An ab Initio Study of the Reaction of Propargyl Cation with Ammonia

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The reaction of propargyl cation with NH_3 was investigated at the CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) theory level by performing a statistical thermodynamics analysis of the theoretical results. Three different reactive channels starting at an association complex were found. The first one is the $C_2H_4 + HCNH^+$ channel, which proceeds under the energy level corresponding to reactants and is the most exothermic one, −34.1 kcal/mol in Gibbs energy, but which implies complex molecular rearrangements giving rise to several adducts much more stable than reactants. The other two channels are the c-$C_3H_2 + NH_4^+$ channel, which is exothermic by only 3.3 kcal/mol, and the $H_2CCC + NH_4^+$ channel, which presents an energy barrier of 8.8 kcal/mol owing to its endothermicity. The c-$C_3H_2 + NH_4^+$ channel proceeds through a TS for the cyclization of $HCCCH_2^+$ efficiently catalyzed by NH_3 and presents the largest Gibbs energy barrier, 24.2 kcal/mol. For the cyclization of H_2CCC, we have found two different pathways with energy barriers of 79.4 and 38.0 kcal/mol. Therefore, according to our theoretical results, obtaining a cyclic product, c-C_3H_2, is energetically disfavored. The product distribution experimentally reported can be rationalized assuming that at low pressure the reaction between propargyl cation and ammonia proceeds along the two reaction channels $H_2CCC + NH_4^+$, with a low energy barrier, and $C_2H_4 + HCNH^+$, dynamically disfavored. At higher pressure, the dynamically disfavored pathway would give rise to two channels: $C_2H_4 + HCNH^+$ and $C_3H_3{\cdot}NH_3^+$.

Introduction

The ion $C_3H_3^+$ has received considerable attention because of its controversial participation in the chemistry of combustion as a precursor to soot[1−9] and its role in the chemistry of interstellar clouds as a precursor to several molecules observed in this medium.[10−14] $C_3H_3^+$ can exist in two low-energy isomeric forms: the acyclic propargyl ion, $HCCCH_2^+$, and the cyclopropenyl ion, c-$C_3H_3^+$, which is the most stable isomer by 24.9 kcal/mol.[15] Experimental studies have shown that $HCCCH_2^+$ is markedly more reactive than c-$C_3H_3^+$ with alkenes, alkynes, aromatic hydrocarbons, simple alcohols, and O and N atoms.[3,5,16−18] Very different results have been found for the reaction of $C_3H_3^+$ with C_2H_2 at low and high pressures.[11,19−22] It has been observed that at low pressures, using ion cyclotron resonance (ICR) and Fourier transform ion cyclotron resonance (FTICR), $HCCCH_2^+$ is unreactive with C_2H_2, whereas at higher pressure using selected ion flow tube (SIFT), $HCCCH_2^+$ reacts rapidly with C_2H_2. In a posterior experimental study of the reactions of a variety of neutral reactants including H_2, NH_3, C_2H_2, CH_3OH, and CH_3CN, it has been found that the ion−molecule chemistry of $C_3H_3^+$ is characterized by association reactions taking place via a long-lived complex.[23] The propargyl cation associates much more rapidly than does c-$C_3H_3^+$ because of the greater ease of forming bonds between the associating species and a terminal C atom of the acyclic structure. The $HCCCH_2^+$ isomer is reactive with NH_3, whereas c-$C_3H_3^+$ is unreactive. Two different channels appear at low pressure in the ICR: $C_2H_4 + H_2CN^+$ (40%) and c-$C_3H_2 + NH_4^+$ (60%) (it has been reported that energy constraints show that this proton-transfer channel requires cyclization of the neutral C_3H_2 product). At higher pressure in the SIFT experiments, the formation of the stabilized association adduct $C_3H_3^+{\cdot}NH_3$ (25%) is detected in addition to the two bimolecular channels $C_2H_4 + H_2CN^+$ (20%) and $C_3H_2 + NH_4^+$ (55%). In light of these results, the capture of NH_3 by $HCCCH_2^+$ to yield the complex $(HCCCH_2^+{\cdot}NH_3)^*$ has been proposed as a plausible mechanism for the reaction. The appearance of the $C_2H_4 + H_2CN^+$ channel in both ICR and SIFT experiments provides evidence that further rearrangement within the complex may be taking place.[23]

Previous quantum mechanical investigations have addressed the study of $C_3H_6N^+$ ions and some rearrangements related to the reactions $C_2H_4 + H_2CN^+ \rightarrow C_3H_6N^+$ and $CH_3^+ + CH_3CN \rightarrow C_3H_6N^+$.[24−27]

Because considerable insight into the mechanism of chemical processes can be gained from theoretical electronic structure calculations, in the present work, we address an ab initio study of the mechanism of the reaction of the acyclic propargyl ion, $HCCCH_2^+$, with NH_3 to determine the energy and the structures of the most important species involved and to be able to rationalize the experimental behavior reported.

