Theoretical Study of the $SC_3H_m^+$ Systems, $m = \{3, 4\}$

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A comprehensive theoretical study of the potential energy surfaces of the lowest-lying doublet and quartet electronic states of the $SC_3H_4^+$ system has been performed by means of a combination of density functional and ab intio methods. The potential energy surfaces corresponding to the lowest doublet and quartet electronic states have turned out to be extremely complex. Twenty-six doublet species and twenty-four quartet species have been identified, some of them having several stable conformations. The quartet states are normally much higher in energy than the doublet states. The absolute minimum is the methylthioketene cation, but the 2H-thiete cation, the thioacrolein cation, and the methylthiirene cation lie very close in energy; all of them are doublet states. The most stable quartet species is the thioxyallyl cation. In addition, a rather detailed analysis of the fragmentation of this system has been made. All of the products that are obtained in the $S^+ + CH_3CCH$ reaction, which is an important step in the generation of sulfur-containing cumulenes of astrophysical significance, have been included in this analysis, namely, a number of states of the $SC_3H_3^+$, HCS^+, $C_3H_3^+$, C_2H_3, and $C_3H_4^+$ systems. Special attention has been paid to the $SC_3H_3^+$ system. In addition, the interaction between S^+ and CH_3CCH through a number of electronic states has been studied by means of a multireference configuration interaction approach. The results suggest that an intersystem crossing process leading to the doublet potential energy surface of the $SC_3H_4^+$ system may play a key role. Some potentially crucial reaction mechanisms have been proposed.

Introduction

The $SC_3H_m^{+n}$ systems ($m = \{3, 4\}$, $n = \{0, 1\}$) are, in general, poorly studied. Thioacrolein has been obtained by the pyrolysis of diallyl sulfide, and its photoelectron spectrum was recorded by Bock and co-workers.[1] They have accompanied their experimental work with semiempirical MNDO computations of 13 isomers; this is the only comprehensive theoretical study known to us. Their results suggest that thioacrolein is the most stable structure but also that there are many low-lying species. The microwave spectrum of thioacolein has been recorded by Kroto and Georgiou,[2] its laser excitation spectrum, accompanied by ab initio computations of the lowest-lying electronic states, has been reported by Moule et al.,[3] and the Fourier transform infrared spectrum has been obtained by Korolev and Baskir.[4] Among the purely theoretical studies, we would cite that of Bachrach and Jiang,[5] who have studied through ab initio computations the Diels−Alder reactions of thioacrolein with a number of compounds. In Korolev and Baskir's work, the photoisomerization of matrix-isolated thioacrolein into methylthioketene has also been studied. The microwave spectrum of the latter species (produced by the pyrolysis of 4- and 5-methyl-1,2,3-thiadiazole) has been recorded by Holm et al.[6] The infrared spectrum of methylthioethyne has been obtained by Moritz[7] whereas Frolov et al.[8] have performed MP2/6-31G* ab initio computations to analyze it. Rodler and Bauder have recorded the microwave spectrum of 2H-thiete (thiacyclobutene);[9] its dipole moment has been measured, and the substitution structure has been almost completely resolved. Propargylthiol has also been the subject of intense microwave analysis.[10,11] Cyclopropanethione has been the subject of theoretical ab initio work.[12−14] Methylenethiirane has also been studied theoretically[13,14] and has been found to be the product of the gas-phase reaction of $S(^1D)$ or $S(^3P)$ with allene at high pressure.[15] 1-Cyclopropenethiol has been included, as well as some of the species mentioned so far, by Petersson and co-workers in their studies of the enolization enthalpies of a number of thiocarbonil compounds[16] whereas 2-cyclopropene-1-thiol has been considered by Xidos et al.[17] in their theoretical study of the Diels−Alder reactions of 3-substituted cyclopropenes with butadiene. McAllister and Tidwell[18] have included 2-cyclopropene-1-thiol and mercaptoallene in their ab initio Hartree−Fock calculations of the effect of substituents on the structures and energies of the allenes. Furuhata and Ando[19] have performed ab initio multiconfiguration Hartree−Fock calculations of the lowest electronic states of thioxyallyl to understand the outcome of the flash vacuum pyrolysis of tetramethylallene episulfide and tetramethylpyrazoline-4-thione. Kikuchi et al.[20] have studied the electronic structures of methylenethiirane, cyclopropanethione, and thioxyallyl and the corresponding isomerization barriers.

Some of the $SC_3H_4^+$ cations, at least the thioacrolein, the thiete, and the methylthioketene cations, can be obtained by dissociative ionization or direct ionization of suitable precursors, as shown by Lahem and co-workers.[21] They have also computed ab initio, at the QCISD(T)/6-31G(d,p) level, the thioacrolein and thiete cations and the corresponding isomerization saddle point. Koppel and co-workers[22] have made, within their study of the aromaticity of the substituted cyclopropenes, ab initio G2-MP2 computations on cyclopropanethione and the 1-cyclopropenethiol cation.

Finally, $SC_3H_3^+$ is one of the products of the reaction between S^+ and propyne, which has been studied by Smith and co-workers[23] by means of the selected ion flow-tube technique (SIFT). This reaction could be an important step in the

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generation of some sulfur-containing cumulenes in dense interstellar clouds, namely, SC_3H_m, $m = \{0-2\}$. From a theoretical point of view, the reaction is interesting because it presents as many as four different channels

$$S^+ + CH_3CCH \rightarrow SC_3H_3^+ + H \qquad (0.6)$$

$$S^+ + CH_3CCH \rightarrow C_3H_3^+ + SH \qquad (0.2)$$

$$S^+ + CH_3CCH \rightarrow HCS^+ + C_2H_3 \qquad (0.15)$$

$$S^+ + CH_3CCH \rightarrow C_3H_4^+ + S \qquad (0.05)$$

where the branching ratios are given in parentheses. The reaction intermediates are, of course, the different states of the $SC_3H_4^+$ system. There are a few studies of the $SC_3H_3^{+n}$ ($n = \{0, 1\}$) systems. Habara and Yamamoto have produced the methyl ethynyl thio radical by discharging a gaseous mixture of propyne and carbon disulfide and have recorded its Fourier transform microwave spectrum.[24] The study by Koppel and co-workers mentioned above includes 2-cyclopropen-1-ylium, 1-mercapto.[22] Thietium has been the subject of B3LYP/6-311+G** computations performed by Wang and Schleyer, which are included in their extensive study of the aromaticity of six- and four-membered ring compounds.[25]

