Ab Initio MO Study of the Global Potential Energy Surface of C₄H₄ in Triplet Electronic State and the Reactions of C(3Pj) with C₃H₄ (Allene and Propyne) and C₂(A³Πₓ) with C₂H₄(X¹A₁g⁺)

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Abstract: The global potential energy surface of C₄H₄ in the lowest triplet electronic state has been studied at the G2M(RCC,MP2) level. Of 28 distinct isomers the most stable are aromatic cyclobutenes q3 (1A₁g,Dₓ) and linear butyne c1 (3E,Dₓ), and 66 transition states for various isomerization and dissociation pathways have been found. The information about the global PES is applied to describe the potential energy surfaces for the C(3Pj) + H₂CCCH₂, C(3Pj) + H₂CCCH, and C(3Πₓ) + C₂H₄ reactions, recently studied experimentally in crossed molecular beams. The reaction of the carbon atom with allene is shown to occur by a barrierless addition of C to the C≡C bond to yield the three-member ring structure t₁ and/or to the central carbon atom of allene to form the branching structure b₁ which isomerizes to t₁ with a low barrier. t₁ undergoes ring opening to c₁ with a barrier of 9.4 kcal/mol, and the latter emits a H atom to give the major reaction product n-C₃H₄ with an exit barrier of 2.2 kcal/mol. The minor reaction product, i-C₃H₃, is formed through a 1,2-H shift in c₁ leading to c₃, followed by the hydrogen loss. The reaction of the carbon atom with methylacetylene starts with a barrierless C addition to the β-C-atom of H₂CCCH to form c₆. to the α-C-atom to give b₂ or b₂', or to the acetylenic C≡C bond to yield the cyclic isomers t₄ or t₄'. c₆, b₂, and b₂' are metastable and would rapidly rearrange to the linear isomer c₅ or to the cyclic t₄ and then to t₄' with low barriers. The latter ring opens to c₅ with a barrier of 14.7 kcal/mol. At high collision energies, the major reaction product n-C₃H₄ is formed through the methyl hydrogen emission in c₅ with an exit barrier of 5.8 kcal/mol. The second product i-C₃H₃ can be reached via a H-shift from c₅ to e₄ and subsequent hydrogen elimination. Cyclic isomers C₃H₃ p₃ and p₄ can originate from t₄, t₄', and t₅. The reaction of C₂(3Πₓ) with ethylene proceeds through a C₂ addition to a carbon atom of C₂H₄ to yield the chain isomer c₂ with an entrance barrier of ~4 kcal/mol. c₂ rearranges to linear c₁ in several steps via the four-member ring intermediate q₁ or the three-membered ring structures b₂ and t₁. c₁ loses a H atom to yield n-C₃H₄ or undergoes a hydrogen migration to c₃ followed by a H emission producing n- or i-C₃H₃. Similarly to C(3Pj) + allene, n-C₃H₃ is expected to be the major product of C₂(3Πₓ) + C₂H₄, while i-C₃H₃ to give a minor contribution.

Introduction

Formation of various structural isomers of hydrocarbon radicals and their chemical reactivity is relevant to chemical processes in hydrocarbon-rich planetary atmospheres,⁴ outflow of dying carbon stars, interstellar clouds, and hot molecular cores.⁵ The reactivity of such radicals is also of major importance in combustion chemistry.⁶ Take, for instance, C₃H₃. In oxygen-deficient combustion, n- and i-C₃H₃ isomers are believed to play a crucial role in formation of the first aromatic ring, the phenyl radical C₆H₅, via the reaction with acetylene.⁷ On the other hand, cyclic isomers are expected not to form aromatic species. The distinct isomers of C₄H₄ can be produced in the carbon–hydrogen exchange channel in the reactions of atomic carbon C(3Pj) with two structural isomers of C₃H₄, allene CH₂CCCH₂, and methylacetylene (propyne) CH₃CCH, as was recently demonstrated by crossed molecular-beam experiments.⁸ Similar carbon–hydrogen exchange reactions occur when C(3Pj) attacks acetylène (the products are I/C=C₃H₂+H), ethylene (producing C₄H₄ + H), C₃H₆ (producing C₅H₅ + H), C₃H₃ (producing C₄H₅ + H), and C₂H₅ (producing CH₂ + H).⁹ The molecular-beam measurements carried out in the single collision conditions support the hypothesis that C₄H₄ isomers are likely to be formed in such extraterrestrial environments as cold molecular clouds and planetary atmospheres of Jupiter, Saturn, Uranus, and Neptune as well as the moons Titan and Triton.⁵,⁶

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10.1021/ja993529n CCC: $19.00 © 2000 American Chemical Society
Published on Web 02/11/2000
The use of the crossed molecular-beam technique allows us to elucidate the intimate chemical dynamics of the neutral reaction of atomic carbon C(P) or carbon dimer C2 with unsaturated hydrocarbons, to gain information at the center-of-mass angular flux and translational energy distributions of the reaction products and to derive energy-dependent triply differential cross-sections. On the other hand, chemically accurate (within 0.1 eV) ab initio molecular orbital (MO) calculations of potential energy surfaces (PES) for these reactions can serve as a complimentary approach which gives a deeper insight into the reaction mechanism and allows us to surmise the most important reaction channels and to predict branching ratios of various products based on RRKM calculations of reaction rate constants. Recently, experimental measurements were performed for the reactions C(P) + CH2CCH2, C(P) + CH2H2, and C2(P) + C2H2. All three reactions explore different regions of the triplet PES for the C4H4 system. Our goal in the present paper is to investigate the global PES for triplet C4H4, i.e., to find all (or almost all) possible isomers of this species, to examine isomerization pathways connecting the local minima, and to study various dissociation channels. After that, we can closely analyze the potential energy surfaces for the reaction of atomic carbon with allene and propyne and C2 with ethylene.

Computational Methods

The geometries of various isomers of triplet C4H4, transition states for isomerization and dissociation, as well as dissociation products, have been optimized using the hybrid density functional B3LYP method,9 with the 6-311G(d,p) basis set.10 Vibrational frequencies, calculated at the B3LYP/6-311G(d,p) level, have been used for characterization of stationary points and zero-point energy (ZPE) correction without scaling. All the stationary points have been positively identified for minimum (number of imaginary frequencies NIMAG = 0) or transition state (NIMAG = 1). All the energies quoted and discussed in the present paper include the ZPE correction. In some cases mentioned in Discussion, geometries and frequencies were also calculated at the MP2/6-311G(d,p)11 and CCSD(T)/6-311G(d,p)12 levels.

To obtain more reliable energies of the most important equilibrium structures and transition states, we used the G2M(RCC,MP2) method,13 which gives an approximation to the RCCSD(T)/6-311+G(3df,2p)14 energy. It is known that the expected accuracy of this and other G2-type calculational schemes is within 1–2 kcal/mol.15-16 The GAUSSIAN 94,17 MOLPRO 96,18 and ACES–II19 programs were employed for the calculations.

Results and Discussion

Isomers of Triplet C4H4. To survey various possible isomers of triplet C4H4, we consider different arrangements of four carbon atoms and different distributions of four hydrogens between them. Four C atoms can form a chain, a branch with the central carbon with three CC bonds, a three-membered ring with an out-of-ring CC bond, a four-membered ring, and a bicyclic structure where two three-membered rings are fused together. Figure 1 shows optimized structures of various isomers. In this figure, chain isomers are denoted with the letter “c”, branching structures with “b”, three-member rings with “t”, and four-member rings and bicyclic structures with “q”.

