Ab Initio MO Study of the Triplet C_3H_4 Potential Energy Surface and the Reaction of $C(^3P_j)$ with Ethylene, C_2H_4

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The potential energy surface for the reaction of $C(^3P_j)$ with ethylene, $C_2H_4(X^1A_g)$, has been investigated using the G2M method. Structures of the stationary points and transition states for various isomerization and dissociation pathways of triplet C_3H_4 have been studied. The results show that at the initial step of the $C(^3P_j) + C_2H_4(X^1A_g)$ reaction carbon atom attacks the π-orbital of the C_2H_4 molecule yielding cyclopropylidene **i1** without entrance barrier. **i1** then isomerizes to the triplet allene **i3** via ring opening. The latter either splits a hydrogen atom producing the propargyl radical **p3** + H or undergoes a 1,2-H shift to vinylmethylene, which in turn gives H_2CCCH (**p3**) + H. The propargyl radical is concluded to be a nearly exclusive product of the $C(^3P) + C_2H_4$ reaction. At the internal energy of 9.2 kcal/mol above the reactants level, Rice−Ramsperger−Kassel−Marcus calculations show about 93% of H_2CCCH comes from fragmentation of triplet allene and 7% from vinylmethylene. The formation of $CH_2(^3B_1) + C_2H_2$ via the vinylmethylene intermediate gives only 2% of the reaction products; the formation of triplet $C_3H_2 + H_2$ is unlikely. This study completes a comprehensive investigation of the $C(^3P_j) + C_2H_4$ reaction; its rate constants have been measured in a broad temperature range from 10 to 800 K, the reaction dynamics has been unraveled by crossed molecular beam experiments, and the reaction potential energy surface has now been explored by ab initio calculations.

Introduction

The formation of various structural isomers of hydrocarbon radicals and their reactivities are relevant to chemical processes in hydrocarbon-rich planetary atmospheres,[1] outflow of dying carbon stars, interstellar clouds, hot molecular cores,[2] and in combustion chemistry.[3] The propargyl radical in its $^2B_1$ ground state has received considerable attention. The recombination of two propargyl radicals (2-propynyl, H_2CCCH), followed by unimolecular rearrangement, is now considered as a principle source of the first aromatic ring. This mechanism, proposed by Wu and Kern,[4] is supported by numerous experimental results and theoretical calculations.[5−13] The analogous reaction of C_3H_3 with C_3H_2 species might be involved in part to form the phenyl radical.[9] In addition, the 2-propynyl radical is expected to be present in flames in relatively high abundance owing to its stability with respect to pyrolysis and its low reactivity[3c,5,10] toward molecular oxygen and other closed shell species due to delocalization of the unpaired electron.[14] Current combustion models postulate that soot formation and synthesis of polyaromatic hydrocarbons (PAHs) are strongly correlated and initiated by recombination of two C_3H_3 radicals to C_6H_6 isomers [$k(295\ \mathrm{K}) = 1.2 \cdot 10^{-10}\ \mathrm{cm^3\ s^{-1}}$] followed by stepwise ring growth to large PAHs.[9] The rate constant for the mutual reaction of propargyl was determined by Alkemade et al.[5] as $5.6 \cdot 10^{-11}\ \mathrm{cm^3\ s^{-1}}$ at 650 K and 2.3−4.5 Torr, and by Morter et al.[10] as $1.2 \pm 0.2 \cdot 10^{-10}\ \mathrm{cm^3\ s^{-1}}$ for 298 K and 16 Torr using IR absorption spectroscopy. However, the synthetic route to form the propargyl is far from being characterized satisfactorily. Some reactions were suggested,[3d,15,16] such as the reactions of $CH(X^2\Pi)$ and $CH_2(a^1A_1)$ with C_2H_2, the thermal decomposition of C_3H_4 via C−H bond rupture. For instance, Peeters et al.,[16a] reporting the first spectroscopic observation of $CH_2(a^1A_1)$ in a hydrocarbon flame and discussing its formation, has first put forward the fast reaction $CH_2(a^1A_1) + C_2H_2 \rightarrow C_3H_3 + H$ as a source of higher poly-unsaturated hydrocarbons in flames. Earlier, this elementary reaction was kinetically characterized by Canosa-Mas et al.[16b] Besides its relevance in combustion chemistry, the propargyl isomer is expected to exist in interstellar and planetary environments.[1,2,17] The results of Herbst et al.[18] for the reaction of $C(^3P_j) + C_2H_4$ in a generic chemical model of the circumstellar envelope surrounding the evolved star IRC + 10216 postulate the existence of a C_3H_3 product, but did not outline the particular isomers.

Previous mechanistic information on the C/C_2H_4 system was derived from radioactive tracer studies of suprathermal $^{11}C(^3P_j)$ and $^{11}C(^1D_2)$ recoil atom reactions with C_2H_4, C_2D_4, C_2H_4/O_2, and C_2H_4/Ne mixtures under bulk conditions.[19−28] Recently, the rate constants for the gas-phase $C(^3P) + C_2H_4$ reaction were measured at low temperatures down to 15 K.[29] In addition, crossed molecular-beam experiments of $C(^3P) + C_2H_4$ yield compelling evidence of the propargyl radical product.[30] Our goal in this article is to investigate the global potential energy surface (PES) for the triplet C_3H_4 system. This will provide a deeper, detailed insight into the reaction mechanism, surmising the most important reaction channels and predicting branching ratios of various products based on Rice−Ramsperger−Kassel−Marcus (RRKM) calculations.

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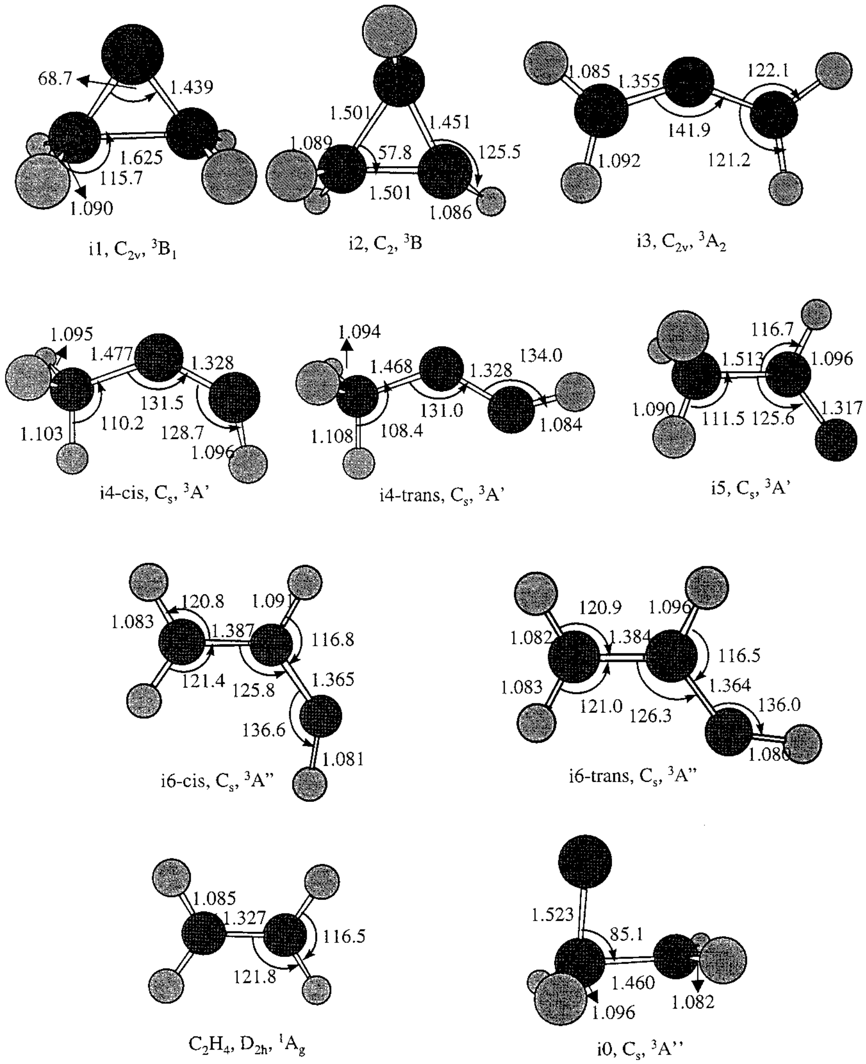