Methods

Ab initio calculations were performed with the Gaussian 98 series of programs.[28] Stable species were fully optimized and transition states (TSs) located using Schlegel's algorithm[29] at the MP2-FULL/6-31+G(d,p) theory level.[30] All of the critical points were further characterized, and the zero-point vibrational energies (ZPVEs) were evaluated by analytical computations of harmonic vibrational frequencies at the MP2-FULL/6-31+G(d,p) level. Single-point calculations on the MP2-FULL/6-31+G(d,p) geometries were also carried out at the CCSD(T)/6-311+G(2df,2p) level.

MP2-FULL/6-31+G(d,p) or MP2-FULL/6-31G(d) intrinsic reaction coordinate (IRC) calculations starting at each saddle point verified the two minima connected by that TS using the

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TABLE 1: Relative Energies in kcal/mol of Chemically Important Structures Located for the Reaction of $HCCCH_2^+$ with NH_3

species	ΔE^a	ΔE_{ZPVE}	ΔE^b	$\Delta H^{c,d}$	$-T\Delta S^d$	ΔG^d
			Reactants			
$HCCCH_2^+ + NH_3$	0.0	0.0	0.0	0.0	0.0	0.0
			Minimum Structures			
M1	−20.6	1.5	−19.8	−18.5	7.3	−11.2
M2	−22.4	2.8	−23.2	−20.6	7.7	−12.9
M3	−72.4	6.4	−71.3	−66.6	11.7	−54.9
M4	−59.3	5.8	−55.0	−51.0	12.1	−38.9
M5	−36.5	2.9	−37.7	−35.9	10.6	−25.3
M6	−101.5	6.8	−98.5	−93.8	12.4	−81.4
M7	−96.9	6.7	−94.1	−89.2	12.3	−76.9
M8	−44.6	3.9	−42.9	−40.6	11.4	−29.2
M9	−45.6	3.9	−43.7	−41.3	11.2	−30.1
M10	−92.4	4.8	−87.7	−84.5	11.7	−72.8
M11	−44.2	5.1	−39.9	−36.8	12.3	−24.5
M12	−88.1	7.4	−83.9	−79.1	13.4	−65.7
M13	−49.2	1.4	−46.2	−45.4	8.8	−36.6
M14	−66.7	6.6	−61.1	−56.5	12.5	−44.0
M15	−50.8	3.1	−45.2	−42.9	7.9	−35.0
M16	−45.3	2.8	−40.3	−38.4	7.8	−30.6
			Transition States			
TS1-2	−19.6	−0.4	−19.2	−20.1	7.5	−12.6
TS1-3	−15.9	1.3	−15.5	−14.8	8.1	−6.7
TS3-4	−16.1	1.9	−15.6	−15.8	12.6	−3.2
TS3-14	8.9	4.3	9.4	11.7	12.5	24.2
TS4-5	−29.3	2.6	−30.2	−29.0	11.2	−17.8
TS5-6	−32.9	2.9	−32.3	−31.2	12.2	−19.0
TS6-7	−90.7	6.2	−88.0	−84.0	12.9	−71.1
TS7-8	−36.9	1.7	−34.4	−34.8	12.7	−22.1
TS8-9	−36.1	3.2	−33.4	−32.3	12.7	−19.6
TS9-10	−28.9	1.8	−30.0	−30.0	12.1	−17.9
TS9-11	−27.3	2.9	−26.7	−25.9	12.1	−13.8
TS11-12	−39.6	5.3	−35.4	−32.6	13.3	−19.3
TS11-13	−35.6	2.5	−33.5	−32.5	11.5	−21.0
TS14-15	−47.0	2.7	−41.6	−39.9	8.6	−31.3
TS15-16	−45.2	1.3	−40.0	−39.9	8.7	−31.2
			Products			
$H_2CCC + NH_4^+$	8.4	2.0	6.7	8.7	0.1	8.8
c-$C_3H_2 + NH_4^+$	−11.1	2.9	−6.6	−4.2	0.9	−3.3
c-$C_3H_3^+ + NH_3$	−32.6	1.4	−28.1	−27.2	0.7	−26.5
$C_2H_4 + HCNH^+$	−38.3	0.3	−35.2	−35.4	1.3	−34.1

[a] MP2-FULL/6-31+G(d,p) relative energies without including the ZPVE correction. [b] CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) relative energies without including the ZPVE correction. [c] Relative enthalpies using the CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) relative energies including the ZPVE (MP2-FULL) correction. [d] 298.15 K, 1 atm.

Gonzalez and Schlegel method[31] implemented in Gaussian 98 with the default step size.

ΔH, ΔS, and ΔG values were also calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations.[32] A pressure of 1 atm and a temperature of 298.15 K were assumed in the calculations.

Results and Discussion

We present first the results obtained for the reaction of the more reactive $C_3H_3^+$ isomer, propargyl cation, with ammonia. Second, we analyze the possibility of forming a cyclic product C_3H_2. Finally, we compare our results with experiment.