The largest number of isomers, 13, is found for the chain arrangement. The most stable of them is H2CCCH3H. It has a linear geometry with D2d symmetry and 3E electronic state. c1 can be described as a triplet butyne with the central triple C≡C bond, two single C–C bonds, and two radical centers (unpaired electrons) on the terminal carbons. However, the triple bond, 1.25 Å, is longer than the regular triple bond (1.20 Å in acetylene)20 and the single bonds are much shorter than regular single bonds. This indicates a presence of some contributions from the H2C≡C≡C=CH2 and H2C≡C=C≡CH2 resonance structures in the wave function of c1. At the G2M(RCC,MP2) level c1 lies 41.1 kcal/mol higher in energy than singlet butatriene H2C≡C≡C=CH2. The next in the order of stability chain isomer is e5, H2CCHCH, which is 6.9 kcal/mol less favorable than c1. In terms of resonance structures, e5 can be described as a mixture of H2C≡C≡C=CH2 and H2C≡C≡C=CH2 resonance structures. In the present study e5 has no symmetry, and the geometry is substantially nonlinear, with the CCH angle of 160°, but two CCC angles are close to 180°. Next two isomers c4 (H2C≡CH≡C≡CH2) and c3 (H2C≡C=CH=CH2 ↔ H2C≡C=CH=CH2) have C5 symmetry and 3A electronic state and lie, respectively, 13.2 and 20.1 kcal/mol higher in energy than c1.

Three configurations are about 32–33 kcal/mol less stable than c1. c10, HC≡CH=CH=CH2, is C2-symmetric, has a 4A electronic state and exhibits a typical carbene structure with the CCH angle of 133° (ca. with 136° for HCH in triplet CH2).20 c9 and e9 are different conformers of HC≡CH=CH=CH2.

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Figure 1. Optimized geometries (bond lengths are in Å, bond angles are in degrees) of various local minima for triplet C₄H₄.

c₉ (3B₂,C₂) is 0.3 kcal/mol more favorable than c₉ (3A',C₄). Interestingly, the e₉ → e₉' isomerization occurs by the hydrogen in-plane scrambling rather than by rotation around the double C≡C bond, and the barrier is relatively low, about 4 kcal/mol. More different conformers of triplet CHCHCHC may exist, but we do not consider them here since they are expected to have similar energies with c₉ and e₉' and are not relevant for the title reactions.

c₇ (3A'',C₄) lies 42.7 kcal/mol higher than c₁. Its electronic structure can be described as a resonance of H₃CC(C)CH. They are 17.7 and 15.7 kcal/mol less stable than the isomer c₂. Isomer c₆, H₂C≡C≡CH≡C*, with possible small contribution from H₂C≡C≡C≡C, making the central CC bond shorter, is C₄-symmetric with 3A'' electronic state. The least stable isomer among the chain structures is c₁₁, C₄-symmetric with 3A'' electronic state. The electronic configuration can be expressed in terms of three resonance structures, H₂C≡C≡C≡C, H₂C≡C≡C≡C, and H₂C≡C≡C≡C, which lies 85.6 kcal/mol higher in energy than c₁. As will be seen in subsequent sections, c₁₁ dissociates to singlet acetylene and triplet vinylidene with a barrier of only 0.1 kcal/mol.

Three distinct branching isomers are found. b₁ is the most stable of them, 50.6 kcal/mol higher in energy than c₁. The geometry of b₁ is C₄-symmetric, with B electronic state. The electronic configuration can be expressed in terms of three resonance structures, H₂C≡C≡C≡C, H₂C≡C≡C≡C, and H₂C≡C≡C≡C, which makes all three CC distances close to each other, 1.42 Å for C=C and 1.38 Å for C=C. b₂ and b₂' correspond to cis and trans conformers of C₄H₄. They are 32–34 kcal/mol higher than b₁. Both structures have C₄ symmetry, 3A'' electronic state and H₂C≡C≡C≡C≡H ≡ H₂C≡C≡C≡C≡H electronic configuration.

Most of eight three-membered ring isomers are more stable than the branching structures. For instance, t₁, t₃, t₅, and t₅' lie 32–34 kcal/mol above c₁. t₁ (3A',C₄) has the electronic configuration described by the B3LYP frequencies. Therefore, the assignment of the photoelectron spectrum of C₄H₄ may not be completely accurate.
resonance. The electronic structure of C$_2$-symmetric t3 in the 3B state can be expressed as a mixture of

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

Thus, the double bond is delocalized between the carbon–carbon bonds with the bond lengths of 1.38–1.40 Å. t5 and t5′ are two conformers of

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

and both have C$_s$ symmetry and 3A′′ electronic state. Nonsymmetric structures t4 and t4′ are 45.3 and 43.3 kcal/mol less stable than c1, respectively. Their geometries and electronic structures are quite similar and differ only by the position of the ring double bond. One can express the structure of t4 and t4′ as

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

According to this bond arrangement, t4 has the CH$_3$ group deviating out of the ring plane, while in t4′ the CH hydrogen is out-of-plane and the methyl carbon is in-plane. t4 and t4′ have similar energies and rearrange to each other with a small barrier of 3.3 kcal/mol with respect to more stable t4′. In the corresponding transition state t4-t4′ the two bonds, C=C(H) and C=C(CH$_3$), exchanging the double bond character have similar lengths of 1.34–1.37 Å. By the energetic order, the next three membered ring isomer is t6, 50.6 kcal/mol less stable than c1. t6 does not have any symmetry and its structure is described as

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

Finally, t2 is the least stable three-member ring isomer lying 63.4 kcal/mol above c1. The structure of t2 (5B$_2$) is C$_3$-symmetric and the electronic configuration is

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

The last interesting group of triplet C$_4$H$_4$ isomers is represented by four-membered ring and bicyclic structures. Within this group we find the most stable configuration of triplet C$_4$H$_4$, q3, which lies 0.4 kcal/mol below the chain isomer c1. q3, triplet cyclobutene, is a structural analogue of singlet cyclobutadiene. The latter is well established to be a highly antiaromatic system. 22 On the contrary, triplet (3A′′) cyclobutene is aromatic according to its symmetric D$_4h$ geometry. All four CC bonds in the cycle have the same length of 1.44 Å. Therefore, the only double bond in q3 is delocalized among four carbon–carbon bonds and two unpaired electrons are also delocalized on all C atoms. Despite of its aromaticity, triplet cyclobutene lies ~7.0 kcal/mol higher than antiaromatic singlet cyclobutadiene at the

\[
\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_2
\]

q2 is 22.1 kcal/mol less favorable than q3 and has C$_s$ symmetry with 3A′′ electronic state. q1 is a triplet analogue of singlet cyclobutene studied by Schaefer and co-workers. 24 This isomer which also can be described as a triplet cyclobutene lies 47.4 kcal/mol higher in energy than aromatic triplet cyclobutene q3. The energy difference can be attributed to the aromatic electron delocalization. The delocalization increases in the row q1-q2-q3, as does the relative stability. The bicyclic structure q4 is similar to tetrahedrane, but with a CC bond broken giving two unpaired electrons. This isomer is 42.4 kcal/mol less favorable than the square structure q3. Interestingly, in the singlet electronic state the energy difference between antiaromatic cyclobutadiene and tetrahedrane is notably smaller, 26.0 kcal/mol at the G2 level of theory. 25 Thus, the planar four-membered ring structure is stabilized in the triplet state, and the nonplanar bicyclic structure is destabilized.