i1, C_{2v}, $^3B_1$ i2, C_2, ^3B i3, C_{2v}, $^3A_2$

i4-cis, C_s, $^3A'$ i4-trans, C_s, $^3A'$ i5, C_s, $^3A'$

i6-cis, C_s, $^3A''$ i6-trans, C_s, $^3A''$

C_2H_4, D_{2h}, ^1A_g i0, C_s, $^3A''$

Figure 1. Optimized geometries (bond lengths are in angstroms; bond angles are in degrees) of various local minima for triplet C_3H_4. Symmetry point groups and electronic states are also shown.

Computational Methods

The geometries of various isomers of the triplet C_3H_4, transition states for isomerization and dissociation, and the C_3H_3 dissociation products, have been optimized using the hybrid density funtional B3LYP method[31] with the 6-311G(d,p) basic set.[32] Vibrational frequencies calculated at the same 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 a minimum (number of imaginary frequencies, NIMAG = 0) or a transition state (NIMAG = 1). When necessary, intrinsic reaction coordinate (IRC) calculations have been performed to confirm the identity of a transition state and the two equilibrium structures it connects. All the energies quoted and discussed in this article include the ZPE correction. In some cases mentioned in discussion, geometries and frequencies were also calculated at the MP2/6-311G(d,p)[33] level.

To obtain more reliable energy of the most important equilibrium structures and transition states, we used the G2M-(RCC,MP2) method,[35] which gives an approximation to the RCCSD(T)/6-311+G(3df,2p)[34] energy. The expected accuracy of this and other G2-type calculational schemes is within 1−2 kcal/mol.[35−38] The Gaussian 98[39] program was used for the calculations.

According to the RRKM theory,[40] rate constant $k(E)$ at available energy E for a unimolecular reaction $A^* \rightarrow A^\# \rightarrow P$ can be expressed as

$$k(E) = \frac{\sigma}{h}\cdot\frac{W^\#(E - E^\#)}{\rho(E)},$$

where σ is the symmetry factor, $W^\#(E - E^\#)$ denotes the total number of states of the transition state (activated complex) $A^\#$ with the barrier $E^\#$, $\rho(E)$ represents the density of states of the reactant molecule A^*, and P is the product or products. The saddle point method[40] was applied to evaluate $\rho(E)$ and $W(E)$. The RRKM calculations were performed for zero-pressure conditions, because no energy transfer by collisions occurs in crossed molecular beam experiments, and for different internal energies in excess of the reactants zero-point level.

Results and Discussion

Optimized structural parameters at the B3LYP/6-311G(d,p) level are displayed in Figures 1, 2, and 3. The intermediates and the dissociation products (C_3H_3) are denoted with the letters **i** and **p**, respectively. The notation tsxy designates a transition state (ts), connecting equilibrium structures x and y. Calculated total, zero-point vibrational, and relative energies for all structures obtained at various levels of theory are summarized

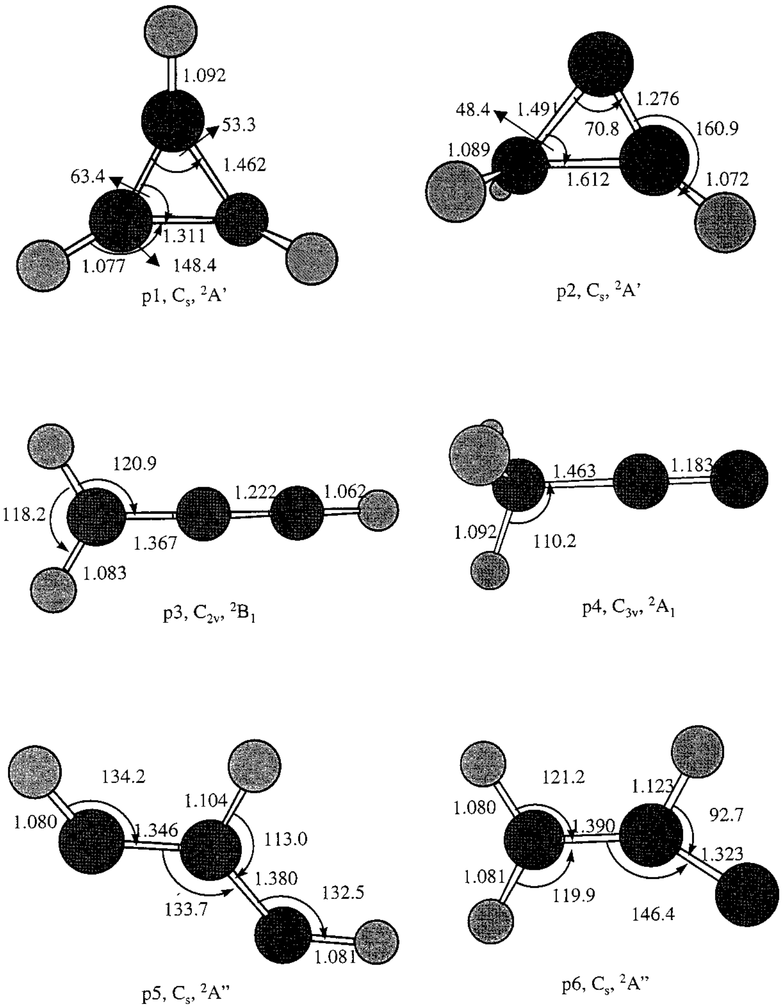


Figure 2. Optimized geometries (bond lengths are in angstroms; bond angles are in degrees) of various C_3H_3 radicals. Symmetry point groups and electronic states are also shown.

in Table 1. Table 2 shows vibrational frequencies calculated at the B3LYP/6-311G(d,p) level. Table 3 compiles RRKM rate constants for different initial internal energies above the reactants zero-point level. Table 4 presents branching ratios for distinct reaction channels.