We have performed a theoretical study of the $SC_3H_n^+$ systems $n = \{3, 4\}$, paying particular attention to their role in the $S^+ + CH_3CCH$ reaction. The corresponding potential energy surfaces are very complex, having a large number of species that often present several possible conversion and fragmentation paths. This complexity is not surprising because it has also been encountered in a recent theoretical study of a related system, SC_5H_4.[26]

Computational Methods

The local minima and the saddle points have been determined through the density functional theory by means of the B3LYP approach[27] in combination with the triple split-valence plus polarization 6-311G** basis set[28] (i.e., we have employed the B3LYP/6-311G** level). Harmonic vibrational frequencies have also been computed at the B3LYP/6-311G** level. The degree of spin contamination is, in general, rather low.[29] The role of the transition structures in the dynamics has been checked by means of the intrinsic reaction coordinate method[30] whenever the analysis of the normal mode having an imaginary frequency was not considered conclusive. Using the B3LYP/6-311G** geometries, we have performed quadratic configuration interaction[31] computations with singles and doubles terms as well as with perturbative triples terms in combination with the 6-311G(2df,p) basis set[32] (the QCISD(T)/6-311G(2df,p) level). To bring the relative energies computed in this way to a degree of accuracy comparable to that of the Gaussian 2 (G2) procedure[33] in its G2(QCI) form,[34] we have taken on the following steps:

- Vibrational frequencies and zero-point energies have been scaled by a factor of 0.9662 by comparison between the experimental[8] and the computed values of methylthioethyne (CH_3SCCH).
- An empirical high-level correction $HLC = -Bn_\alpha - An_\beta$ has been defined to correct for basis set and other deficiencies, as in G2 theory, by the following procedure. The parameter B has been given the original G2(QCI) value, and A has been determined such that the experimental and theoretical values of $E = D_0(CH_3SH \rightarrow C + 4H + S) + 2(D_0(C_2H_2 \rightarrow 2CH) + D_0(C_2H_4 \rightarrow 2CH_2) + D_0(C_2H_6 \rightarrow 2CH_3))/3 + D_0(CH_2 \rightarrow CH + H)$ coincide. $D_0(CH_3SH \rightarrow C + 4H + S)$ is the atomization energy of methylthiol, and the rest of the D_0's are bond dissociation energies; the experimental values have been taken from ref 33. In fact, several multiply polarized basis sets have been tested up to 6-311+G(3df,2p) for a few species, but the results, when including the corresponding HLC corrections, are very similar to those obtained with the 6-311G(2df,p) set. Given the rather large number of species that have to be studied, we have used the relatively economical 6-311G(2df,p) basis set. Our final values are $A = 0.005938$ and $B = 0.000190$, which may be compared to the G2(QCI) values $A = 0.00513$ and $B = 0.00019$[34] (all values are given in hartrees).

We will refer to the energies computed in this way as G2-type values. In addition, we have performed wave function analysis through the Mulliken[35] and the atoms in molecules (AIM)[36,37] methods. All of these computations have been performed with the Gaussian 98 program package.[38]

To study the interaction of S^+ with propyne, we have performed multireference configuration interaction (MRCI) calculations[39] using the MOLPRO program package.[40]

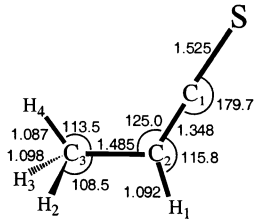
Potential Energy Surface of the $SC_3H_4^+$ System

We have studied a number of conformations on the lowest doublet and quartet potential energy surfaces (PES), obtained the local minima, and located the saddle points that connect them. We have also determined the reaction paths and energy profiles corresponding to the fragmentation of the most-stable species.

A. Doublet States of the $SC_3H_4^+$ System. We have found a number of minima on the PES corresponding to the lowest-lying doublet electronic state. Their B3LYP/6-311G** optimized geometries together with those of the transition states for the isomerization and fragmentation processes are shown in Figure 1. Scheme 1 presents the possible paths for the interconversion of the doublet intermediates. Absolute and relative energies of the doublet and quartet states together with those of the transition states are given in Table 1. In addition, we have performed Mulliken and AIM analyses of the HF/6-311G** and B3LYP/6-311G** wave functions. We will note the intermediates according to increasing energy. When giving energy differences, we will always refer to G2-type values. There are many details of our computations that are not given in the present paper but that are available as Supporting Information. This is the case for the dihedral angles not shown in Figures 1−3.

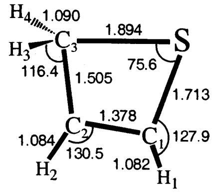
The most stable form, noted as M1, is the methylthioketene cation, which has a $^2A''$ electronic state with a leading electron configuration $[...15a'^2 3a''^2 4a''^1]$. Note that the most stable form of the neutral system is thioacrolein, according to the MNDO computations of Bock et al.[1] M1 has a rather short S−C bond; in fact, the wave function analysis indicates that it is average between double and triple whereas the C1−C2 bond is average between single and double. It is also a very polar bond; the atomic charges are $Q(S) = 1.10$, $Q(C1) = -0.76$ (we will normally give AIM charges). S and C2 share the unpaired electron. In most species, sulfur retains a good portion of the positive charge, and the rest is very much divided between the other atoms, often with important contributions from the hydrogen atoms. We will only describe the electron distribution in detail when it does not fit this pattern. Besides, we will give the electronic state and leading electron configuration except when the species has no symmetry.

M1 may transform into M4, the methylthiirene cation, through the transition structure TS14 (transition structures will be named by putting together the numbers of the two intermediates involved). M4 presents a $^2A''$ electronic state with the leading