**Isomerization Pathways.** Possible isomerization pathways of triplet C$_4$H$_4$ are illustrated in Figure 2. The relative energies (in kcal/mol) with respect to C(3P) + C$_2$H$_4$ (allene) of various isomers and transition states are shown in this figure in italic numbers. The energies of transition states are positioned near the lines connecting different local minima. Optimized geometries of transition states are drawn in Figure 3. The notation of TS’s includes the names of the isomers connected by these transition states. For example, the transition state for the c1 → c3 isomerization is denoted as c1-c3. Figure 2 represents a graph describing the triplet PES of C$_4$H$_4$ and various routes from one local minimum to another can be found in this graph.

The rearrangements of C$_4$H$_4$ can be classified as hydrogen shifts and ring opening/closures related to three- and four-membered ring isomers. Chain structures can isomerize to each other by hydrogen migrations. For example, c1 can eventually rearrange into c5 by three consecutive H shifts via c3 and c4. Typically, barriers for the hydrogen migrations are in the range of 40–60 kcal/mol. Transition state c1-c3 for the 1,2-H shift leading from c1 to c3 lies 61.7 and 40.6 kcal/mol higher than the former and the latter, respectively. Isomers c3 and c4 are connected by two transition states, c3-c4 and c3-c4′. The former corresponds to the 2,3-H shift and the latter to the 1,4-H shift in c3 and lies about 6 kcal/mol higher in energy than c3-c4. The 1,4-H shift is also possible in c1 directly yielding c5; however, the transition state c1-c5 has an unfavorable highly bent structure, and the barrier is very high, 88.6 kcal/mol relative to c1. In less stable chain isomers the hydrogen shift barriers can be low. For instance, c6 is separated from c5 by the barrier of only 0.2 kcal/mol. Thus, c6 is kinetically unstable and should rapidly rearrange to c5 by the 1,2-H shift to the terminal carbene-like carbon. As will be seen below, this fast isomerization can play an important role for the C(3P) + C$_2$H$_4$ (propyne) reaction.

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that for the similar process in the singlet state, 3.3 and 4.1 kcal/mol relative to $c_4$.

The branching structures, but also to more stable chain isomers. The other routes connecting chain isomers include Figure 2.

The other routes connecting chain isomers include $c_3 \to c_6 \to e_8 \to e_9 \to e_9' \to c_11, c_6 \to c_7 \to c_2, c_8 \to c_2 \to c_{10}$, and $c_8 \to c_4$. The latter corresponds to the vinylvinylene $\to$ vinylacetylene rearrangement in triplet electronic state. The calculated barrier, 6.5 kcal/mol relative to $e_8$, is somewhat higher than that for the similar process in the singlet state, 3.3 and 4.1 kcal/mol at the CISD/D95(d,p)21 and G2M(rcc,MP2)26 levels. The relative energy of $C_4^r(H) + C_2H_6$ is given at the RCCSD(T)/6-311+G(3df,2p) + ZPE[B3LYP/6-311G(d,p)] level (see text for more detail).

The reverse barriers characterize kinetic stability of the four-member ring structures. For instance, nonaromatic cyclobutene $q_1$ can isomerize to the very stable isomer $c_1$ with the barrier of 20.3 kcal/mol at the G2M(rcc-MP2) level. The analogous process in the singlet state was calculated to have the classical barrier of 41.3 kcal/mol at the CCSD(T)/DZP level, but Schaefer and co-workers24 gave the best estimate for the cyclobutene $\to$ butatriene rearrangement barrier as $\sim25$ kcal/mol. In any case, triplet cyclobutene $q_1$ is expected to be less stable with respect to the ring opening than singlet cyclobutene. On the other hand, aromatic triplet cyclobutene $q_3$ is much more stable; the ring opening barrier is 57.4 kcal/mol. Bicyclic structure $q_4$ is produced from $q_3$ with a barrier of 47.5 kcal/mol. The triplet tetrahedrane is not expected to be kinetically stable, since the reverse barrier for $q_4 \to q_3$ is only 5.1 kcal/mol. 1.2-Hydrogen migrations connect $q_1$, $q_2$, and $q_3$. The barrier heights for the $H$ shifts range between 46 and 72 kcal/mol. Interestingly, the more favorable path for the rearrangement of $q_1$ to $q_2$ is not the direct $H$ shift $q_1 \to q_2$ but the multistep mechanism involving ring opening, hydrogen migration, and ring closure: $q_1 \to c_1 \to c_3 \to q_2$.

The third most stable isomer of $C_4H_3$ is $c_4$. It can be produced in two conformations $p_2$ and $p_2'$ which are very close in energy. $i-C_4H_3$ is formed from $c_3$ and $c_4$ with low exit barriers of 1.4 and 2.7 kcal/mol and from less stable $c_9$ and $c_{10}$ with higher exit barriers (5–7 kcal/mol). In the energetical order, $p_1$ and $p_2$ are followed by cyclic structures of $C_4H_3$, $p_3$, $p_{11}$, and $p_4$ lying the corresponding barriers are higher, 21–22 kcal/mol. Hydrogen migrations which do not destroy the three-membered cycles in the $c$-isomers, $t_1 \to t_5, t_1 \to t_6, t_3 \to t_6$, and $t_4 \to t_6$, exhibit very large barriers of 50–65 kcal/mol. Hence, the three-membered ring isomers would rather rearrange to the chain structures than to each other.

Four-membered ring isomers can be formed from the chain structures by ring-closures: $c_1 \to q_1, c_2 \to q_1, c_3 \to q_2, c_8 \to q_2, c_{10} \to q_2, c_{11} \to q_2$, and $c_9' \to q_3$. However, the barriers for such processes are usually high, except for relatively unstable isomers $c_{11}, c_2, \text{and } c_8$. The reverse barriers characterize kinetic stability of the four-member ring structures. For instance, nonaromatic cyclobutene $q_1$ can isomerize to the very stable isomer $c_1$ with the barrier of 20.3 kcal/mol at the G2M(rcc-MP2) level. The analogous process in the singlet state was calculated to have the classical barrier of 41.3 kcal/mol at the CCSD(T)/DZP level, but Schaefer and co-workers24 gave the best estimate for the cyclobutene $\to$ butatriene rearrangement barrier as $\sim25$ kcal/mol. In any case, triplet cyclobutene $q_1$ is expected to be less stable with respect to the ring opening than singlet cyclobutene. On the other hand, aromatic triplet cyclobutene $q_3$ is much more stable; the ring opening barrier is 57.4 kcal/mol. Bicyclic structure $q_4$ is produced from $q_3$ with a barrier of 47.5 kcal/mol. The triplet tetrahedrane is not expected to be kinetically stable, since the reverse barrier for $q_4 \to q_3$ is only 5.1 kcal/mol. 1.2-Hydrogen migrations connect $q_1$, $q_2$, and $q_3$. The barrier heights for the $H$ shifts range between 46 and 72 kcal/mol. Interestingly, the more favorable path for the rearrangement of $q_1$ to $q_2$ is not the direct $H$ shift $q_1 \to q_2$ but the multistep mechanism involving ring opening, hydrogen migration, and ring closure: $q_1 \to c_1 \to c_3 \to q_2$.