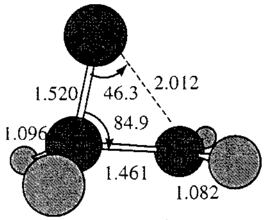
A. Stationary Points on the Triplet C_3H_4 Surface. The most stable triplet C_3H_4 isomer **i3** has C_{2v} symmetry and $^3A_2$ electronic state. It is bound by 81.9 kcal/mol with respect to the separated reactants, $C(^3P) + C_2H_4$, cf. Figure 4. Triplet allene has been a subject of numerous investigations by ab initio methods.[41−46] Calculations by Seeger et al.[41] indicated that it has a planar C_{2v} open-shell structure with 3π electrons. Further studies[47] showed the lowest triplet state of allene is $^3A_2$ with the electronic configuration as $(4b_2)^2(1b_1)^2(6a_1)^1(1a_2)^1$, which lies 2.4 kcal/mol higher than the corresponding excited singlet state ($^1A_2$). Theoretical studies by Jackson et al.[48] gave the adiabatic singlet−triplet separation for allene as 50.8 kcal/mol at the CCSD(T)/6-311+G(3df,2p) level with B3LYP/6-311G-(d,p) ZPE corrections. The geometry we obtained (Figure 1) does not differ markedly from those reported earlier.[46,48−49]

Triplet *cis*/*trans*-vinylcarbenes or vinylmethylenes are the next stable structures. **i6-cis** and **i6-trans** have C_s ($^3A'$) symmetry and can be obtained by 1,2-H-migrations in triplet allene or methylacetylene. The results of Yoshimine et al.[50] showed that the triplet vinylmethylene has two isoenergetic minima (*cis* and *trans*), which have allylic planar structures and lie 45.9 kcal/mol above the X^1A_1 state of methylacetylene. Theoretical investigation by Feller et al.[51] together with experimental observations[52,53] also indicated the presence of two similar *cis*- and *trans*-isomers. The discussions centered on whether the triplet ground state may best be described as a delocalized carbene with an allylic π structure. All our calculated geometric parameters compare well with the theoretical values of Yoshimine et al.[50b] At the G2M level, *cis*/*trans*-vinylcarbenes lie 1.4 and 1.1 kcal/mol higher than allene, respectively.

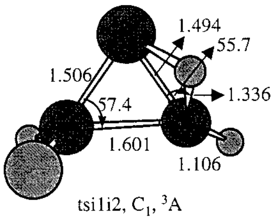
Triplet cyclopropylidene (**i1**) has C_{2v} symmetry and a $^3B_1$ electronic state and is 30.2 kcal/mol less favorable than **i3**. The triplet cyclopropylidene has been a subject of many investigations.[50a,54−55] The studies of Rauk et al.[47] showed that **i1** has the electronic configuration $(1a_2)^2(5a_1)^2(3b_2)^2(6a_1)^1(2b_1)^1$, and the singlet−triplet separation energy was calculated at the HF/6-31G* level as 38.5 kcal/mol. This result is far from those of Bettinger et al.,[49] who obtained ΔE_{ST} as 14.0, 14.9, and 11.1 kcal/mol at the B3LYP/TZP, CCSD(T)/TZ2P, and MR−CISD/TZ2P levels, respectively. Our B3LYP results are very close to those of Bettinger et al.[49]

Several articles have reported the geometry of singlet cyclopropene[50,56] with C_{2v} symmetry. However, up to now, the triplet cyclopropene has not been studied. The energy calculated at the G2M level for cyclopropene (**i2**) with C_2 symmetry (^3B), is only 2.4 kcal/mol higher than that of cyclopropylidene (**i1**).

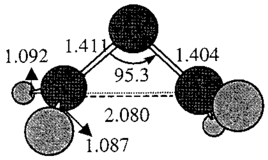
The next two isomers, *cis*- and *trans*-methylacetylene (**i4-cis** and **i4-trans**), have C_s symmetry, the $^3A'$ electronic state, and lie 33.1 and 40.3 kcal/mol higher in energy than triplet allene