Mechanisms for the Reaction of Propargyl Cation with Ammonia. Unless otherwise indicated, we will give in the text the CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) energies including the MP2 ZPVE corrections. Table 1 collects the relative energy of the different structures located along the reaction coordinate for this process, and Figure 1 displays the corresponding energy profile. Figure 2 presents the optimized geometry of those structures. The corresponding absolute energies and ZPVE corrections are listed in Table 1S available in the Supporting Information.

The first critical structure located for the reaction between $HCCCH_2^+$ and NH_3 is an association complex, **M1**, 18.3 kcal/mol more stable than separate reactants,[33] in which the N atom is linearly interacting with the hydrogen atom of the terminal CH group of the propargyl cation. This complex can evolve along two different channels. One corresponds to a proton transfer from $HCCCH_2^+$ to ammonia to give $NH_4^+ + H_2CCC$, 8.7 kcal/mol above reactants. This channel goes through a TS, **TS1-2**, connecting **M1** with an intermediate **M2**, which is 2.1 kcal/mol more stable than **M1**. **TS1-2** lies below **M1** in energy when including the ZPVE correction. Finally, **M2** evolves along a monotonically increasing energy profile to give the products.

On the other hand, **M1** can evolve through a TS 4.1 kcal/mol above it, **TS1-3**, to form a C−N bond and give an adduct **M3**, 64.9 kcal/mol more stable than reactants, which corresponds to the N-protonated 1-aminopropanodiene. This adduct isomerizes through the TS for H shift, **TS3-4**, and formation of a cycle to give an N-protonated 2-methylaziridine, **M4**, which is 49.2 kcal/mol more stable than reactants. This aziridine can undergo a two-step rearrangement, which consists of a ring-opening through **TS4-5** with an energy barrier of 21.6 kcal/mol and a 1,2-H shift through **TS5-6** with an energy barrier of 5.4 kcal/mol, to yield the most stable species located along the reaction coordinate, N-protonated *trans*-propene imine, **M6**, which is 91.7 kcal/mol more stable than reactants. **M6** can rearrange into its isomer N-protonated *cis*-propene imine, **M7**, through TS **TS6-7** with an energy barrier of 9.9 kcal/mol. **M7** can undergo a 1,4-H shift to yield the C-protonated *cis*-propene imine, **M8**, 39.0 kcal/mol under reactants, through TS **TS7-8** with an energy barrier of 54.7 kcal/mol. **M8** transforms into its trans isomer, **M9**, 0.8 kcal/mol more stable than **M8**, through an energy barrier of 8.8 kcal/mol (**TS8-9**). **M9** can evolve through a TS for a H-shift from the carbon atom bonded to N, **TS9-10**, to yield protonated ethyl cyanide, **M10**, 82.9 kcal/mol below reactants. Alternatively, **M9** can evolve through a TS for a 1,2 H-shift from the terminal carbon atom, **TS9-11**, 16.0 kcal/mol above it, to give **M11**, 34.8 kcal/mol below reactants. **M11** can render a cyclic structure, **M12**, 76.5 kcal/mol below reactants, through the TS **TS11-12**. **M11** can also lead to the product complex **M13**, 10.0 kcal/mol more stable than **M11**, through the TS **TS11-13** with an energy barrier of 3.8 kcal/mol. **M13** dissociates into the final products $C_2H_4 + HCNH^+$ along a monotonically increasing energy profile. The process is exoergic by 34.9 kcal/mol. It is interesting to note that the routes $HCNH^+ + C_2H_4$ → **M13** → **TS11-13** → **M11** → **TS9-11** → **M9** → **TS9-10** → **M10** and $HCNH^+ + C_2H_4$ → **M13** → **TS11-13** → **M11** → **TS11-12** → **M12** constitute competitive alternatives to the pathways previously reported from ab initio calculations.[27]

A route has also been located that connects **M3** with the products c-$C_3H_2 + NH_4^+$. This reaction path goes through a TS for the cyclization of the $C_3H_3^+$ moiety, 13.7 kcal/mol above reactants, **TS3-14**, to give the intermediate **M14**, 54.5 kcal/mol more stable than reactants. **M14** evolves through the TS **TS14-15**, 15.6 kcal/mol above it, to give the intermediate **M15**, 42.1 kcal/mol below reactants, in which the NH_3 moiety interacts with one of the H atoms of the $C_3H_3^+$ fragment. This intermediate **M15** can either dissociate directly into c-$C_3H_3^+ + NH_3$, 26.7 kcal/mol below reactants, or evolve into the intermediate **M16** through a TS for a H transfer, **TS15-16**, which lies below **M16** in energy when the ZPVE correction is taken