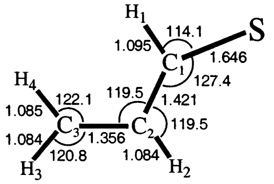
$< C_1C_2C_3H_3 = 122.9$

M1

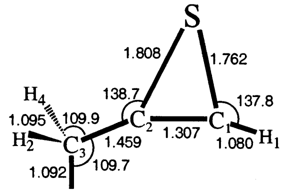


$< C_1SC_3H_3 = 117.0$

M2

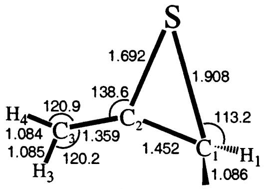


M3



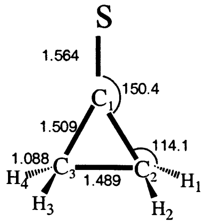
$< C_1C_2C_3H_2 = 120.9$

M4



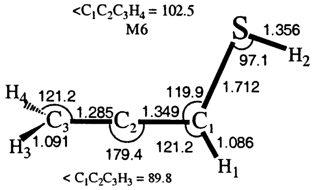
$< H_1C_1C_2C_3 = 79.5$

M5



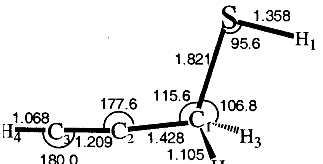
$< C_1C_2C_3H_4 = 102.5$

M6



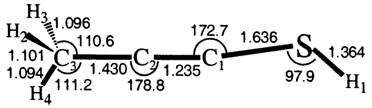
$< C_1C_2C_3H_3 = 89.8$

M7



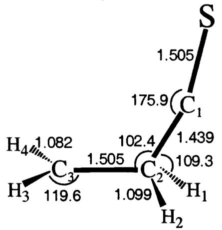
$SC_1C_2H_3 = 121.8$

M21



$< C_2C_3H_2 = 108.9$

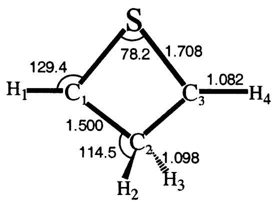
M8



$<C_1C_2C_3H_4 = 86.0$

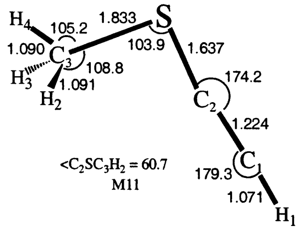
$<C_1C_2C_3H_1 = 117.8$

M9



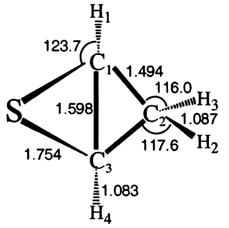
$< SC_1C_2H_2 = 118.0$

M10



$<C_2SC_3H_2 = 60.7$

M11



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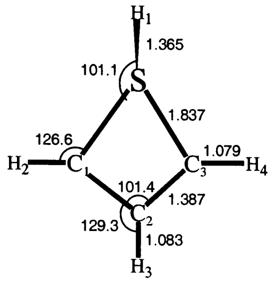
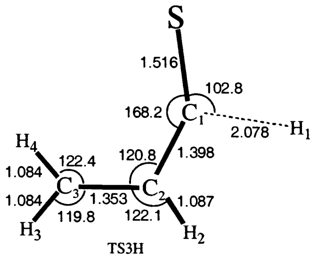
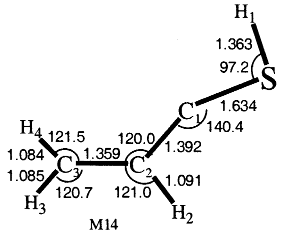


$< H_1SC_3C_2 = 101.7$

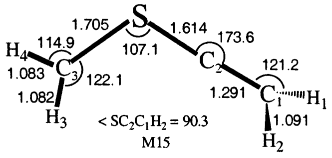
M13



TS3H

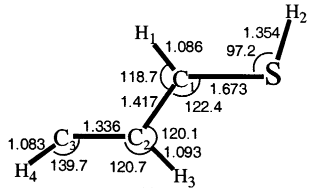


M14



$< SC_2C_1H_2 = 90.3$

M15



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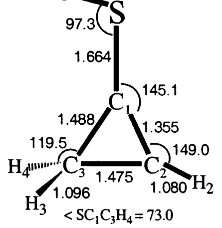
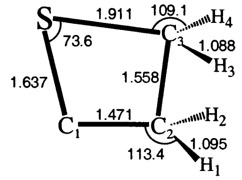


$< SC_1C_3H_4 = 73.0$

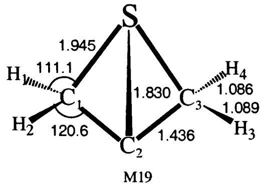
M17



$< SC_3C_2H_2 = 116.0$

$< SC_3C_2H_4 = 111.7$

M18



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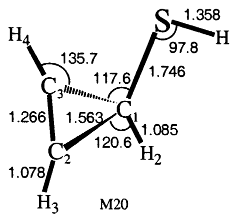

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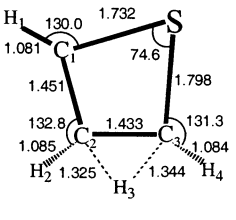

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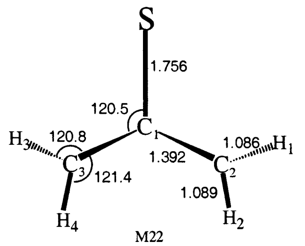

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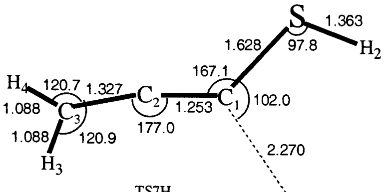
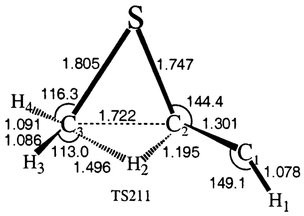


TS7H



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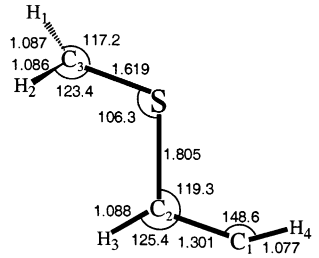

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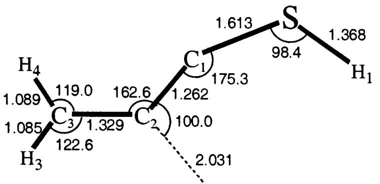

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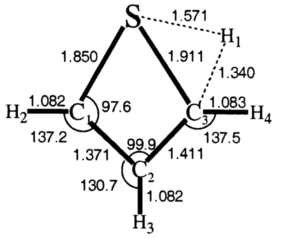

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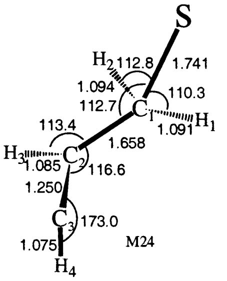