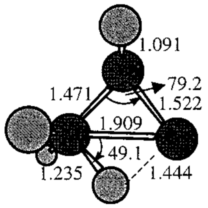
tsi0i1, C_s, $^3A''$



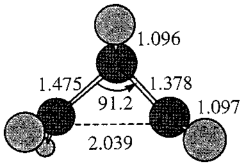
tsi1i2, C_1, ^3A



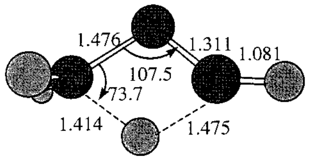
tsi1i3, C_1, ^3A



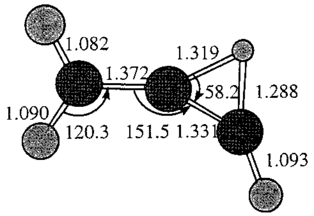
tsi2i5, C_1, ^3A



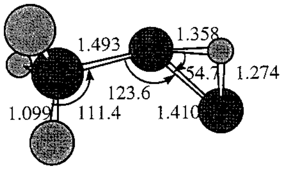
tsi2i6, C_1, ^3A



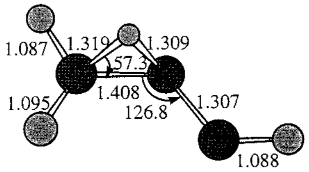
tsi3i4, C_s, $^3A'$



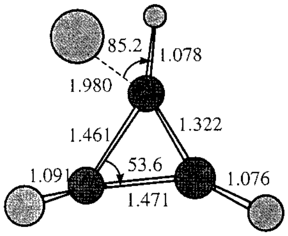
tsi3i6, C_s, $^3A''$



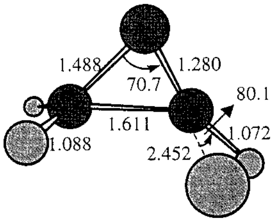
tsi4i5, C_1, ^3A



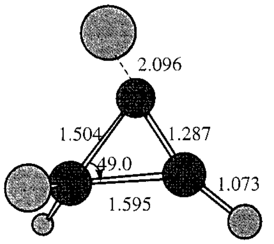
tsi4i6, C_1, ^3A



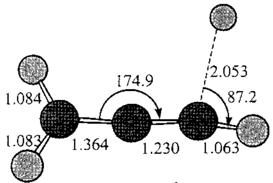
tsi2p1, C_1, ^3A



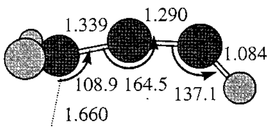
tsi1p2, C_1, ^3A



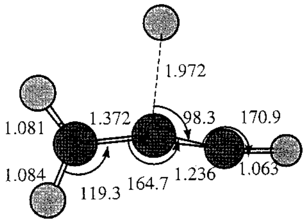
tsi2p2, C_1, ^3A



tsi3p3, C_s, $^3A''$



tsi4p3, C_1, ^3A



tsi6p3, C_s, $^3A''$

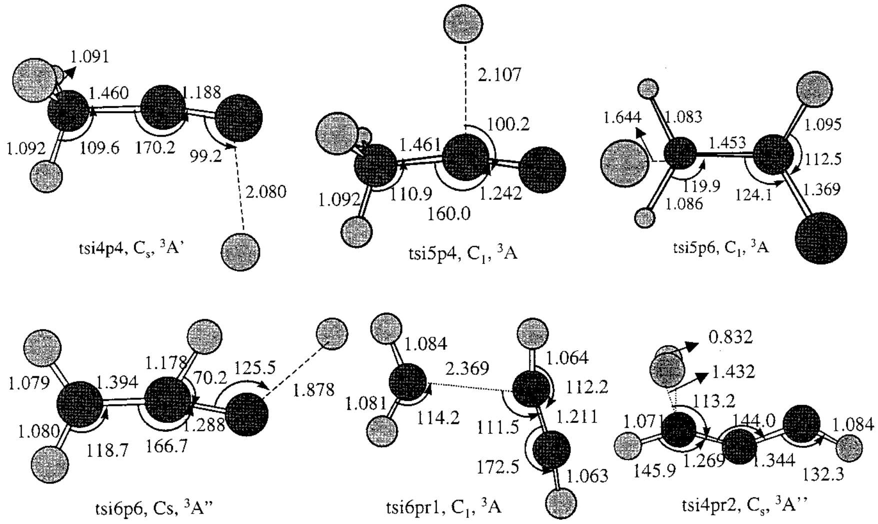


Figure 3. Optimized geometries (bond lengths are in angstroms; bond angles are in degrees) of various transition states. Symmetry point groups and electronic states are also shown.

TABLE 1: Calculated Total, Zero-point Vibrational, and Relative Energies of the C_3H_4, C_3H_3 Isomers, Transition States for C_3H_4 Isomerization and Dissociation, Calculated at Different Levels of Theory

species	B3LYP 6-311G(d,p)	ZPE (kcal/mol)	MP2 6-311G(d,p)	CCSD(T) 6-311G(d,p)	MP2 6-311+G(3df, 2p)	G2M[a] (kcal/mol)
reactants	−116.46997	31.88	−116.08918	−116.15038	−116.15017	0.0
i0	−116.51284	31.91	−116.11881	−116.18025	−116.18556	22.3
i1	−116.56112	34.28	−116.17898	−116.23020	−116.24629	51.7
i2	−116.55773	33.40	−116.17216	−116.22410	−116.24042	49.3
i3	−116.61429	32.69	−116.21169	−116.27339	−116.28152	81.9
i4-cis	−116.55546	33.14	−116.16546	−116.22364	−116.23296	48.8
i4-trans	−116.54312	33.11	−116.15311	−116.21184	−116.22086	41.6
i5	−116.54049	33.74	−116.15063	−116.21535	−116.21480	40.9
i6-cis	−116.60994	33.15	−116.21254	−116.27409	−116.28009	80.5
i6-trans	−116.61060	32.99	−116.21275	−116.27439	−116.28034	80.8
p1 + H	−116.48597	26.55	−116.11140	−116.15501	−116.18088	13.6
p2 + H	−116.47125	26.96	−116.09013	−116.14327	−116.15842	5.0
p3 + H	−116.53952	25.69	−116.14676	−116.20428	−116.21611	45.3
p4 + H		29.38	−116.08288	−116.14174	−116.14986	0.8
p5 + H	−116.41553	23.73	−116.01983	−116.08318	−116.08560	31.0
p6 + H	−116.46180	24.66	−116.06505	−116.12941	−116.13241	1.9
pr1	−116.51917	27.70	−116.14377	−116.19343	−116.20891	33.8
pr2	−116.55127	22.22	−116.13982	−116.20994	−116.20749	51.2
tsi0i1	−116.51259	31.71	−116.11909	−116.18027	−116.18587	22.6
tsi1i2	−116.47640	31.12	−116.09059	−116.14244	−116.16106	1.7
tsi1i3	−116.53723	31.21	−116.14593	−116.20148	−116.21572	38.3
tsi2i5	−116.46718	30.47	−116.07783	−116.13553	−116.14498	4.0
tsi2i6	−116.51308	31.17	−116.10766	−116.17720	−116.17668	22.6
tsi3i4	−116.50283	29.60	−116.11056	−116.16800	−116.17945	18.3
tsi3i6	−116.52921	28.78	−116.12497	−116.18665	−116.19613	32.2
tsi4i6	−116.50438	30.26	−116.10380	−116.16402	−116.17430	16.1
tsi5i4	−116.47525	29.59	−116.07917	−116.14150	−116.14644	0.7
tsi1p2	−116.47141	27.46	−116.08601	−116.14145	−116.15470	3.6
tsi2p1	−116.48331	27.48	−116.09635	−116.14834	−116.16720	9.3
tsi2p2	−116.46861	27.51	−116.08677	−116.13712	−116.15542	0.9
tsi3p3	−116.53770	26.67	−116.14447	−116.19794	−116.21460	40.8
tsi4p3	−116.50139	27.69	−116.09179	−116.16110	−116.16164	16.5
tsi6p3	−116.53554	26.56	−116.13060	−116.19584	−116.20013	39.2
tsi4p4		30.34	−116.07639	−116.13465	−116.14462	3.8
tsi5p4		30.1	−116.07179	−116.13769	−116.13860	2.5
tsi5p6	−116.42846	27.63	−116.05521	−116.12680	−116.12213	6.8
tsi6p6		25.57	−116.06528	−116.12698	−116.13487	3.0
tsi4pr2		30.01	−116.05901	−116.12516	−116.13076	7.2
tsi6pr1	−116.51381	28.77	−116.12016	−116.18301	−116.18673	27.1

[a] Relative energies.

(**i3**). As seen in Scheme 1, the $H_3C{-}C$ distances are close to each other with a difference of 0.003 Å, but the C−CH distance in singlet methylacetylene[57] is 1.190 Å as compared with 1.328 Å in the triplet state. Further, the $\angle H_1C_1C_2$ angle bends to 128.7°, because two unpaired electrons in the triplet methylacetylene are delocalized at different carbon atoms, C_1 and C_2. The **i4-cis** to **i4-trans** isomerization occurs by the hydrogen in-plane scrambling rather than by rotation around the double C−C bond. **i4-trans** lies 7.2 kcal/mol higher in energy than **i4-cis**.