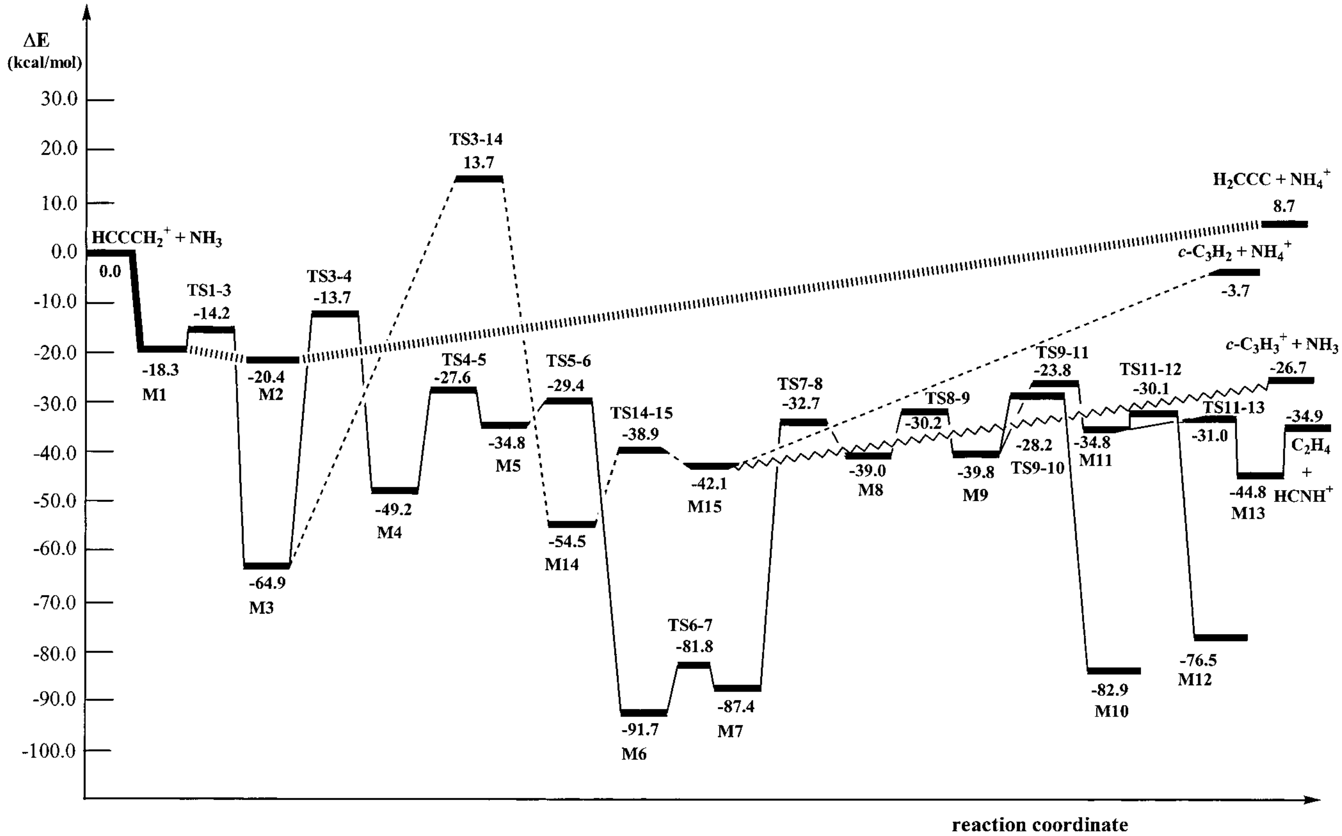

Figure 1. CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p)+ZPVE(MP2) energy profiles of the reaction channels located for the reaction of $HCCCH_2^+$ with NH_3.

TABLE 2: Relative Energies in kcal/mol of Chemically Important Structures Located for the Isomerization Reaction of H_2CCC into c-C_3H_2

species	ΔE^a	ΔE_{ZPVE}	ΔE^b	$\Delta H^{c,d}$	$-T\Delta S^d$	ΔG^d
H_2CCC	0.0	0.0	0.0	0.0	0.0	0.0
TSC1A	83.6	−3.9	81.6	79.5	−0.1	79.4
MC1A	13.5	−1.5	12.5	12.0	−0.2	11.8
TSC2A	68.8	−2.6	64.9	66.0	−0.2	65.8
TSC1B	33.0	−1.3	36.5	31.4	−0.2	31.2
MC1B	33.0	−1.1	36.7	32.0	−0.9	31.1
TSC2B	40.3	−2.1	45.9	37.6	0.4	38.0
***c*-C_3H_2**	−19.5	0.9	−13.3	−19.1	0.8	−18.3

[a] MP2-FULL/6-31+G(d,p) relative energies without including the ZPVE correction. [b] CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) relative energies without including the ZPVE correction. [c] Relative enthalpies using the CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) relative energies including the ZPVE (MP2-FULL) correction. [d] 298.15 K, 1 atm.

into account. Finally, **M16** yields directly the products *c*-C_3H_2 + NH_4^+, 3.7 kcal/mol more stable than reactants.

Given that some of the TSs located imply a H transfer, we have tried to estimate the tunneling effect by calculating the Wigner coefficient[34] for **TS3-4**, **TS3-14**, **TS5-6**, **TS7-8**, **TS9-10**, and **TS9-11**. The values obtained are, respectively, 2.79, 1.35, 1.46, 1.77, 1.31, and 1.18. Because the electronic energy barriers, including the ZPVE correction, corresponding to **TS3-4**, **TS3-14**, and **TS7-8** are, respectively, 51.2, 78.6, and 54.7 kcal/mol, the effect of tunneling would be practically null in these cases. On the other hand, for **TS5-6**, **TS9-10**, and **TS9-11**, the energy barriers are lower (5.4, 11.6, and 16.0 kcal/mol, respectively), but the small value of the Wigner coefficients calculated seems to indicate that the tunneling effect, while present in these three cases, would not play a very important role.