Dissociation Channels. Numerous hydrogen elimination routes shown in Figure 4 lead from chain and cyclic isomers of triplet $C_4H_3$ to various structures of the $C_3H_2$ radical (Figure 5). Normal $C_3H_2$ ($n-C_3H_2$, $p_1$), the most stable isomer, can be produced from $c_1, c_3, c_4,$ and $c_5$. Our calculations give the CH bond strength in $c_1$ as 53.7 kcal/mol. The reverse reactions $n-C_3H_2 + H$ on the triplet PES are found to have barriers varying from 2.2 kcal/mol to produce $c_1$ to 6.0 kcal/mol to form $c_3$. Transition states for hydrogen splitting shown in Figure 3 all have a late character (close to separated $C_3H_2 + H$) with the CH distances for the breaking bond between 1.9 and 2.3 Å. It is worth mentioning that singlet $C_3H_4$ can be formed from $C_3H_2 + H$ without barrier. The geometry of $n-C_3H_2$ is of special interest. B3LYP/6-311G(d,p) optimization converges to a linear structure of $C_2P$ symmetry which has no imaginary frequencies. However, earlier ab initio MO calculations at different levels of theory showed27 that the linear $C_2P$ structure actually is an inversion transition state and the minimum has a nonlinear geometry. Therefore, we reoptimized the structure of $p_1$ at the CCSD(T)/6-311G(d,p) level and confirmed that $n-C_3H_2$ is nonlinear and the linear geometry corresponds to the transition state. The energy difference between $p_1$ and linear TS is only 255 cm$^{-1}$ at the CCSD(T)/6-311G(d,p) level with ZPE.

The second most stable isomer of $C_3H_2$ is $i-C_3H_2$, about 11 kcal/mol higher than $p_1$. It can be produced in two conformations $p_2$ and $p_2'$ which are very close in energy. $i-C_3H_2$ is formed from $c_3$ and $c_4$ with low exit barriers of 1.4 and 2.7 kcal/mol and from less stable $c_9$ and $c_{10}$ with higher exit barriers (5–7 kcal/mol). In the energetical order, $p_1$ and $p_2$ are followed by cyclic structures of $C_3H_3$, $p_3$, $p_{11}$, and $p_4$ lying.
Three-membered ring $p_3$ is produced from $t_1$ and $t_6$ with exit barriers of 1.4 and 9.7 kcal/mol and from $t_3$ and $t_4$ without exit barriers. $p_4$ which also has a three-membered ring structure can be formed from $t_3$ without reverse barrier and from $t_5$ with small exit barrier of 1.3 kcal/mol. Hydrogen elimination in $q_2$ leads to the four-membered ring $C_4H_3$ isomer $p_{11}$, and no exit barrier was found.
Another chain isomer p5 of the C4H3 radical, 34.2 kcal/mol above p1, can be obtained by hydrogen elimination from c4 (no barrier), c2 (exit barrier of 1.7 kcal/mol), c7 (no barrier), and c8 (0.8 kcal/mol barrier). Slightly less stable three-membered ring structure p9 is formed from t4 without barrier. The chain CH3CCC structure p8, 41.0 kcal/mol less stable than n-C4H3, can react with H on the triplet PES yielding c7 with a barrier of only 0.6 kcal/mol. The other C4H3 isomers, such as chain p7, three-membered ring p6, four-membered ring p12, and bicyclic p10, are 47–58 kcal/mol higher than p1 and their production from triplet C4H4 is significantly endothermic and occurs without barrier. The q1 → p10 + H reaction is an exception; the reverse barrier reaches 11.7 kcal/mol. This can be attributed to that the hydrogen loss in q1 is accompanied with the formation of extra CC bond and the structure changes from a four-membered ring to a bicycle. Indeed, the critical CC distance decreases from 2.10 Å in q1 to 1.79 Å in TS q1-p10 and 1.59 Å in the product. Summarizing, we can say that

Figure 4. Various dissociation pathways for triplet C4H4. The numbers show relative energies (in kcal/mol) for each isomer and dissociation product with respect to C(Πg) + C3H4 (allene), calculated at the G2M(RCC,MP2) level. The numbers marking arrows correspond to the relative energies of dissociation transition states. The notation "n/b" means that a dissociation channel proceeds without an exit barrier.
yielding cyclo-C$_3$H with exit barrier of 3.1 kcal/mol and from singlet (1)
13 distinct isomers of the C$_4$H$_3$ radical can be produced from angles are in degrees) of various local minima for the C$_4$H$_3$ radical. 

**Optimized geometries (bond lengths are in angstroms, bond angles are in degrees) of various local minima for the C$_4$H$_3$ radical.**

Figure 5.

Dissociation products other than C$_4$H$_3$ are also possible. Branching and some three-membered ring structures can lose a carbon atom giving C($^1$P) + C$_3$H$_4$ (allene and propyne) without exit barrier. c2 can eliminate triplet C$_2$ producing ethylene. We will consider the reverse reactions in the subsequent sections. Dissociation of t3 can result in CH$_2$ (t1) + cyclo-C$_2$H$_2$ without barrier and with endothermicity of 61.2 kcal/mol. Methyl radical CH$_3$ can be emitted through the single CC bond cleavage in t4 yielding cyclo-C$_2$H with exit barrier of 3.1 kcal/mol and from c5 and c7 without barrier. The CH$_3$ loss in c5 and c7 leads to the linear C$_2$H isomer. The structure c9 can decompose to the singlet ($^2$Sigma$^+$) and triplet ($^2$B$_2$) acetylenes. This reaction is endothermic by 46.8 kcal/mol and the reverse barrier is only 1.1 kcal/mol. Finally, the unstable isomer c11 fragments to acetylene and triplet ($^2$B$_2$) vinylidene with a barrier of only 0.1 kcal/mol and the energy gain is 1.9 kcal/mol.

We should mention that the B3LYP approach is not always successful in finding dissociation transition states. For some channels we were not able to locate any TS at this level and the B3LYP TS optimization converged to the dissociation products. In this case, we tested the existence or nonexistence of TS’s using MP2/6-311G(d,p) optimization. In most occasions the MP2 and B3LYP results agree. However, two transition states, c5-p8 and c2-C$_2$, were located only at the MP2 level.

**PES of the C($^1$P) + H$_2$CCCH$_2$ Reaction.** Now we are in position to apply our knowledge of the global C$_4$H$_4$ potential energy surface in triplet state to the reactions of our interest. First, we consider the reaction of carbon atom with allene which was recently studied by the crossed molecular-beam technique.$^6$ The profile of PES for this reaction is illustrated in Figure 6. We showed there only energetically preferable channels, other, less important reaction mechanisms can be found on the PES graph in Figure 2.