TABLE 2: Unscaled B3LYP/6-311G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) of the Various Intermediates, Products, and Transition States on the Triplet C_3H_4 PES

species	frequencies (cm^{-1})
i0	131, 430, 432, 802. 826, 941, 1031, 1133, 1204, 1452, 1488, 2986, 3048, 3157, 3264
i1	675, 793, 805, 982, 1029, 1046, 1049, 1053, 1272, 1454, 1486, 3049, 3052, 3113, 3121
i2	670, 697, 786, 840, 935, 997, 1072, 1086, 1105, 1289, 1436, 3066, 3122, 3130, 3138
i3	304, 444, 744, 762, 766, 902, 1019, 1138, 1393, 1458, 1471, 3050, 3060, 3178, 3178
i4-cis	211, 369, 612, 897, 950, 995, 1074, 1374, 1437, 1461, 1708, 2948, 3024, 3076
i4-trans	181, 335, 607, 855, 952, 1023, 1094, 1369, 1409, 1462, 1695, 2895, 3044, 3077, 3166
i5	162, 464, 585, 915, 960, 1064, 1279, 1393, 1478, 1480, 1600, 3010, 3019, 3069, 3123
i6-cis	400, 510, 642, 785, 845, 949, 1022, 1203, 1232, 1410, 1493, 3097, 3141, 3221, 3238
i6-trans	423, 528, 562, 794, 825, 906, 1013, 1210, 1237, 1416, 1501, 3032, 3147, 3238, 3246
p1	614, 695, 885, 915, 978, 985, 1032, 1236, 1663, 3047, 3238, 3284
p2	632, 645, 768, 879, 1005, 1042, 1079, 1506, 1767, 3061, 3142, 3332
p3	351, 403, 470, 639, 680, 1031, 1089, 1455, 2011, 3141, 3232, 3467
p4	399, 399, 994, 1080, 1080, 1431, 1508, 1508, 2660, 3103, 3194, 3194
p5	130, 361, 491, 718, 772, 931, 1154, 1212, 1417, 2952, 3228, 3236
p6	88, 444, 676, 705, 807, 1041, 1148, 1472, 1582, 2851, 3167, 3272
tsi0i1	122i, 428, 433, 802, 826, 940, 1033, 1131, 1203, 1452, 1487.5, 2984, 3045, 3156, 3264
tsi1i2	1952i, 646, 777, 816, 898, 963, 1020, 1059, 1204, 1321, 1512, 2256, 3034, 3093, 3174
tsi1i3	574i, 110, 669, 765, 823, 899, 956, 1097, 1234, 1419, 1463, 3044, 3060, 3144, 3152
tsi2i5	771i, 406, 708, 773, 910, 1004, 1092, 1124, 1222, 1296, 1406, 2096, 3059, 3069, 3149
tsi2i6	1244i, 497, 618, 667, 777, 844, 1008, 1061, 1217, 1277, 1452, 3005, 3028, 3122, 3230
tsi3i4	1805i, 403, 616, 619, 910, 954, 955, 1013, 1070, 1435, 1566, 1698, 3082, 3173, 3213
tsi3i6	2148i, 179, 349, 542, 728, 763, 850, 1009, 1084, 1451, 1583, 2277, 3027, 3079, 3212
tsi4i6	1482i, 379, 505, 687, 923, 961, 1040, 1138, 1193, 1447, 1488, 2097, 3018, 3200, 3163
tsi5i4	1073i, 153, 398, 478, 852, 952, 966, 1329, 1353, 1442, 1446, 2199, 2979, 3051, 3104
tsi1p2	155i, 142, 193, 645, 651, 789, 878, 1006, 1045, 1075, 1503, 1737, 3064, 3146, 3333
tsi2p1	605i, 293, 401, 608, 751, 887, 914, 968, 973, 1046, 1215, 1592, 3057, 3235, 3281
tsi2p2	581i, 210, 338, 586, 652, 787, 880, 987, 1009, 1076, 1496, 1680, 3066, 3152, 3323
tsi3p3	1546i, 280, 392, 458, 591, 598, 664, 972, 1040, 1055, 1471, 2053, 3194, 3306, 3455
tsi4p3	1558i, 262, 350, 571, 574, 748, 805, 1026, 1060, 1112, 1445, 1967, 3101, 3168, 3181
tsi6p3	655i, 154, 423, 436, 448, 482, 621, 703, 1028, 1084, 1453, 1903, 3146, 3247, 3454
tsi4p4	1124i, 81, 278, 420, 519, 1008, 1067, 1089, 1426, 1502, 1505, 2836, 3102, 3193, 3199
tsi5p4	1009i, 195, 431, 481, 587, 974, 1076, 1086, 1428, 1505, 1508, 2289, 3102, 3197, 3199
tsi5p6	1608i, 200, 312, 570, 694, 917, 957, 982, 1072, 1238, 1428, 1540, 3072, 3122, 3220
tsi6p6	1088i, 239, 255, 444, 454, 494, 584, 829, 1032, 1113, 1482, 1742, 2630, 3233, 3355
tsi4pr2	2359i, 257, 478, 510, 646, 876, 954, 956, 1108, 1495, 1749, 2061, 3236, 3244, 3424
tsi6pr1	345i, 63, 207, 334, 358, 594, 636, 757, 768, 1128, 1965, 3096, 3315, 3408, 3494

TABLE 3: RRKM Rate Constants in s^{-1} at Internal Energies of 0.0, 4.1, and 9.2 kcal/mol above the Reactants Zero-point Level

	0.0 kcal/mol	4.1 kcal/mol	9.2 kcal/mol
k_1	1.49×10^{13}	1.79×10^{13}	2.18×10^{13}
k_2	9.17×10^{6}	8.41×10^{7}	5.25×10^{8}
k_3	8.03×10^{11}	1.17×10^{12}	1.76×10^{12}
k_4	6.49×10^{10}	1.08×10^{11}	1.86×10^{11}
k_{-4}	2.51×10^{10}	4.14×10^{10}	7.15×10^{10}
k_5	2.08×10^{8}	4.99×10^{8}	1.24×10^{9}
k_6	7.67×10^{11}	1.18×10^{12}	1.85×10^{12}
k_7	1.50×10^{11}	2.87×10^{11}	5.74×10^{11}

TABLE 4: Product Yield in Percent at Internal Energies of 0.0, 4.1, and 9.2 kcal/mol above the Reactants Zero-point Level

	0.0 kcal/mol	4.1 kcal/mol	9.2 kcal/mol
H_2CCCH^a	6.1	6.6	7.1
H_2CCCH^b	92.7	91.8	90.7
$CH_2(^3B_1) + C_2H_2$	1.2	1.6	2.2

[a] From **i6**. [b] From **i3**.

The least stable triplet C_3H_4 isomer, propenylidene (**i5**), has C_s symmetry and a $^3A'$ electronic state. No experimental data are available on the multiplicity of the ground state for this structure. Several theoretical calculations by Honjou et al.[50a] indicated that the closed-shell $^1A'$ state is 41 kcal/mol more stable than the open-shell $^3A'$ state. Our G2M-calculated results show that triplet propenylidene is less stable than triplet allene by about 41 kcal/mol.