Cyclization of $HCCCH_2^+$ and H_2CCC. Previous theoretical investigations have been performed on the interconversion of the two more stable $C_3H_3^+$ isomers. Two different mechanisms have been found for the propargyl−cyclopropenyl rearrangement.[35,36] One is a two-step route presenting a rate-limiting energy barrier of 49.2 kcal/mol, whereas the other one is a concerted pathway with an energy barrier of 88.0 kcal/mol.[36] Therefore cyclization of propargyl cation is energetically unfavorable. It is interesting to note that the pathway from $HCCCH_2^+$ + NH_3 to *c*-$C_3H_3^+$ + NH_3 located in the present work (see above) constitutes a very efficient catalytic route for the isomerization of propargyl cation into cyclopropenyl cation with a low energy barrier of 13.7 kcal/mol corresponding to **TS3-14** (see Figure 1).

A recent theoretical investigation has been carried out on the propadienylidene−cyclopropenylidene isomerization.[37] Two different pathways have been found for this process. The first one is a two-step route with a rate determining barrier of 75.9 kcal/mol. The second one is a concerted route with an energy barrier of 41.7 kcal/mol.

According to our results, the cyclization of propadienylidene, H_2CCC, can take place along two two-step routes. Figure 3 displays the two corresponding energy profiles, Figure 4 collects the optimized critical structures involved, and Table 2 shows their relative energy. The corresponding absolute energies and the ZPVE corrections are listed in Table 2S available in the Supporting Information. The first pathway proceeds through a TS, **TSC1A**, for a 1,3 H-shift in which the H atom transferred is situated midway in front of C2. This TS is analogous to that previously reported as the rate-limiting step in a two-stage mechanism.[37] The energy barrier corresponding to this TS is 77.7 kcal/mol. **TSC1A** evolves to an intermediate, **MC1A**, 11.0 kcal/mol above H_2CCC. **MC1A** is the C_s structure of prope-