C($^1$P) can add without entrance barrier to one allenic C≡C bond of H$_2$CCCH$_2$ to form the cyclic isomer t1 which is stabilized by 63.4 kcal/mol with respect to the reactants. t1 ring opens with a barrier of 9.4 kcal/mol to much more stable linear structure c1 which is bound by 96.7 kcal/mol relative to C($^1$P) + allene. In addition, t1 can lose a hydrogen atom yielding the C$_4$H$_3$ isomer p3. This product channel has the overall exothermicity of 13.4 kcal/mol and the exit barrier only 1.4 kcal/mol above c3 + H. c1 can emit a H atom to form the n-C$_4$H$_3$ isomer p1 through a product like transition state located 2.2 kcal/mol above n-C$_4$H$_3$ + H. The reaction exothermicity for this channel is calculated as 43.0 kcal/mol. This amount is available for the translational and internal energy of the products in the molecular-beam experiment.$^9$ c1 can also undergo a 1.2-H migration to form isomer c3. The barrier for this migration lies 36.0 kcal/mol below the reactants but 4.8 kcal/mol higher than the barrier for the hydrogen elimination. c3 can fragment via CH bond cleavage to three different C$_4$H$_3$ isomers, p1, p2, and p7, but the pathway to p7 is overall 15.0 kcal/mol endothermic. The formation of i-C$_4$H$_3$ p2 + H from C($^1$P) + H$_2$CCCH$_2$ has the exothermicity of 32.1 kcal/mol. The exit barriers of the pathways leading from c3 to p1 and p2 are 6.0 and 1.4 kcal/mol, respectively. Hydrogen migrations can continue in c3 leading to c4 and c5, which in turn can eliminate a hydrogen atom forming n- and i-C$_4$H$_3$ as well as some other isomers of this radical. However, our earlier RRKM calculations based on this PES demonstrated$^6$ that the isomerization of c3 is unlikely in the conditions of the molecular-beam experiment and the n- and i-C$_4$H$_3$ products are almost exclusively formed from c1 and c3.

In another reaction, channel C($^3$P) could attack the central carbon atom of the allene molecule without an entrance barrier to form the branching structure b1. The initial reaction step is less exothermic than the one leading to t1; the energy gain is 46.1 kcal/mol. The fate of b1 can be 3-fold if we rule out an H migration to b2$^-$ because it has a very high barrier, 54.7 and 8.6 kcal/mol above b1 and the reactants, respectively. First, the barrier to ring closure yielding t1 is only 3.0 kcal/mol. After the b1 → t1 isomerization, this pathway merges with the channel described in the previous paragraph. Second, a H atom migration combined with a ring closure can form another three-membered ring isomer t3 through the transition state b1-t3, 15.7 kcal/mol above b1. t3 is stabilized by 65.1 kcal/mol with respect to the reactants. CH bond rupture in t3 can yield either the C$_4$H$_3$ isomers p3 or p4. The total reaction exothermicities of the p3 and p4 product channels are 13.4 and 11.2 kcal/mol, respectively. t3 could also ring open through a barrier of 12.1 kcal/mol to c3. Additionally, t3 might split the CH$_2$ group yielding CH$_2$ ($^2$B$_1$) and c-C$_3$H$_2$ without an exit barrier, but the reaction exothermicity is only 3.9 kcal/mol, making this channel unlikely. Third, b1 might undergo a ring closure to form t2 through a barrier of 34.7 kcal/mol. In principle, t2 can show a barrierless CH bond rupture to produce the C$_3$H$_4$ isomer p6, however, this product channel is endothermic by 8.1 kcal/mol and unlikely to happen. The t2 ring opens to isomer c2 (the barrier is 9.6 kcal/mol) prior to CH bond rupture to form the C$_3$H$_4$ isomer p5. The channel leading from C($^3$P) + H$_2$CCCH$_2$ to C$_4$H$_3$ p5 + H is exothermic by 8.8 kcal/mol and the exit barrier is 1.7 kcal/mol. Also, c2 could fragment to C$_3$($^3$Π$_u$) + C$_2$H$_4$, but...
this channel is energetically unfavorable as compared with the formation of p5. We shall address this pathway in detail in the section devoted to the C2(3Πg) + C2H4 reaction. Finally, c2 can isomerize to the four-member ring q1 and then to the chain structure c1 by consecutive ring closure and ring opening with the barriers of 15.0 and 20.3 kcal/mol, respectively. Transition states c2-q1 and q1-c1 lie 18.7 and 29.4 kcal/mol below the reactants.

Our calculations show that a direct insertion of the carbon atom into the allenic CH bond to form c3 cannot occur. The latter can be produced only stepwise after the addition of C(3P) to the C≡C bond or to the central C atom. We also considered earlier6 the possibility of intersystem crossing (ISC) in the reaction leading the system onto the singlet C4H4 PES. ISC can occur in the vicinity of the isomer b1 during its ring closure to t1. Singlet t1 would isomerize to linear butatriene which emits a H atom to form n-C4H3 without exit barrier. However, the derived center-of-mass translational distribution P(Et) for the C4H3 product peaks at 7−12 kcal/mol indicating existence of a transition state for the decomposition of the C4H4 intermediate to the products. On this basis, we concluded earlier6 that if ISC provides a reactive scattering signal of the C(3P) + H2CCCH2 reaction, this contribution is likely small.

The RRKM calculations based on the PES described in this section showed that the major reaction product (more than 98.4%) should be n-C4H3 p1. The dominant portion of p1, 97−99%, is formed directly from the c1 intermediate, and the rest comes from c3, with insignificant contributions from c4 and c5. Therefore, the H migration from c1 to c5 plays a very minor role in the reaction. The second reaction product (less than 1.6% at the experimental collision energies of 4.7 and 9.3 kcal/mol) is i-C4H3 p2 produced predominantly from c3. The results of theoretical calculations are in line with experimental observations in molecular beams.5 For instance, the high energy cutoff of the P(Et) strongly suggest the formation of the n-C4H3 isomer p1 and possibly i-C4H3 p2. The analysis of chemical dynamics for the C(3P) + H2CCCH2 reaction showed that the carbon atom attacks the π-orbital of allene barrierless via a loose, reactant-like transition state located at the centrifugal barrier. The initially formed three-membered ring intermediate t1 rotates in a plane almost perpendicular to the total angular momentum vector around its C-axis and undergoes ring opening to the chain intermediate c1. The latter decomposes via hydrogen atom emission to the n-C4H3 isomer. As the collision energy increases, the approach geometries with a small impact parameter very likely show an enhanced contribution leading possibly to a barrierless attack of C(3P) to the central carbon atom in H2-CCCH2 allene.