B. Stationary Points on Doublet C_3H_3 Surface. The geometrical parameters of the C_3H_3 isomers are shown in Figure 2. Our computed results are very close to those of Vereecken et al.[58] In this article, six different isomers have been confirmed. The most stable structure is 2-propynyl (**p3**) with C_{2v} symmetry and the $^2B_1$ electronic state. 2-Propynyl + H lies 36.6 kcal/mol higher in energy than allene. The next two cyclic isomers are cycloprop-2-enyl (**p1**) and cycloprop-1-enyl (**p2**). Theoretical studies by Chipman and Miller,[59] Collin et al.[60] and Vereecken et al.[58] provided results similar to our calculations. We predict **p1** and **p2** to be 31.7 and 40.3 kcal/mol higher than **p3**, respectively. The next isomer in the order of energies is 1-propynyl radical, **p4**. Our earlier calculations[61] showed that in the ground electronic state **p4** has C_{3v} symmetry and $^2A_1$ electronic term. At the G2M level 1-propynyl is less stable than 2-propynyl (**p3**) by 44.5 kcal/mol.

A less stable C_3H_3 isomer, 2-propene-1-yl-3-ylidene (**p6**), has C_s symmetry and the $^2A''$ electronic state. 2-Propene-1-yl-3-ylidene is 47.2 kcal/mol less favorable than **p3**. At last, we surveyed the least stable C_3H_3 isomer, 1-propene-1-yl-3-ylidene (**p5**) with C_s symmetry ($^2A''$). According to our calculations, **p5** lies 76.3 kcal/mol above **p3**, compared with 76.5 kcal/mol reported by Walch[62] for the *cis-cis* geometry.

C. The Pathways of C_3H_4 Isomerization. The isomerization mechanisms of C_3H_4 in singlet electronic state have been carefully studied.[50,56] In this article, we focus on the isomerization and dissociation mechanisms of C_3H_4 in the triplet electronic state which are related to the $C(^3P) + C_2H_4$ reaction. Kaiser et al.[30] suggested that a carbon atom can add to the double bond of ethylene forming the triplet cyclopropylidene without an entrance barrier. Our calculations have confirmed this conclusion. In addition, we investigated another mechanism

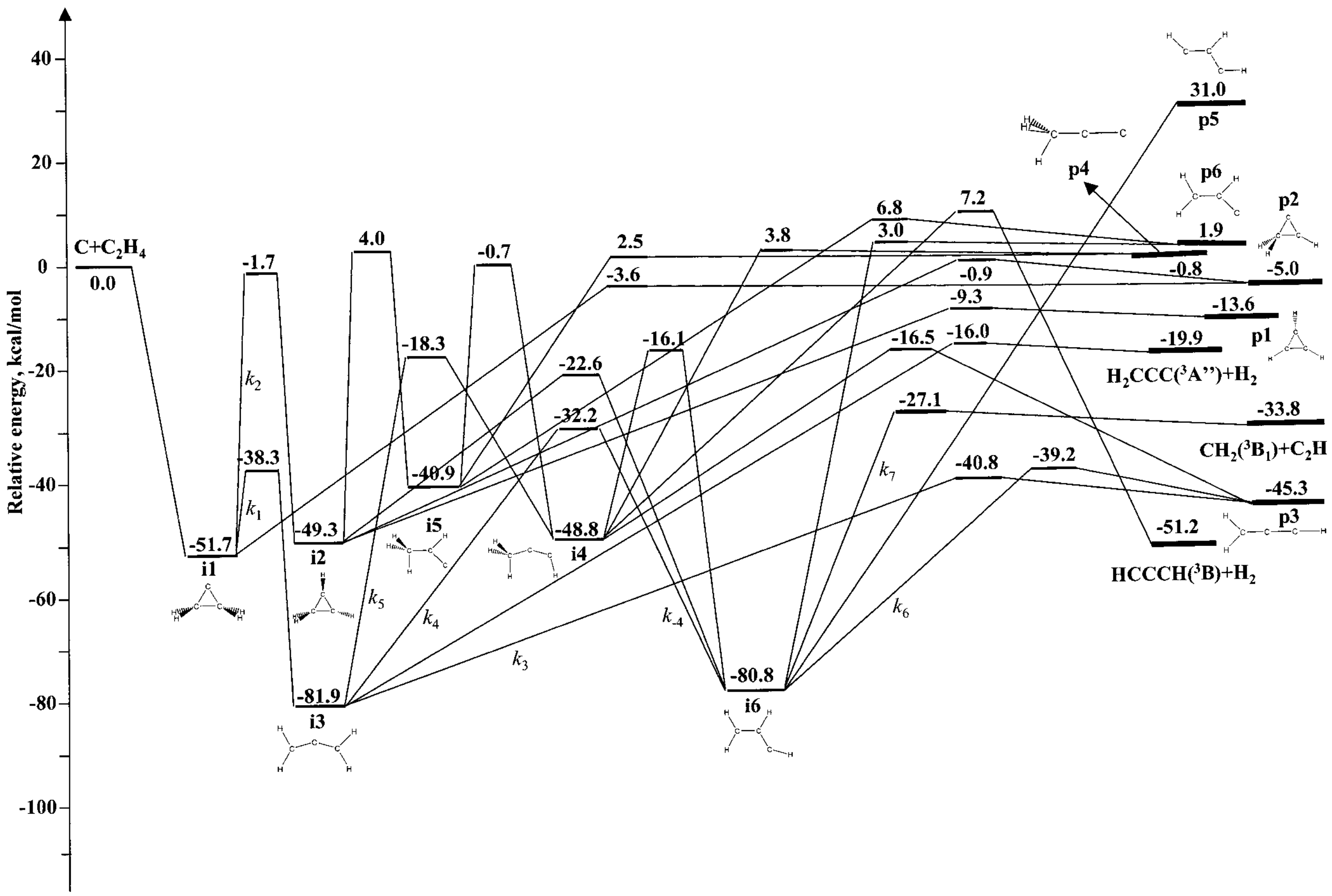
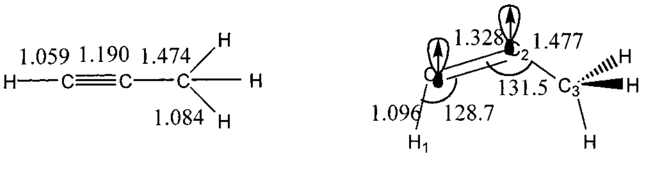


Figure 4. Schematic potential energy surface of the $C(^3P_j) + C_2H_4(X^1A_g)$ reaction. The relative energies are calculated at the G2M(RCC,MP2) level.