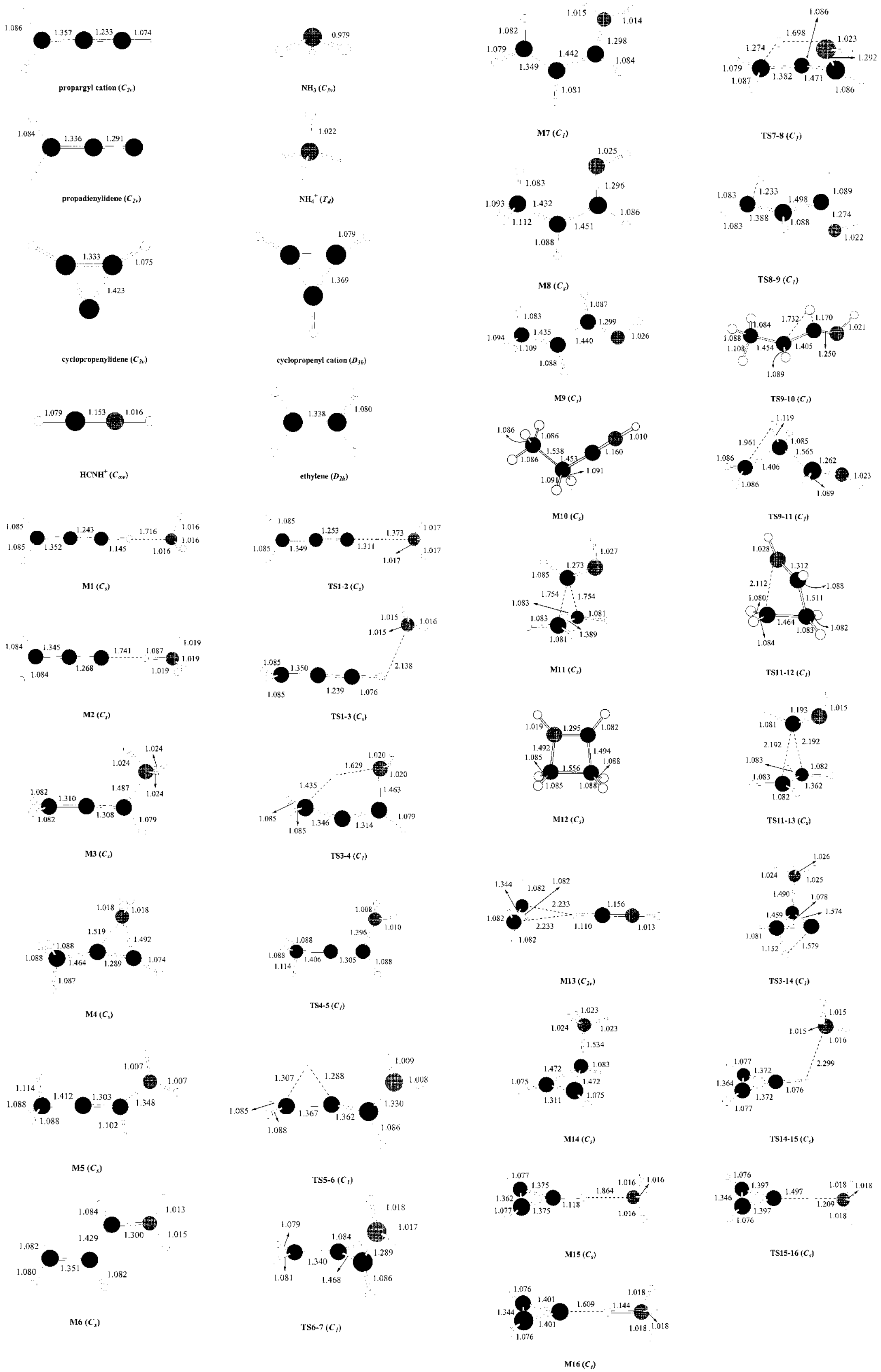

Figure 2. MP2-FULL/6-31+G(d,p) optimized geometries of the chemically important structures located for the reaction of propargyl cation with ammonia. Distances are given in angstroms.

nylidene and can undertake cyclization with a simultaneous 1,2 H-shift through the TS **TSC2A**, 62.3 kcal/mol above H_2CCC, to yield cyclopropenylidene, 12.4 kcal/mol more stable than propadienylidene. The second route proceeds through a TS for bending of the carbon skeleton, **TSC1B**, with an energy barrier of 35.2 kcal/mol. **TSC1B** evolves to an intermediate very similar to it both in energy and structure, **MC1B**, 35.6 kcal/mol above propadienylidene (**MC1B** is above **TSC1B** in energy because of the ZPVE correction). **MC1B** yields cyclopropenylidene through a TS for 1,2 H-shift, **TSC2B**, 43.8 kcal/mol above