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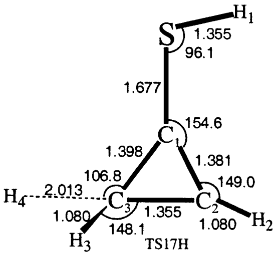

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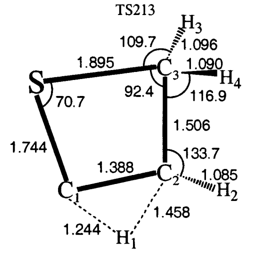

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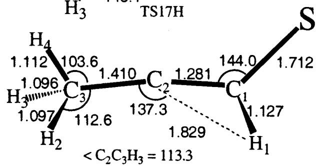
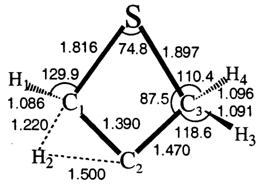


$< C_2C_3H_3 = 113.3$

TS14



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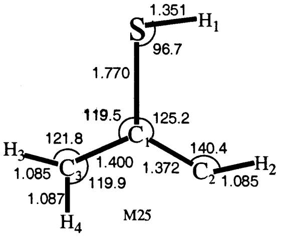

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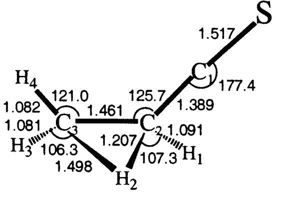

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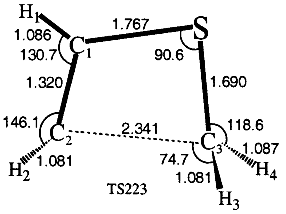

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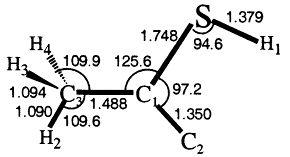
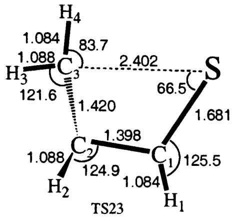


$< SC_1C_3H_4 = 59.6$

M26



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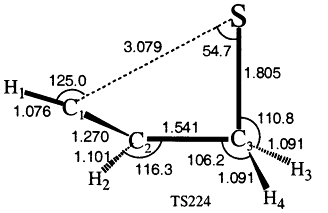
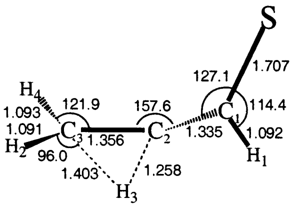
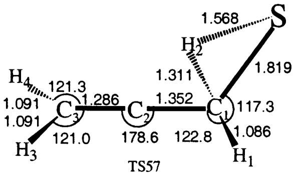