**PES of the C(3P) + H2CCCH Reaction.** The calculated profile of PES for the reaction of carbon atom with methyl-acetylene (propyne) is illustrated in Figure 7 where we show only the channels preferable by energy. At the initial reaction step, five distinct isomers of triplet C4H4 can be formed without an entrance barrier. C(3P) can add to the acetylenic C≡C bond in H2CCCH to yield cyclic isomers t4 and t4′ which are stabilized by 50.8 and 52.8 kcal/mol, respectively, relative to the reactants. t4 would rapidly rearrange to t4′ since the barrier separating them is only 1.3 kcal/mol. t4′ ring opens with a barrier of 14.7 kcal/mol to the stable chain structure c5, H2-CCCH, which is bound by 89.2 kcal/mol with respect to C(3P) + propyne. In addition, t4 and t4′ can lose a hydrogen atom from two different positions (from the methyl group and from the ring CH) yielding the C4H3 isomers p3 and p9. Both H eliminations occur without an exit barrier, and the calculated exothermicities for the C4H3 product channels are 12.8 kcal/mol for p3 and 7.5 kcal/mol for p9. c5 can emit an H atom from CH3 to form the n-C4H3 isomer p1 through the transition state c5-p1 located 5.8 kcal/mol above p1 + H. The reaction exothermicity to produce n-C4H3 + H from C(3P) + H2CCCH is 42.4 kcal/mol. Hydrogen emission from the CH group in c5 would result in C3H3 p8. This channel is overall exothermic by 1.4 kcal/mol and has an exit barrier of 0.7 kcal/mol. Due to unfavorable energetics, the formation of p8 is unlikely. c5 can also show a 1,2-H shift to form isomer c4. The barrier for this rearrangement, 50.8 kcal/mol relative to c5, lies 38.4 and 1.8 kcal/mol below the reactants and the transition state for the H elimination to n-C4H3. In turn, c4 can decompose via CH bond cleavage to three different isomers of C4H3, p1, p2, and p5. The p1 channel is the most favorable; it has a reverse barrier of 7.0 kcal/mol. This is followed by the p2 channel, 31.5 kcal/mol exothermic for the C(3P) + H2CCCH reaction and with the exit barrier of 2.7 kcal/mol. The channel leading to p5 is
the least preferable but still exothermic by 8.2 kcal/mol with no exit barrier. Further isomerization of \textit{c4} by the hydrogen scrambling to \textit{c3} and \textit{c1} is unlikely to play a significant role in the reaction, since the \textit{c4} \rightarrow \textit{c3} barrier is higher than that for \textit{c4} \rightarrow \textit{p1}. The pathways connecting \textit{c4} with \textit{t6}, \textit{c8}, and \textit{q2} may have lower barriers, but these structures would rather isomerize back to \textit{c4} or \textit{c3} than yield some different products. For instance, if \textit{t6} is formed from \textit{c4}, the reverse barrier back to \textit{c4} is only 2.2 kcal/mol, while the barriers to produce \textit{t1}, \textit{t3}, \textit{t4}, \textit{c8}, or \textit{p3} are significantly higher, 41.6, 44.9, 44.6, 13.9, and 42.4 kcal/mol, respectively. If \textit{c8} is produced, the barrier to go back to \textit{c4} is 6.5 kcal/mol and that to form \textit{q2} is 10.3 kcal/mol. The other possibilities are less likely; the barriers for isomerization of \textit{c8} to \textit{t6}, \textit{c9}, \textit{c2}, and \textit{c6} as well as for dissociation of \textit{c8} to \textit{p5} and \textit{p7} are in the range of 19–60 kcal/mol. From \textit{q2}, it is much easier to go to \textit{c3} with a barrier of 29.6 kcal/mol than in any other direction.

In another initial reaction channel C(3P\textsubscript{j}) could attack the CH carbon atom of the propyne molecule to form the chain isomer \textit{c6}, H\textsubscript{1}CCCHC. In principle, two conformations of the C atoms are possible in H\textsubscript{1}CCCHC, cis, like in \textit{c6}, and trans. However, the attempts to optimize the trans structure both at the B3LYP and MP2 levels resulted in \textit{t4}, indicating that the trans conformation does not exist. It is worth mentioning that the cis conformation \textit{c6} also collapsed to \textit{t4} at the B3LYP level but MP2 optimization gives a local minimum. Therefore, the transition state \textit{c6}-t4 was also computed at MP2/6-311G(d,p). \textit{c6} is stabilized by 32.7 kcal/mol relative to the reactants but is very unstable kinetically. The barrier for the H shift from CH to the terminal carbon atom to yield \textit{c5} is as low as 0.2 kcal/mol. \textit{c6} also can easily show ring closure to give \textit{t4} with a barrier of 4.4 kcal/mol. Other hydrogen migrations in \textit{c6}, i.e., \textit{c6} \rightarrow \textit{c7}, \textit{c6} \rightarrow \textit{c3}, and \textit{c6} \rightarrow \textit{c8}, require significantly higher barriers. In Figure 7, we showed only one of these channels, with the lowest barrier of 16.6 kcal/mol. It leads to the H\textsubscript{1}CCCHCC isomer \textit{c7}, 53.4 kcal/mol below the reactants. Methyl hydrogen splitting from \textit{c7} gives the C\textsubscript{4}H\textsubscript{3} isomer \textit{p5} without exit barrier. Emission of the CH hydrogen which takes place with an exit barrier of 0.6 kcal/mol is unfavorable since it yields the C\textsubscript{4}H\textsubscript{3} isomer \textit{p8}, only 1.4 kcal/mol below the reactants. Further hydrogen migration in \textit{c7} to \textit{c2} is unlikely because of a high barrier.

Addition of C(3P\textsubscript{j}) to the carbon atom connected to CH\textsubscript{3} gives trans and cis branching structures \textit{b2}′ and \textit{b2}, 29.8 and 27.8 kcal/mol below the reactants, respectively. \textit{b2}′ undergoes ring closure to \textit{t4}′ with a barrier of only 0.5 kcal/mol. On the other hand, a ring closure accompanied with a hydrogen migration leads \textit{b2} and \textit{b2}′ to the three-membered ring isomers \textit{t5} and \textit{t5}′ with barriers of 6.5 and 8.3 kcal/mol, respectively. \textit{t5} and \textit{t5}′ are stabilized by 63.4 and 62.4 kcal/mol with respect to the reactants. On the next step \textit{t5} show ring opening to yield \textit{c4} with a low barrier of 4.4 kcal/mol. Hydrogen emission from the CH\textsubscript{2} group in \textit{t5} and \textit{t5}′ gives the C\textsubscript{4}H\textsubscript{3} isomer \textit{p4}, and the exit barrier for this process is calculated as 1.3 kcal/mol. The overall exothermicity of the \textit{p4} + H product channel is 10.6 kcal/mol. The rupture of the out-of-ring CH bond in \textit{t5} and \textit{t5}′ occurring without exit barrier is less likely, since the C\textsubscript{4}H\textsubscript{3} + H product lie 8.7 kcal/mol above the reactants. Also, a 1,3-H shift connecting \textit{t5} with \textit{t1} is not feasible because of a very high barrier.
CH3 + C2H products can be formed by the single CC bond cleavage in t4, c5, and c7. In the case of t4, cyclic C2H is formed with an exit barrier of 3.1 kcal/mol and the exothermicity of the C(3P) + HCCCH — CH3 + C-C-H reaction is calculated to be 9.1 kcal/mol. For c5 and c7, the emission of CH3 occurs without an exit barrier, and the total exothermicity for the CH3 + I-C-H channel is 6.7 kcal/mol. Due to unfavorable energetics, the formation of CH3 + CH2 would play at best a minor role in the reaction of C(3P) with propyne. Similarly to the reaction with allene, a direct insertion of the carbon atom into the acetylenic or methyl CH bonds does not occur; the corresponding transition states could not be found. On the other hand, the insertion into the acetylenic bond is nearly direct: C(3P) + H3-CCH — C6 + H3, where the addition intermediate is metastable and separated from c5 by a tiny barrier. The insertion into a methyl CH bond of propyne would give c10. Instead, c10 can be formed by multistep pathways where most of transition states lie below the reactants: ... → c5 → c4 → c3 → q2 → c10 and ... → c6 → c7 or c8 → c10. Finally, note that no C2H4 intermediates relevant for this reaction fulfills requirements for intersystem crossing,5,7 so we do not consider the singlet PES here.