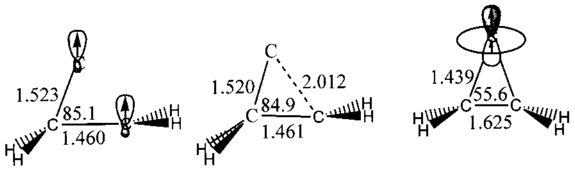
SCHEME 1



C_{3v}, $^1A_1$

C_s, $^3A'$

SCHEME 2



i0

tsi0i1

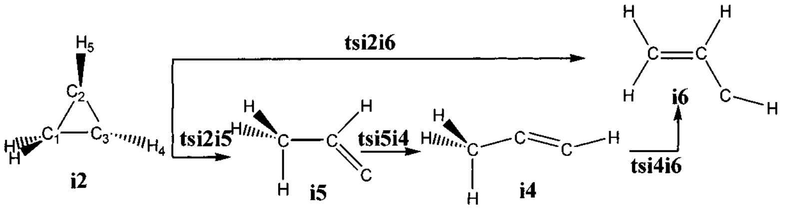
i1

where C (^3P) attacks the ethylene π-bond yielding a 1,3 radical tricarbon chain structure (labeled as **i0**) without a barrier. Scheme 2 shows the conversion between **i0** and **i1** through **tsi0i1**. The geometrical parameters of **i0** are very close to those of **tsi0i1**. If ZPE corrections are included, **i0** lies 0.1 and 0.3 kcal/mol above **tsi0i1** at the B3LYP/6-311G(d,p) and G2M levels, respectively. This indicates that **i0** is not stable and instantly rearranges to **i1**.

Cyclopropylidene (**i1**) can isomerize by the ring opening to allene (**i3**) or by the 1,2-H shift to cyclopropene (**i2**). The results by Rauk et al.[47] at the HF/3-21G level indicated that the isomerization of triplet cyclopropylidene to triplet allene is hindered by a barrier of 23.7 kcal/mol. Our more accurate calculations show that the barrier for the cyclopropylidene-to-allene rearrangement is 13.4 kcal/mol, whereas that for the reverse reaction is 43.6 kcal/mol. The rearrangement of cyclopropylidene to cyclopropene by 1,2-H migration through **tsi1i2** occurs with a barrier of 50.0 kcal/mol, which is 36.6 kcal/mol higher than that for the cyclopropylidene-to-allene isomerization. This means that the route via allene is much more favorable than the pathway via cyclopropene. Triplet allene can be converted to *cis*/*trans* triplet vinylmethylene by 1,2-hydrogen migration. The structure of the corresponding **tsi3i6** (Figure 3) has C_s symmetry and electronic state $^3A''$. Barriers for the 1,2-hydrogen migration typically are in the range of 40−60 kcal/mol. In this case, the conversion from **i3** to **i6** has a barrier of 49.7 kcal/mol. Vinylmethylene (**i6**) can also be formed from **i3** by undergoing a 1,3-H shift to yield methylacetylene (**i4**) followed by 1,2-H migration to **i6** with a barrier of 32.7 kcal/mol. However, barrier for the 1,3-hydrogen shift from **i3** to **i4** is fairly high, about 63.6 kcal/mol.

Cyclopropene (**i2**) can isomerize to vinylmethylene (**i6**) either via a one-step path by ring opening or by a stepwise mechanism, as shown in Scheme 3. The barrier for the reaction from **i2** to **i6** is calculated as 26.7 kcal/mol. In the stepwise mechanism, cyclopropene first undergoes a 1,2-hydrogen shift accompanied with a cleavage of the bond C_1–C_3 to yield propenylidene (**i5**) with a barrier of 53.3 kcal/mol. Isomers **i5** and **i4** are connected by transition state **tsi5i4**, which lies about 17.6 kcal/mol higher in energy than **tsi3i4**. The 1,2-H shift is also possible in **i4**, directly yielding **i6** with a barrier of 32.7 kcal/mol. The transition state connecting cyclopropylidene (**i1**) and cyclopropene (**i2**) is located 36.6 kcal/mol above that leading to triplet allene (**i3**) (see Figure 4).

SCHEME 3



D. The Pathways for C_3H_4 Dissociation. The mechanisms of the C_3H_4 dissociation leading to different doublet C_3H_3 isomers are shown in Figure 4. The most stable isomer, propargyl radical (**p3**), can be produced from **i3**, **i6**, and **i4**. Our calculations give the CH bond strength in **i3** as 36.6 kcal/mol. The reverse reaction **p3** + H on the triplet PES has barriers of 4.5 kcal/mol to produce **i3**, 6.1 kcal/mol to form **i6**, and 28.8 kcal/mol to yield **i4**. Transition states for hydrogen splitting shown in Figure 3 all have a late, product-like character (close to separated C_3H_3 + H) with the CH distances for bond breaking between 2.1 and 2.0 Å, except **tsi4p3** and **tsi5p6,** which exhibit a much earlier character.

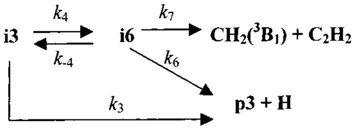
Cycloprop-2-enyl (**p1**) and cycloprop-1-enyl (**p2**) lie 31.7 and 40.3 kcal/mol higher than **p3**. Cycloprop-2-enyl (**p1**) is produced from cyclopropene (**i2**) with an exit barrier of 4.3 kcal/mol. Cycloprop-1-enyl (**p2**) also has a three-member ring structure and can be formed from **i2** with an exit barrier of 4.1 kcal/mol and from **i1** with an exit barrier of about 1.4 kcal/mol.

The other chain isomers **p4** and **p6** are located 44.5 and 47.2 kcal/mol higher in energy than **p3**. 1-Propynyl (**p4**) can be obtained by hydrogen elimination from **i4** with an exit barrier of 4.6 kcal/mol and from **i5** with a smaller barrier of 3.3 kcal/mol. 2-Propene-1-yl-3-ylidene (**p6**) is also produced from **i5** with an exit barrier of 4.9 kcal/mol. **p6** can react with H on the triplet PES yielding **i6** with a barrier of only 1.1 kcal/mol. The least stable isomer, 1-propene-1-yl-3-ylidene (**p5**), lies 76.3 kcal/mol higher than **p3** and can be formed by barrierless hydrogen loss in **i6**.

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 transition state at this level, and the B3LYP transition state optimization converged to the dissociation products. In this case, we tested the existence or nonexistence of transition states using MP2/6-311G(d,p) optimization. In most occasions the MP2 and B3LYP results agree, but three transition states, **tsi4p4**, **tsi6p6**, and **tsi4pr2**, were located only at the MP2 level. More definite conclusions about the existence of these transition states can be made using higher level geometry optimization, for example, by the quadratic configuration interaction including single and double excitations (QCISD) method. However, because they do not lie on the most important reaction pathway, we did not explore this question further.

In addition, we considered other channels leading to fragmentation products $CH_2(^3B_1)$ + HCCH (**pr1**), $HCCCH(^3B)$ + H_2 (**pr2**), and H_2CCC (C_s, $^3A''$) + H_2 (**pr3**). The product **pr1** lies 11.5 kcal/mol above **p3** and is formed by breaking C−C bond in **i6**. Our calculation give the CC bond strength in vinylmethylene as 47.0 kcal/mol. The $HCCCH(^3B)$ + H_2 products (**pr2**) lie 51.2 kcal/mol below the reactants and can be formed by the molecular hydrogen elimination from **i4**. However, the barrier for H_2 loss from **i4** to **pr2** is fairly high, about 56.0 kcal/mol. At last, molecular hydrogen elimination from the triplet allene is also possible.[48] The products, H_2CCC (C_s, $^3A''$) + H_2, lie 19.9 kcal/mol below the reactants, $C(^3P)$ + C_2H_4, and the exit barrier was calculated as 3.9 kcal/mol.