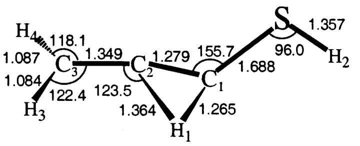
TS224



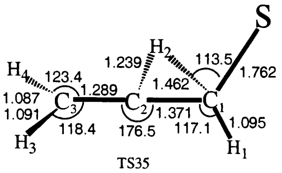
TS34



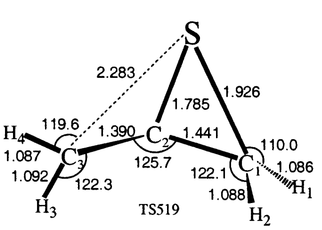
TS57



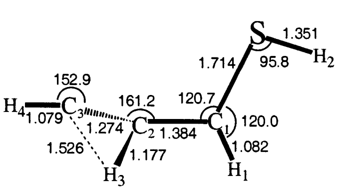
TS714



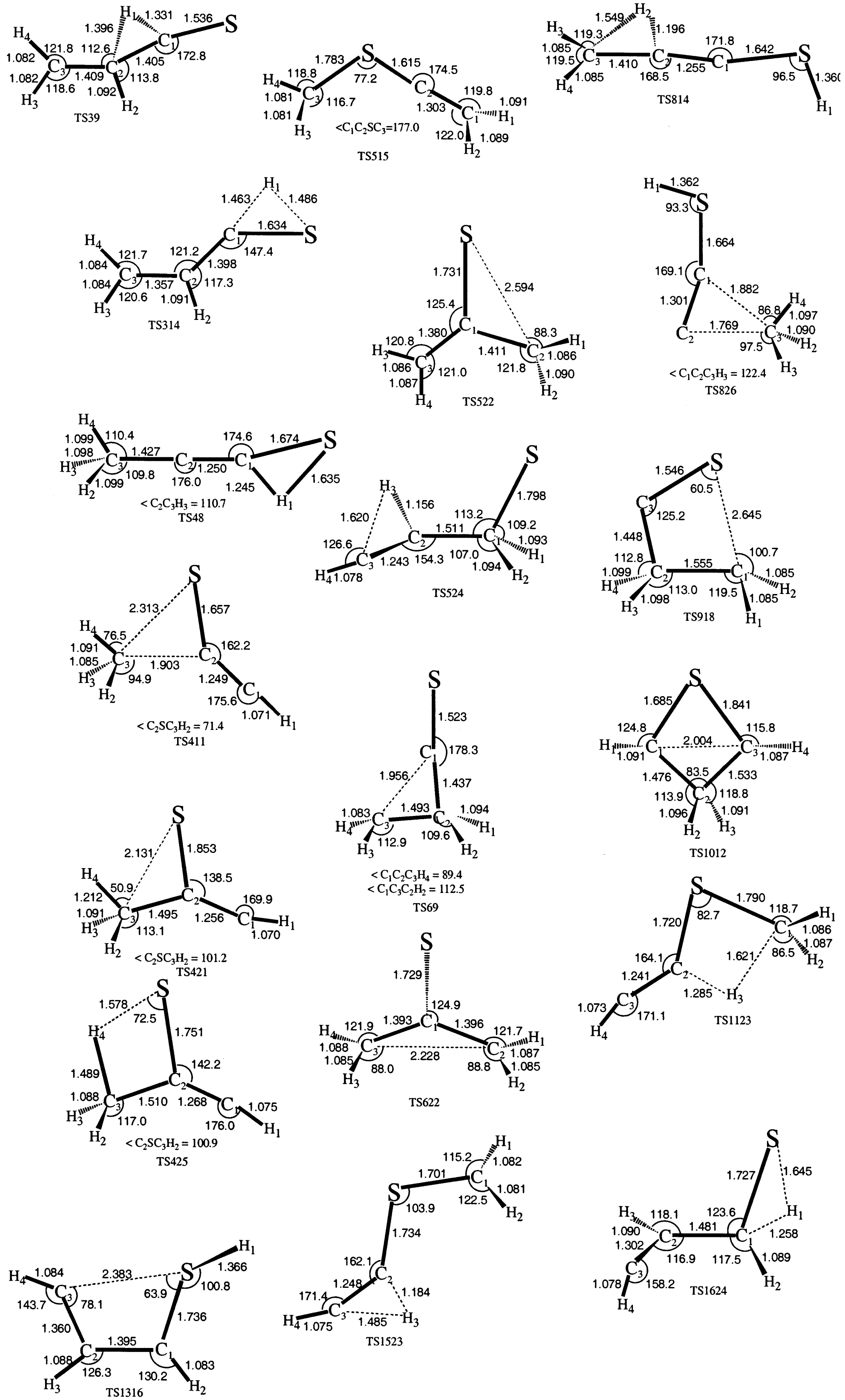
TS35



TS519



TS716


TS39
H1 1.331 1.536 S
1.396 C1
H4 121.8 112.6
1.082 C3 C2 1.405 172.8
1.082 1.409 113.8
118.6 1.092
H3 H2
TS515
S
1.783 1.615 174.5
H4 118.8 77.2 C2
1.081 C3 116.7 119.8
1.081 1.303 C1 1.091 H1
H3 <C1C2SC3=177.0 122.0 1.089 H2
TS814
1.549 H2
H3 119.3 1.196
1.085 171.8 1.642 S
119.5 C3 1.410 C2 1.255 C1
H4 1.085 168.5 96.5 1.360
H1
TS314
H1
1.463 1.486
C1 1.634 S
H4 121.7 121.2 147.4
1.084 C3 C2 1.398
1.084 1.357 117.3
120.6 1.091
H3 H2
TS522
S
1.731 2.594
125.4
1.380 C1
H3 120.8 1.411 88.3 H1
1.086 C3 121.0 121.8 C2 1.086
1.087 1.090
H4 H2
TS826
H1 1.362
93.3 S
1.664
169.1 C1
1.301 1.882
86.8 H4
C2 1.769 C3 1.097
97.5 1.090 H2
H3
< C1C2C3H3 = 122.4
TS48
H4
1.099 110.4 174.6 1.674 S
1.098 C3 1.427 C2 C1
H3 109.8 1.250
1.099 176.0 1.245 1.635
H2 H1
< C2C3H3 = 110.7
TS524
S
H3 1.798
1.620 1.156 113.2
109.2
126.6 C2 1.511 C1 1.093
H4 1.078 C3 1.243 154.3 107.0 H1
1.094 H2
TS918
1.546 S
C3 60.5
125.2 2.645
1.448
112.8 100.7
1.099 C2 1.555 C1 1.085
H4 113.0 119.5 H2
H3 1.098 1.085
H1
TS411
S
2.313 1.657
H4 76.5
1.091 C2 162.2
1.085 C3 1.903
H3 94.9 1.249
H2 175.6 C1
1.071 H1
< C2SC3H2 = 71.4
TS69
S
1.523
C1 178.3
1.956 1.437
1.083 1.493 1.094
H4 C3 C2 H1
112.9 109.6
H3 H2
< C1C2C3H4 = 89.4
< C1C3C2H2 = 112.5
TS1012
S
1.685 1.841
124.8 115.8
H1 C1 2.004 C3 H4
1.091 1.087
1.476 83.5 1.533
113.9 C2 118.8
1.096 1.091
H2 H3
TS421
S
2.131 1.853
H4 138.5
1.212 50.9 C2 169.9
1.091 C3 1.495
H3 113.1 1.256 C1 H1
H2 1.070
< C2SC3H2 = 101.2
TS1123
S 1.790
82.7 118.7 H1
1.720 C1 1.086
1.087
164.1 1.621 86.5 H2
C2
1.241 1.285 H3
1.073 C3 171.1
H4
TS425
S
1.578
H4 72.5 1.751
1.489 142.2
1.088 C2
H3 C3 1.510 1.268 C1 1.075
H2 117.0 176.0 H1
< C2SC3H2 = 100.9
TS622
S
1.729
124.9
H4 121.9 1.393 C1 1.396 121.7 H1
1.088 C3 C2 1.087
1.085 88.0 2.228 88.8 1.085
H3 H2
TS1316
H1
H4 1.084 2.383 S 1.366
143.7 C3 78.1 63.9 100.8
1.360 1.736
1.088 C2 1.395 C1 1.083
126.3 130.2
H3 H2
TS1523
H1
115.2 1.082
1.701 C1
S 1.081
103.9 122.5 H2
1.734
162.1
1.248 C2
171.4 C3 1.184
H4 1.075 1.485 H3
TS1624
S
1.727 1.645
H3 118.1 123.6 H1
1.090 C2 1.481 C1 1.258
1.302 116.9 117.5 1.089
1.078 C3 158.2 H2
H4