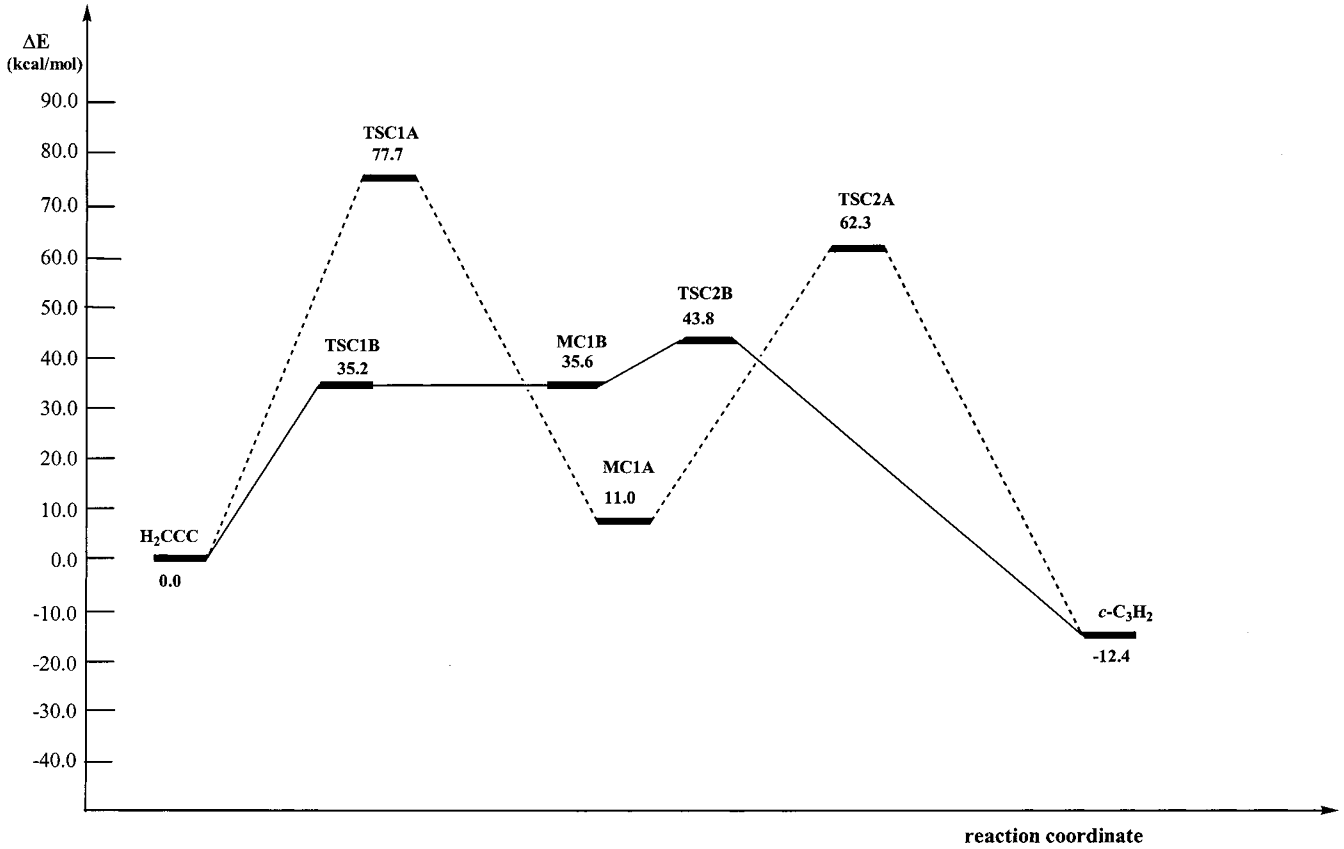

Figure 3. CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p)+ZPVE(MP2) energy profiles for the isomerization of H_2CCC into c-C_3H_2.

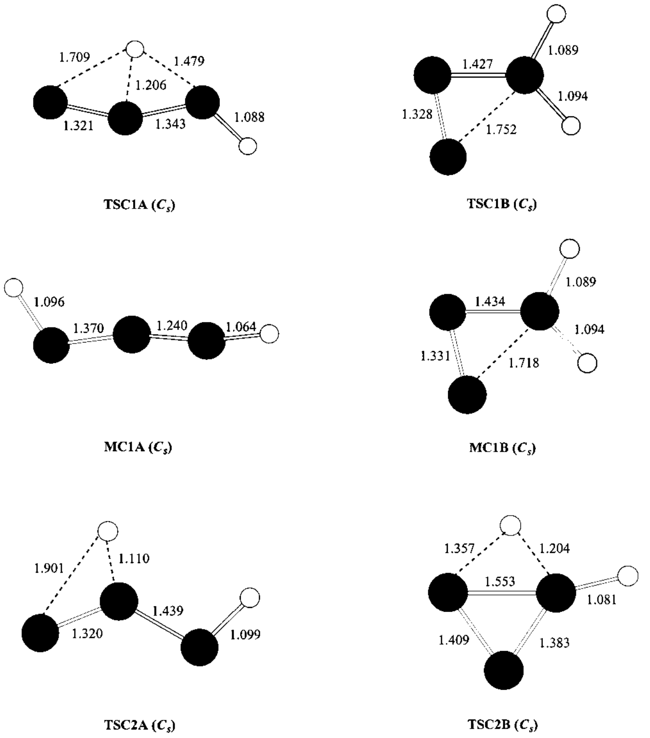

Figure 4. MP2-FULL/6-31+G(d,p) optimized geometries of the chemically important structures located for the isomerization reaction of H_2CCC into c-C_3H_2. Distances are given in angstroms.

H_2CCC. This TS is analogous to that previously reported for the concerted route.[37] Therefore, the cyclization of H_2CCC is also energetically unfavorable. The calculated electronic energy barriers (including ZPVE) for **TSC1A**, **TSC2A** and **TSC2B** are so high that no tunneling effect is to be expected along these cyclization routes.

Discussion and Comparison with Experiment. To more readily compare our results with experiment a statistical thermodynamics analysis of our computational data was carried out at 298.15 K and 1 atm. Table 1 collects the ΔH, ΔS, and ΔG values obtained. Unless otherwise stated, Gibbs energies will be reported in this section.

Thermal corrections are relatively small for all of the channels for the reaction between propargyl cation and ammonia so that ΔH profiles display the critical structures 0.0−2.2 kcal/mol more stable than reactants compared with the electronic energy profiles. On the contrary, entropy destabilizes all of the critical structures except products in about 7.3−12.9 kcal/mol. Except for **TS4-5**, **TS11-13**, and **TS14-15**, all of the TSs undergo a decrease of entropy with respect to the previous minimum energy structures of 1.7−5.4 cal/(K mol). In both **TS5-6** and **TS8-9**, which present the most important entropy decrease (5.4 and 4.4 cal/(K mol), respectively), an internal rotor is lost. Correspondingly, these two TSs would have the lowest Arrhenius *A*-factors. **TS4-5** and **TS11-13** have slightly loose structures, and consequently, they present a moderate entropy increase (3.0 and 2.7 cal/(K mol), respectively) and would have higher *A*-factors. The most significant increase in entropy (13.1 cal/(K mol)) takes place for **TS14-15**, which presents a very loose character, which would determine a high Arrhenius *A*-factor.

According to our results for the reaction between propargyl cation and ammonia there are three different reactive channels and a fourth channel for the dissociation to c-$C_3H_3^+ + NH_3$ corresponding to the cyclization of $HCCCH_2^+$ catalyzed by an ammonia molecule. The $H_2CCC + NH_4^+$ channel presents an energy barrier of 8.8 kcal/mol owing to its endothermicity, whereas the $C_2H_4 + HCNH^+$ channel is exothermic by 34.1 kcal/mol and proceeds under the energy level of the separate reactants. Both the reaction channels c-$C_3H_2 + NH_4^+$ and the isomerization process giving c-$C_3H_3^+ + NH_3$ present a rate-determining energy barrier of 24.2 kcal/mol and are exothermic by 3.3 and 26.5 kcal/mol, respectively. As expected by experimentalists, we located the adduct $HCCCH_2^+{-}NH_3$ (**M3**) 54.9 kcal/mol more stable than reactants (66.6 kcal/mol in enthalpy to compare with the reported value of 62.9 kcal/mol[15]) and four more stable isomers, $C_3H_3{\cdot}NH_3^+$ (**M6**, **M7**, **M10**, and **M12**) 81.4, 76.9, 72.8, and 65.7 kcal/mol below reactants, respectively.