SCHEME 4



E. Most Favorable Mechanism of the $C(^3P)$ + C_2H_4 Reaction. According to the schematic potential energy surface for $C(^3P)$ + C_2H_4 (see Figure 4), the reaction starts with addition of the carbon atom to the π-bond of ethylene yielding a cyclopropylidene without barrier. **i1** can isomerize to triplet allene **i3** or to triplet cyclopropene **i2**. However, the latter process is very unlikely because it has a barrier 36.6 kcal/mol higher than that for the former. This conclusion is confirmed by the RRKM rate coefficients in Table 3. Triplet allene dissociates to propargyl **p3** + H with a barrier of 41.1 kcal/mol or isomerizes to vinylmethylene **i6**; the isomerization to methylacetylene **i4** and the elimination of H_2 are much slower (Table 3). Intermediate **i6** in turn will dissociate to **p3** + H with a barrier of 41.6 kcal/mol, whereas other **i6** pathways cannot compete. Thus, the $C(^3P)$ + C_2H_4 reaction is expected to almost exclusively produce the propargyl radical H_2CCCH and a hydrogen atom. Formation of C_3H_2 + H_2 is highly unlikely and indeed was not observed in the crossed molecular beam experiment.[30]

Using the rate constants k_3, k_4, k_{-4} (**i6** → **i3**), and k_6 (**i6** → **p3** + H), we solved the kinetic rate equations for the reaction scheme shown in Scheme 4: using the steady-state approximation.[40] The results (Table 4) show that at initial internal energy 9.2 kcal/mol above the reactant level, 97.8% of the reaction products are p3 + H which are produced mostly from the triplet allene (90.7%) and from the vinylmethylene **i6** (7.1%). The formation of $CH_2(^3B_1)$ + C_2H_2 gives only 2.2% of the reaction products.

Collision energy in a crossed molecular beam experiment never converts solely into vibrational energy of the initial adduct, but goes for a part depending on the total angular momentum into rotational energy with a quite different effect on the microcanonical rate constant. Therefore, the internal energy above the reactants zero-point level is somewhat lower than collision energy and when J-distribution for the individual encounters is not known, RRKM theory by itself may not predict the outcome of crossed molecular beam experiments accurately. Meanwhile, according to Table 4, the calculated branching ratios are not sensitive to the initial internal energy above the reactants in the range of 0−9.2 kcal/mol.

F. Comparison with the Crossed Beam Reaction of $C(^3P_j)$ with C_2H_4. Recently, the reaction of ground-state carbon atoms, $C(^3P_j)$, with ethylene was studied at two collision energies of 4.1 and 9.2 kcal/mol under single-collision conditions using the crossed molecular beams technique. Only the atomic carbon versus hydrogen atom replacement was observed; no molecular hydrogen elimination could be sampled. In strong agreement with our electronic structure calculations, a forward-convolution fitting of the experimental data yielded compelling evidence on the formation of the propargyl radical in its $^2B_1$ electronic ground state via a distinct exit transition state.

The reaction dynamics inferred from the experimental data indicate two microchannels, both initiated by attack of the carbon atom to the π-orbital of the ethylene molecule via a loose, reactant-like transition state located at the centrifugal barrier. Following C_s symmetry on the ground state $^3A''$ surface, the initially formed triplet cyclopropylidene complex rotates in a plane roughly perpendicular to the total angular momentum vector around its *C*-axis, undergoes ring opening to triplet allene, and decomposes via hydrogen emission through a distinct transition state to the propargyl radical. The initial and final orbital angular momenta $\mathbf{L}$ and $\mathbf{L}'$ are weakly coupled and result in an isotropic center-of-mass angular distribution. A second microchannel arises from A-like rotations of the cyclopropylidene complex, followed by ring opening and H-atom elimination. In this case, a strong $\mathbf{L}$ - $\mathbf{L}'$ correlation leads to a forward-scattered, center-of-mass angular distribution.

Both the experimental and theoretical approaches are highly complementary. The crossed beam experiments could not identify the minor contribution from a decomposing vinylmethylene intermediate **i6**, as well as formation of $CH_2(^3B_1) + C_2H_2$, whereas our theoretical investigation fails to account for the direct reaction mechanism via triplet allene complexes rotating around their *A*-axis. This is a typical example of synergistic information based on a combined crossed beam and theoretical study of an elementary reaction relevant to chemistry in extraterrestrial environments and combustion processes.

G. Implications to Interstellar Chemistry. The explicit identification of the propargyl product in the reaction of atomic carbon with ethylene represents an alternative, one-step approach to build up carbon-bearing molecules in interstellar environments and hydrocarbon flames. Hitherto postulated ion−molecule reactions

$$\begin{aligned} C_2H_4 + C^+ &\rightarrow c{-}C_3H_3^{\;+} + H \\ &\rightarrow c{-}C_3H_2^{\;+} + H_2 \\ &\rightarrow l{-}C_3H_2^{\;+} + H_2 \end{aligned}$$

have larger rate constants with $k(C^+ + C_2H_4;\ 293\ K) = 1.2 \pm 0.1 \cdot 10^{-9}\ cm^3\ s^{-1}$ than the atom neutral reaction $k(C + C_2H_4;\ 293\ K) = 2.0 \pm 0.1 \cdot 10^{-10}\ cm^3\ s^{-1}$. But because neutral carbon is more abundant that singly ionized carbon atoms,[63] these data compensate the advantage of the rate of ion−molecule reactions as compared with atom-molecule reactions. In addition, the neutral−neutral reaction forms the propargyl radical in one step compared with successive binary encounters in ion−molecule reactions. Therefore, our findings strongly suggest that the title reaction can form propargyl isomer in interstellar environments.

Conclusions

The reaction between a ground-state carbon atom, $C(^3P_j)$, and ethylene, $C_2H_4(X^1A_g)$, was studied by using the G2M(RCC,-MP2) method. The potential energy surface related to the $C(^3P) + C_2H_4$ reaction, the structures for the stationary points and transition states, and the dissociation pathways of the triplet C_3H_4 leading to various radical C_3H_3 isomers + H have been investigated. We can conclude that at the initial step of the $C(^3P_j) + C_2H_4(X^1A_g)$ reaction the carbon atom attacks the π-orbital of the C_2H_4 molecule yielding cyclopropylidene without entrance barrier. **i1** then isomerizes to the triplet allene **i3** by ring opening. The latter either splits a hydrogen atom producing the propargyl radical **p3** + H or undergoes to a minor amount a 1,2-H shift to vinylmethylene, which in turn gives H_2CCCH (**p3**) + H through a hydrogen atom elimination. The propargyl radical is concluded to be a nearly exclusive product of the $C(^3Pj) + C_2H_4$ reaction, with a minor contribution (2%) of the $CH_2(^3B_1) + C_2H_2$ products. The $C(^3P_j) + C_2H_4(X^1A_g)$ reaction is not thermodynamically controlled because the thermodynamically most favorable reaction pathway to $HCCCH(^3B)$ was not observed.

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