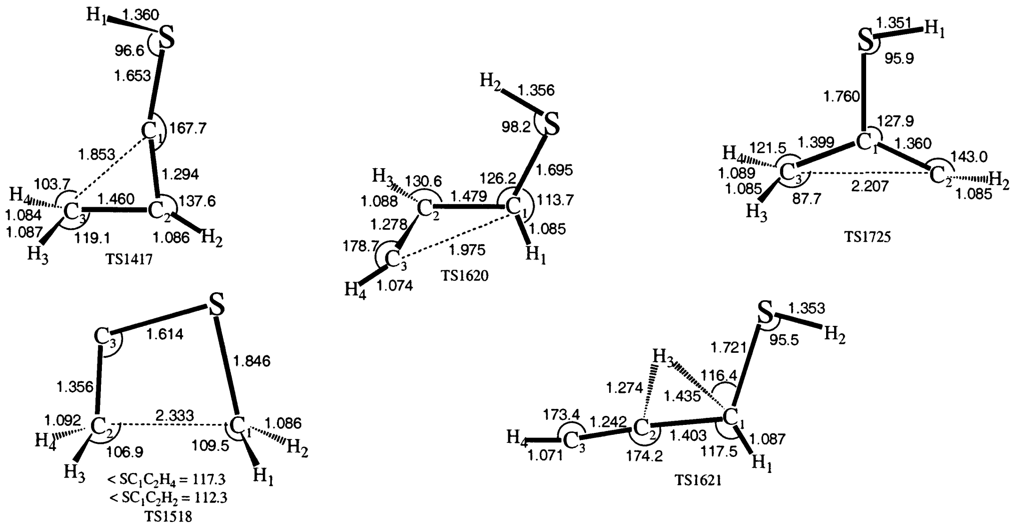
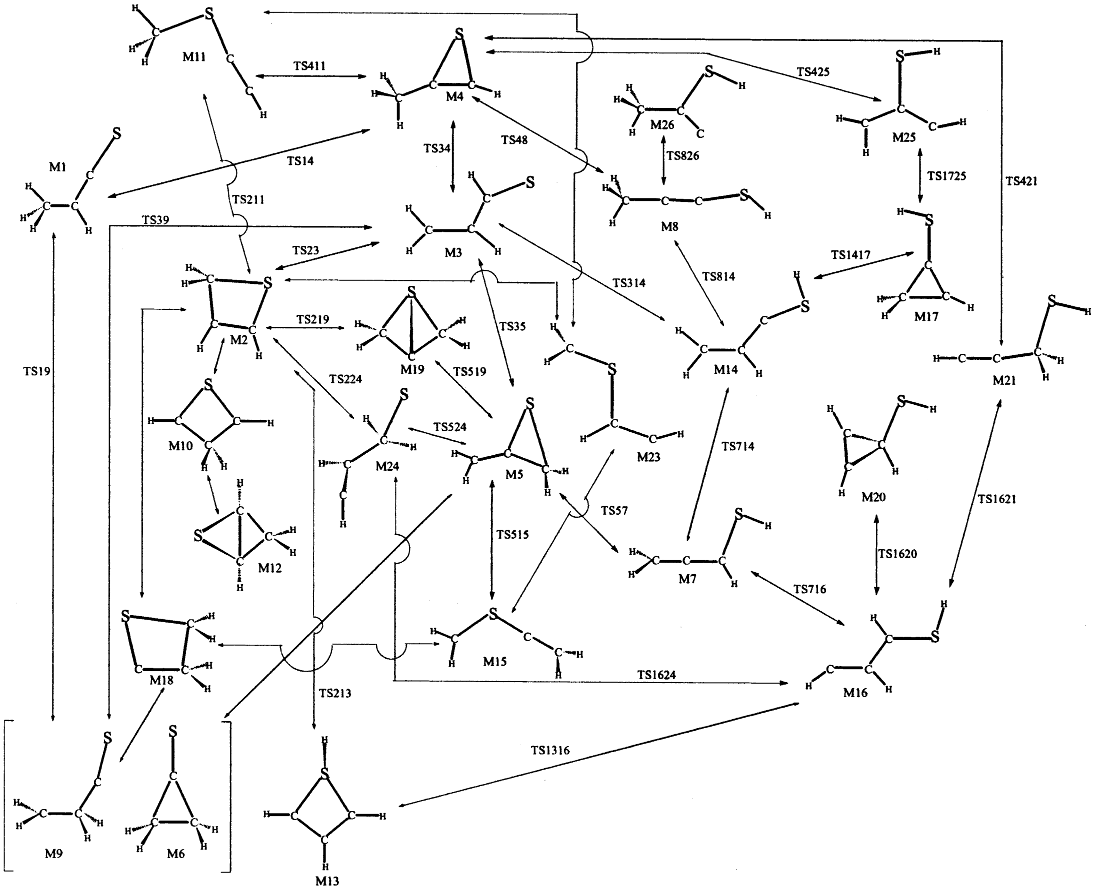


Figure 1. B3LYP/6-311G** optimized geometries (angstroms and degrees) of the most-relevant minima and saddle points of the doublet PES of the $SC_3H_4^+$ system.

SCHEME 1: Evolution of the $SC_3H_4^+$ System on the PES of the Lowest Doublet Electronic State



configuration [...$15a'^2 3a''^2 4a''^1$]. The wave function analysis indicates that the S−C bonds of the thiirene ring are strong single bonds whereas the C1−C2 bond is almost a double bond. The unpaired electron is mostly localized on the sulfur atom.

M4 may isomerize into the thioacrolein cation M3 through TS34. Note that hydrogen atom migration from C3 to C2 entails the simultaneous breaking of the S−C2 bond of M4. The thioacrolein cation is connected to the thiete cation M2 through TS23 but may give another structure with an SCC cycle, namely, the methylenethiirane cation M5.

M3 presents a $^2A'$ state with a dominant electron configuration of [...$15a'^2 3a''^2 16a'^1$]. The wave function analysis indicates that the S−C bond is almost a double bond and also that it is quite polar (Q(S) = 0.745, Q(C1) = −0.39). The C2−C3 bond is average between single and double whereas the C1−C2 bond is basically a single bond. Most of the spin density is localized on sulfur.

The methylenethiirane cation, M5, presents a $^2A''$ electronic state arising from a [...$15a'^2 3a''^2 4a''^1$] electron configuration. The S−C2 and C2−C3 bonds are average between single and double. The unpaired electron is divided between C3 and S.

M5 may transform into a rather high-lying open structure, the thioxyallyl cation M22. The existence of this species is dubious—although it is a local minimum at the B3LYP/6-311G-

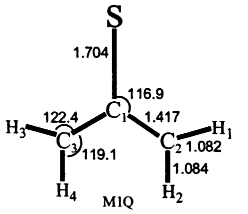
TABLE 1: Energies (hartrees) and Relative Energies with Respect to Ground-State S^+ + Propyne (kcal/mol) for the Intermediates and Transition States of the Doublet and Quartet PESs[a]