As mentioned above, theoretical results indicate that the formation of a cyclic product, C_3H_2, presents a large energy barrier. In effect, on one hand, the uncatalyzed cyclization of the original reactant, propargyl cation, is penalized by strong energy barriers. On the other hand, the cyclization of H_2CCC presents energy barriers of at least 43.8 kcal/mol, and even the catalyzed route for cyclization of the carbon skeleton described above has an energy barrier of 24.2 kcal/mol. Consequently, our theoretical results would explain the experimental results obtained at low pressure considering that the process would take place along the two reaction channels $H_2CCC + NH_4^+$ and $C_2H_4 + HCNH^+$. The first channel would imply surmounting 8.8 kcal/mol, whereas the second channel would be dynamically disfavored given that along it several H-shifts, cyclizations, and ring openings take place. According to experimental data,[23] only 13% of collisions are reactive at low pressure. This is a consequence of the initial complexes formed dissociating back into reactants. At higher pressure, the effect of third body collisions would remove enough energy of the initial complexes as to prevent them from dissociating back into reactants, allowing thus 87% of the collisions between reactants to be reactive. Further along the reaction coordinate, about 25% of the $C_3H_3{\cdot}NH_3^+$ adducts would stabilize by multiple third body collisions.[23] Thus, the reaction pathway dynamically disfavored would split into two channels, $C_2H_4 + HCNH^+$ and $C_3H_3{\cdot}NH_3^+$. This $C_3H_3{\cdot}NH_3^+$ channel would be disfavored by high temperature so that, given the well depths obtained in our calculations and the mean thermal energy available to the system at different temperatures, this adduct channel is expected to practically disappear at about 1900 K.

To investigate the effect of pressure on the Gibbs energy barriers, we performed the statistical thermodynamics analysis of the CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) calculations at 298.15 K and 10^{-10} and 10^{-4} atm besides 1 atm. For all of the TSs located, the Gibbs energy barrier remains practically unchanged except for **TS1-3**. For this TS, the Gibbs energy barrier with respect to the previous intermediate along the reaction channel is 8.2 (10^{-10} atm), 4.6 (10^{-4} atm), and 4.5 kcal/mol (1 atm). Thus, according to our results, the Gibbs energy barrier for the unimolecular process **M1** → **M3** does not change with pressure from 10^{-4} atm at 298.15 K.

In summary, we located three reactive channels for the title reaction: the $C_2H_4 + HCNH^+$ channel, which is the most exothermic one (−34.1 kcal/mol), the c-$C_3H_2 + NH_4^+$ channel, which is only slightly exothermic (−3.3 kcal/mol) and presents the largest energy barrier (24.2 kcal/mol), and the $H_2CCC + NH_4^+$ channel, which presents an energy barrier of 8.8 kcal/mol owing to its endothermicity. The three reactive channels start at an association complex and the two exothermic ones go through adduct formation in agreement with experimental findings. Given that obtaining a cyclic product is disfavored by higher energy barriers, the product distribution experimentally reported could be rationalized assuming that at low pressure the process proceeds along the two reaction channels $H_2CCC + NH_4^+$ and $C_2H_4 + HCNH^+$, the first one requiring surmounting 8.8 kcal/mol and the second one dynamically disfavored. At higher pressure, the dynamically disfavored channel would give rise to a new channel, $C_3H_3{\cdot}NH_3^+$, owing to adduct collisional stabilization. A fourth pathway has also been located on the PES giving c-$C_3H_3^+ + NH_3$. Along this channel, the isomerization from propargyl cation into cyclopropenyl cation takes place with a very efficient catalytic action by NH_3.

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Supporting Information Available: Table 1S, MP2-FULL/6-31+G(d,p) and CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) absolute energies (hartree) and zero-point vibrational energies (kcal/mol) corresponding to the chemically important structures located for the reaction of $HCCCH_2^+$ with NH_3; Table 2S, MP2-FULL/6-31+G(d,p) and CCSD(T)/6-311+G(2df,2p)//MP2-FULL/6-31+G(d,p) absolute energies (hartree) and zero-point vibrational energies (kcal/mol) corresponding to the chemically important structures located for the isomerization reaction of H_2CCC into c-C_3H_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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$$Q = 1 + \frac{1}{24}\left(\frac{h|\nu|}{k_B T}\right)^2$$

where h is the Planck constant, k_B is the Boltzmann constant, T is the absolute temperature, and ν is the imaginary vibrational frequency corresponding to the TS.

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