From the experimental study of the C(3P) + H3CCH reaction in crossed molecular beams,3 a conclusion was made that the reaction proceeds by the carbon atom attack to the π-orbitals of methylacetylene via a loose reactant-like transition state at the centrifugal barrier with initial formation of triplet 1-methylpropadienylidene complex c6. c6 rotates in a plane almost perpendicular to the total angular momentum vector around the B/C axis and undergoes a H migration to triplet 1-methylpropargylene c5. Within 1–2 ps, the latter decomposes via CH-bond cleavage to n-C3H4. The initial intermediates b2, b2′, t4, and t4′ were considered less likely because of uneven spin density distribution on two triply bound carbons and the sterical hindrance of the CH4 group which reduces the cone of acceptance at the α-C-atom and the range of reactive impact parameters. For instance, a simultaneous attack of C(3P) to α- and β-C-atoms to produce t4 or t4′ would give maximum impact parameter of 0.6 Å, while only narrow range of impact parameters between 1.19 and 2.24 Å actually contributes to the reactive scattering signal. From the PES presented here, it is difficult to judge what are relative initial concentrations of the b2, b2′, c6, t4, and t4′ intermediates in the reaction, since all of them are formed exothermically without entrance barrier. Further studies including variational RRKM are needed to address this question.

At higher collision energies for both C3H4 isomers, crossed molecular beam data show almost identical data, indicating the two reactions produce similar products, major n-C3H4 and minor i-C3H4. The result is in line with the reaction PES which shows that the formation of n-C3H4 through intermediate c5 is most favorable energetically and i-C3H4 can be reached via intermediate c4. At lower collision energies, the center of mass distributions differ significantly,5 indicating that the reactions of carbon atom with propyne and allene form distinct isomers. On the basis of the high energy cutoff of the center of mass translational energy distribution, the authors suggested the formation of a higher energy isomer, possibly a cyclic one. On the basis of the present calculations, we can suggest that this isomer could be p3 which can be produced from t4′ without exit barrier. Formation of p4 is much less likely because it has to go through the t5 intermediate formed from b2. However, b2 would rather isomerize to t4 than to t5. In the reaction with allene (Figure 6) the p3 product can be generated from t1. The ring-opening barrier in t1 is 5.3 kcal/mol lower than the corresponding barrier for t4′. Therefore, the lifetime of t4′ should be longer than that of t1, so the former might have enough time to emit a hydrogen atom. To quantify our consideration of the product branching ratios in the C(3P) + HCCCH reaction, detailed RRKM calculations are now underway for different collision energies and with variation of initial concentrations of the b2, b2′, c6, t4, and t4′ intermediates.

**PES of the C2(t1)+ + C2H4 Reaction.** First, we look into the question what is the relative energy of C2(t1)+ + C2H4 with respect to C2(3P)+ + HCCCH which was chosen as zero on the PES map shown in Figure 2. From experimental heats of formation,28 the C(3P)+ + HCCCH → C2(3Σ+)+ + C2H4 reaction is exothermic by 2.9 kcal/mol. Experimentally,29 the t1 state of C2 lies 2 kcal/mol higher in energy than 3Σ+, so the C(3P)+ + HCCCH → C2(t1)+ + C2H4 reaction exothermicity is 0.9 kcal/mol. At the G2M(RCC,MP2) level, we found that the reaction leading to the singlet C2 is exothermic by 9.8 kcal/mol, while that leading to the triplet C2 is endothermic by 1.3 kcal/mol. Thus, in this approximation the energy gap between C2 3Σ+ and t1 is greatly overestimated. G2(M-RCC,MP2) includes RCCSD(T)/6-311G(d,p), MP2/6-311G(d,p), and MP2/6-311+G(3df,2p) calculations in order to estimate the RCCSD(T)/6-311+G(3df,2p) energy. The energy difference between 3Σ+ and t1 is computed as 2.4 kcal/mol at RCCSD(T)/6-311G(d,p) and 0.8 and 6.5 kcal/mol at MP2 with smaller and larger basis sets, respectively. Thus, the MP2 method performs unsuccessfully for C2, which could be foreseen taking into account a multireference character of the wave function in the carbon dimer. The singlet—triplet energy gap in C2 at G2M(M-RCC,MP2) is further exaggerated due to the HLC correction.13,14 The 3Σ+ state formally has an extra electron pair as compared to t1, so the HLC correction adds 3 kcal/mol into the stabilization of singlet C2. On the other hand, the coupled cluster method provides satisfactory results; the RCCSD(T)/6-311+G(3df,2p) calculated 3Σ+—t1 energy gap in C2 is 1.8 kcal/mol. Therefore, we used this level to compute the energy difference between C(3P)+ and allene and C2H4 + C2 in singlet and triplet states. The results, 5.3 and 3.5 kcal/mol for C2 3Σ+ and t1, respectively, overestimate the experimental exothermicities by ~2.5 kcal/mol, which is close to the accuracy usually expected for the heats of reactions from the G2-type methods. Hence, we use for C2(t1)+ + C2H4 the RCCSD(T)/6-311+G(3df,2p) relative energy in comparison with G2M(RCC,MP2) relative energies for the other species on the triplet C2H4 PES. The comparison is warranted since G2M(RCC,MP2) approximates the RCCSD(T)/6-311+G(3df,2p) energy, but the correction scheme fails for C2. Mention also that the HLC correction is not present in relative energies because all species on the PES have the triplet multiplicity.

Now we turn to the PES of the C2(t1)+ + C2H4 reaction shown in Figure 8. In principle, a C2 molecule can add to a C atom of ethylene yielding the triplet C2H5 isomer e2 or to the CC π-bond in a perpendicular or parallel manner producing three-membered ring t2 and four-membered ring q1, respectively. Addition to the carbon atom occurs with an entrance barrier at the transition state c2-C2 (3A′, C′). This is an early TS with forming CC bond distance of 2.12 Å. C2 is located in the plane perpendicular to the C2H4 plane, so the carbon dimer attacks the π-system of ethylene. The entrance barrier height is calculated to be 4.6 and 3.7 kcal/mol at the RCCSD(T)/6-311G-
The parallel addition of C₂(³Πₐ) to the π-bond of ethylene within C₂ᵥ geometry is symmetry-forbidden. In this case, the two components of the C₂(³Πₐ) state split into ³A₁ and ³B₁ states for C₂ + C₂H₄ at infinite separation, while the electronic state of C₂H₄ q₁ is ³B₂. The perpendicular approach can be formally symmetry-allowed; the ³Πₐ state of C₂ splits into the ³B₂ and ³B₁ components for C₂ + C₂H₄ and the electronic state of the product t₂ is ³B₂. However, the electronic configurations for the two ³B₂ states are different: 8a₁⁶a₂¹²b₂¹³b₂⁻¹ for C₂(³Πₐ) + C₂H₄ and 7a₁⁶a₂¹³b₂⁻¹⁴b₂⁻¹ for t₂, so an electron pair has to be moved from the a₁ orbital to b₂. Therefore, q₁ and t₂ can be formed from the reactants either via a seam of crossing or avoided crossing (for the perpendicular approach) of two different electronic states or via nonsymmetric transition states. We located two minima on the seams of crossing, MSX₁ and MSX₂, shown in Figure 9. MSX₁ corresponds to the perpendicular approach where the avoided crossing of two ³B₂ states with different electronic configurations takes place. MSX₂ is related to the parallel approach and is a minimum on the ³A₁-³B₂ seam of crossing. We took the ³A₁ component of the ³Πₐ state of C₂ because it is lower in energy than the ³B₁ component at finite separations between C₂ and C₂H₄. The calculations were carried out at the B3LYP/6-31G(d,p) level using the SEAM program. At this level, MSX₁ and MSX₂, respectively, lie 31.7 and 14.1 kcal/mol higher than the reactants C₂(³Πₐ) + C₂H₄. The result indicates that the direct formation of t₂ or q₁ from the reactants with C₂ᵥ symmetry cannot compete with the formation of c₂ where the entrance barrier is only ~4 kcal/mol. When we tried to search for nonsymmetric transition states leading from the reactants to t₂ or q₁, the optimization converged to TS c₂-C₂ connecting C₂(³Πₐ) + C₂H₄ with the isomer c₂. Thus, the three- and four-membered ring addition complexes are most likely to be formed indirectly, via the chain structure c₂.