species	QCISD(T)/ 6-311G(2df,p)	ZPVE (B3LYP/6-311G**)	G2(QCI)-type energy	G2(QCI)/ relative energy
M1	−513.86194	0.05771	−513.86766	−109.8
M2	−513.85341	0.05964	−513.85726	−103.3
M3	−513.85118	0.05892	−513.85572	−102.3
M4	−513.84565	0.05762	−513.85145	−99.6
M5	−513.83855	0.05836	−513.84364	−94.7
M6	−513.83404	0.05806	−513.83941	−92.1
M7	−513.83048	0.05456	−513.83924	−92.0
M8	−513.82666	0.05443	−513.83555	−89.7
M9	−513.82845	0.05670	−513.83514	−89.4
M10	−513.82865	0.05758	−513.83449	−89.0
M11	−513.81910	0.05625	−513.82622	−83.8
M12	−513.82144	0.05914	−513.82577	−83.5
M13	−513.81559	0.05567	−513.82328	−82.0
M14	−513.81212	0.05541	−513.82005	−79.9
M15	−513.80547	0.05463	−513.81416	−76.2
M16	−513.80318	0.05529	−513.81124	−74.4
M17	−513.80173	0.05480	−513.81025	−73.8
M18	−513.80109	0.05915	−513.80542	−70.8
M19	−513.79975	0.05919	−513.80404	−69.9
M20	−513.79322	0.05382	−513.80269	−69.0
M21	−513.79265	0.05365	−513.80228	−68.8
M22	−513.79456	0.05743	−513.80054	−67.7
M23	−513.78763	0.05485	−513.79611	−64.9
M24	−513.76090	0.05505	−513.76919	−48.0
M25	−513.75567	0.05322	−513.76572	−45.8
M26	−513.74152	0.05338	−513.75143	−36.9
M1Q	−513.78450	0.05573	−513.78639	−58.8
M2Q	−513.76982	0.05572	−513.77171	−49.6
M3Q	−513.76694	0.05566	−513.76889	−47.8
M4Q	−513.75553	0.05584	−513.75731	−40.6
M5Q	−513.74255	0.05632	−513.74386	−32.1
M6Q	−513.73622	0.05249	−513.74122	−30.5
M7Q	−513.73844	0.05546	−513.74059	−30.1
M8Q	−513.73703	0.05617	−513.73848	−28.8
M9Q	−513.73644	0.05597	−513.73808	−28.5
M10Q	−513.72550	0.05253	−513.73047	−23.7
M11Q	−513.72549	0.05302	−513.72999	−23.4
M12Q	−513.72360	0.05310	−513.72802	−22.2
M13Q	−513.72186	0.05150	−513.72783	−22.1
M14Q	−513.71938	0.05275	−513.72414	−19.8
M15Q	−513.71965	0.05689	−513.72041	−17.4
M16Q	−513.70223	0.05258	−513.70716	−9.1
M17Q	−513.70367	0.05478	−513.70646	−8.7
M18Q	−513.69910	0.05457	−513.70210	−5.9
M19Q	−513.69301	0.05320	−513.69734	−2.9
M20Q	−513.69524	0.05719	−513.69570	−1.9
M21Q	−513.68648	0.05242	−513.69156	0.7
M22Q	−513.68831	0.05467	−513.69121	0.9
M23Q	−513.67079	0.05303	−513.67528	10.9
M24Q	−513.66709	0.05159	−513.67297	12.4
TS3H	−513.76619	0.04938	−513.77996	−54.8
TS7H	−513.72330	0.04515	−513.74115	−30.4
TS14H	−513.71828	0.04567	−513.73562	−27.0
TS17H	−513.74218	0.04696	−513.75829	−41.2
TS14	−513.78474	0.05358	−513.79444	−63.9
TS19	−513.79476	0.05405	−513.80401	−69.9
TS23	−513.82410	0.05822	−513.82933	−85.8
TS210	−513.78375	0.05451	−513.79256	−62.7
TS211	−513.70708	0.05195	−513.71837	−16.1
TS213	−513.76509	0.05161	−513.77670	−52.7
TS218	−513.74498	0.05409	−513.75419	−38.6
TS219	−513.74555	0.05436	−513.75450	−38.8
TS223	−513.76411	0.05541	−513.77204	−49.8
TS224	−513.74324	0.05472	−513.75185	−37.1
TS34	−513.76603	0.05348	−513.77583	−52.2
TS35	−513.77259	0.05319	−513.78267	−56.5
TS39	−513.78318	0.05256	−513.79388	−63.5
TS314	−513.77114	0.05219	−513.78219	−56.2
TS48	−513.75028	0.05073	513.76273	44.0
TS411	−513.72964	0.05381	−513.73913	−29.2
TS421	−513.71745	0.05156	−513.72911	−22.9
TS425	−513.70683	0.04933	−513.72064	−17.6
TS57	−513.75340	0.05111	−513.76549	−45.7
TS515	−513.77434	0.05366	−513.78397	−57.3
TS519	−513.78926	0.05789	−513.79480	−64.1
TS522	−513.79407	0.05662	−513.80084	−67.9
TS524	−513.75534	0.05291	−513.76569	−45.8
TS69	−513.82496	0.05695	−513.83141	−87.1
TS622	−513.79469	0.05729	−513.80081	−67.9
TS714	−513.76969	0.04922	−513.78361	−57.1
TS716	−513.76300	0.04968	−513.77647	−52.6
TS814	−513.75885	0.04954	−513.77246	−50.1
TS826	−513.71164	0.05193	−513.72294	−19.0
TS918	−513.76627	0.05586	−513.77378	−50.9
TS1012	−513.79528	0.05751	−513.80119	−68.1
TS1123	−513.71104	0.04903	−513.72514	−20.4
TS1316	−513.77559	0.05395	−513.78494	−57.9
TS1417	−513.78427	0.05340	−513.79415	−63.7
TS1518	−513.74569	0.05323	−513.75574	−39.6
TS1523	−513.73745	0.04938	−513.75122	−36.7
TS1620	−513.78211	0.05264	−513.79272	−62.8
TS1621	−513.74975	0.04950	−513.76340	−44.4
TS1624	−513.71319	0.05058	−513.72580	−20.8
TS1725	−513.75584	0.05279	−513.76631	−46.2
TS4SQ	−513.73346	0.05478	−513.73626	−27.4
TS19Q	−513.71036	0.05338	−513.71451	−13.7
TS115Q	−513.69955	0.05409	−513.70302	−6.5
TS23Q	−513.70482	0.05148	−513.71081	−11.4
TS27Q	−513.72675	0.05276	−513.73150	−24.4
TS29Q	−513.69086	0.05094	−513.69737	−3.0
TS213Q	−513.68224	0.04845	−513.69115	0.9
TS217Q	−513.70003	0.05441	−513.70318	−6.6
TS35Q	−513.68295	0.04984	−513.69052	1.3
TS519Q	−513.67704	0.05261	−513.68193	6.7
TS621Q	−513.65159	0.05069	−513.65834	21.5
TS721Q	−513.65147	0.04953	−513.65934	20.9
TS89Q	−513.65385	0.05003	−513.66125	19.7
TS811Q	−513.67461	0.04921	−513.68278	6.2
TS817Q	−513.69864	0.05453	−513.70168	−5.7
TS1011Q	−513.64122	0.04757	−513.65098	26.2
TS1123Q	−513.63387	0.04836	−513.64287	31.2
TS1124Q	−513.66579	0.05098	−513.67227	12.8
TS1214Q	−513.63826	0.04666	−513.64890	27.5
TS1220Q	−513.65179	0.05436	−513.65499	23.6
TS1316Q	−513.65660	0.04879	−513.66518	17.2
TS1321Q	−513.67151	0.05062	−513.67834	9.0
TS1417Q	−513.65980	0.05242	−513.66488	17.4
TS1418Q	−513.65135	0.04903	−513.65971	20.7
TS1519Q	−513.69026	0.05215	−513.69559	−1.8
TS1622Q	−513.59304	0.04923	−513.60120	57.4
TS1720Q	−513.63417	0.05274	−513.63893	33.7
TS1920Q	−513.62084	0.05327	−513.62509	42.4
TS2124Q	−513.62826	0.04803	−513.63758	34.6