Besides emitting a H atom to yield the C₄H₃ isomer p₅ (5.3 kcal/mol below the reactants), there are two major pathways for c₂ isomerization. First, c₂ can show ring closure to t₂, which in turn would rearrange to b₁ and then t₁, and c₁. This path was described in detail when we addressed PES for the C(³P) + H₂CCCH₂ reaction. c₁ loses a hydrogen atom to produce n-C₄H₃ p₁ with overall exothermicity of 39.5 kcal/mol. The highest barrier on this pathway is located at TS b₁-t₂, 22.5 kcal/mol above t₂ but 7.9 kcal/mol below the reactants. The second route from c₂ to c₁ involves the four-member ring isomer q₁. The ring closure from c₂ to q₁ requires a barrier of 15.0 kcal/mol, and the corresponding transition state is 15.2 kcal/mol lower in energy than the reactants. Then, q₁ undergoes ring...

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**Figure 8.** Profile of potential energy surface for the C₂(³Πₐ) + C₂H₄ reaction calculated at the G2M(RCC,MP2) level.

**Figure 9.** Optimized geometries of the minima on the seams of crossing of two triplet electronic states corresponding to the perpendicular and parallel approach of C₂(³Πₐ) toward C₂H₄ within C₂ᵥ symmetry.
opening along the CH₂-CH₂ bond to yield c₁ with a barrier of 20.3 kcal/mol. The two pathways leading from c₂ to c₁ are expected to compete, and further RRKM calculations are required to quantify their roles in the C₂(3Πu) + C₂H₂ reaction. The other channels of rearrangement of c₂ by hydrogen migrations to c₇, c₈, or c₁₀ have significantly higher barriers than the ring closure and are not expected to play any important role.

From PES shown in Figure 8, we can conclude that for the C₂(3Πu) + C₂H₂ reaction, similarly to C(3P) + allene, n-C₄H₃ + H should be the major product, with possible minor production of i-C₄H₃ via the c₁ → c₃ → p₂ channel. Other isomers of C₄H₃ which might be produced are p₃, p₄, and p₅, but their contribution is not expected to be significant. Of other products, in principle, acetylene could be formed in pair with triplet vinylidene H₂CC(3B₂): q₁ → c₁ → c₃ → q₂ → c₁₁ → C₂H₂ + H₂CC(3B₂), or with triplet acetylene (3B₂): q₂ → q₃ → e₉' → C₂H₂ + C₂H₂(3B₂) or c₂ → c₈ → c₉ → C₂H₂ + C₂H₂(3B₂). Although the two acetylene channels in the C₂(3Πu) + C₂H₂ reaction are exothermic by 9.6 and 12.9 kcal/mol, we do not expect them to compete with the channels yielding n- and i-C₄H₃ because of unfavorable energetic barriers. Detailed RRKM calculations are now underway to predict product branching ratios at various collision energies.

Recent molecular-beam experiments for the C₂ + C₂H₄ reaction⁸ show n-C₄H₃ as the dominant product, and the experimental TOF spectra could be fitted in terms of contributions from two reactions C₃(1Σ⁺g) + C₂H₄ and C₃(3Πu) + C₂H₄. We shall address the experimental data, the results of RRKM calculations for the triplet PES, and the singlet potential energy surface elsewhere.⁸

Conclusions

We have studied the global potential energy surface of C₄H₃ in the lowest triplet electronic state. Twenty eight distinct isomers are located as well as 66 transition states for various isomerization and dissociation pathways. The most stable structures for triplet C₄H₃ are aromatic cyclobutene q₃ (3A₁g,Dₐb) and linear butyne c₁ (3E,Dₐb) lying 0.4 kcal/mol higher in energy than q₃. Other local minima include chains, branching configurations, three- and four-membered rings, and a bicyclic structure. Isomerization mechanisms in triplet C₄H₃ involve hydrogen migrations and ring opening/closures. At triplet PES, C₄H₃ can dissociate to C(3P) + C₂H₄, C₃(3Πu) + C₂H₄, C₂H₄ (thirteen different isomers) + H, CH₂ (3B₁) + c-C₃H₄, CH₃ + l/c-C₃H, and C₂H₂ (1Σ⁺g) + C₂H₂ (3B₂)/H₂CC (3B₂).

The information about the global PES is applied to describe the potential energy surfaces for the C(3P) + H₂CCCH₃, C(3P) + H₂CCCH, and C₃(3Πu) + C₂H₄ reactions, recently studied in crossed molecular-beam experiments.⁵,⁶ The reaction of the carbon atom with allene is shown to occur by the addition of C to the allenic C=C bond to yield the three-membered ring structure t₁ or (in a less extent) to the central carbon atom of allene to form the branching structure b₁ which isomerizes to t₁ with a low barrier. t₁ undergoes ring opening to c₁, and the latter emits a H atom to give n-C₄H₃, the major reaction product. The minor reaction product, i-C₄H₃, is formed through a 1,2-H shift in c₁ leading to c₃ followed by the hydrogen loss.

The reaction of the carbon atom with methylacetylene starts with the C addition to the β-C-atom of H₂CCCH to form c₆, to the α-C-atom to give b₂ or b₂', or to the acetylenic C≡C bond to yield the cyclic isomers t₄ or t₄'. According to experimental impact parameters,⁶ the formation of c₆ at the initial reaction step is most probable. c₆ is metastable and would rearrange to the linear isomer e₅ or to the cyclic t₄ and then to t₄' with low barriers. b₂ and b₂' should also rapidly isomerize to t₄'. The latter ring opens to e₅ with the barrier of 14.7 kcal/mol. The major reaction product n-C₄H₃ is formed through the methyl hydrogen emission in e₅. The second product i-C₄H₃ can be reached via a H-shift from c₅ to c₄ and subsequent hydrogen elimination. Cyclic isomers C₄H₃ p₃ and p₄ (formation of those was postulated from the experimental crossed molecular-beam measurements⁵) can originate from t₄, t₄', and t₅. Further RRKM calculations are required to quantify the product branching ratios in the reaction of C(3P) with propyne.

The reaction of C₃(3Πu) with ethylene proceeds through the C₂ addition to a carbon atom of C₂H₂ to yield the chain isomer c₂ with an entrance barrier of ~4 kcal/mol. c₂ rearranges to linear c₁ in two steps via the four-membered ring intermediate q₁: c₂ → q₁ → c₁, or by a multistep mechanism involving three-member ring structures: c₂ → t₂ → b₁ → t₁ → c₁. c₁ loses an H atom to yield n-C₄H₃ or undergoes a hydrogen migration to c₃ following by a H emission producing n- or i-C₄H₃. Similarly to the C(3P) + allene reaction, n-C₄H₃ is expected to be the major product of C₃(3Πu) + C₂H₄, while i-C₄H₃ to give a minor contribution.

Acknowledgment. This work supported by Academia Sinica and in part by the National Science Council of ROC under Grant NSC 8902113-M-001-034. A partial support from the Petroleum Research Fund of the Republic of China is also appreciated. The authors thank the reviewers for their valuable corrections.

JA9935299