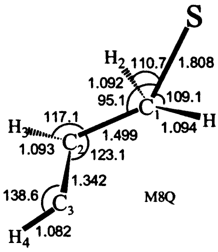
[a] Quartet structures are noted with Q.

(d,p) level, the addition of the zero-point energy brings it to virtually the same energy as that of TS622 (i.e., the saddle point for the M6 ↔ M22 isomerization). The cyclopropanethione cation, M6, which may be viewed as the cyclic analogue of M22, is much lower in energy because it lies only 17.7 kcal/mol above the global minimum M1 (see Table 1). M6 presents a C_{2v} structure with a $^2B_2$ electronic state and a $[...10a_1^2 1a_2^2 3b_1^2 4b_2^2 5b_2^1]$ electron configuration. It has a very polar S−C double bond, and the unpaired electron is mostly localized on sulfur. M6 may isomerize to M9 through TS69, which lies above M9 by only 2.3 kcal/mol. The latter species is very close in energy to M6 because it lies only 2.7 kcal/mol above. Under conditions of high excitation energies, as is the case for the generation of the $SC_3H_4^+$ system in $S^+ + C_3H_4$ collisions, M6 and M9 may be considered to be the same minimum from a dynamical point of view. M9 has a S−C bond that is almost triple and extremely polar ($Q(S) = 1.14$, $Q(C1) = -0.75$). The unpaired electron is localized on the C3 atom. M9 and M6 are important species because they are connected to very low-lying states, namely, M1 and M3 through TS19 and TS39 or M5 through the likely unstable structure M22.

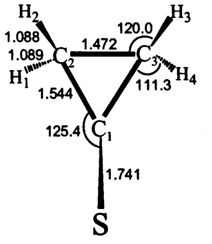
The thiete cation (M2) is only 6.5 kcal/mol higher in energy than M1 (see Table 1). It has a $^2A''$ electronic state with a $[...15a'^2 3a''^2 4a''^1]$ dominant electron configuration. The S−C1



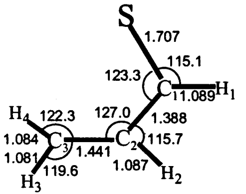
M1Q



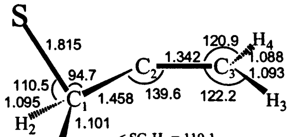
M8Q



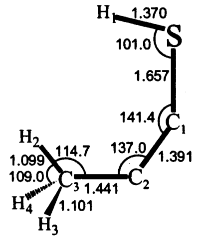
M15Q



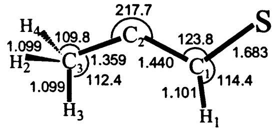
M2Q



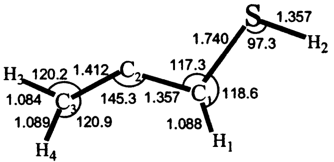
< SC_1H_1 = 110.1
M9Q



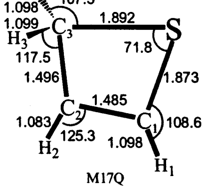
< $C_1C_2C_3H_4$ = 122.0
M16Q



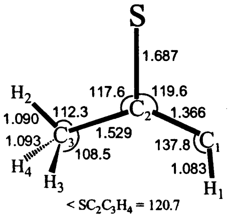
< $C_1C_2C_3H_2$ = 121.8
M3Q



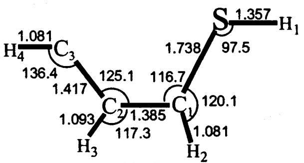
M10Q



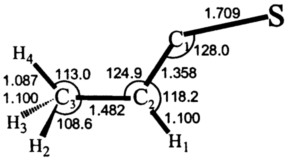
M17Q



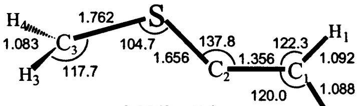
< $SC_2C_3H_4$ = 120.7
M4Q



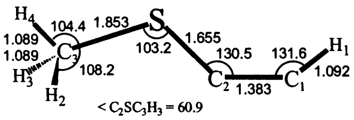
M11Q



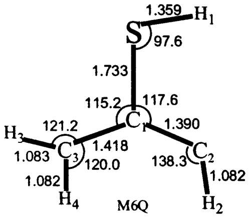
< $C_1C_2C_3H_3$ = 123.0
M5Q



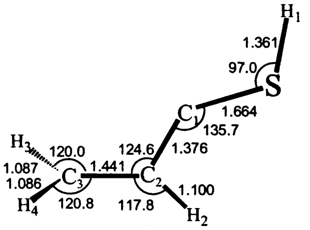
< $C_2SC_3H_3$ = 93.7
M12Q



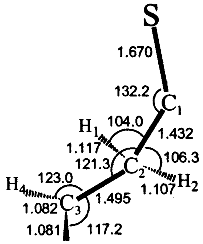
< $C_2SC_3H_3$ = 60.9
M18Q



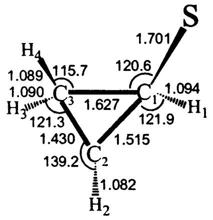
M6Q



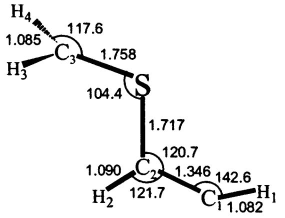
M13Q



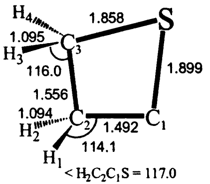
M19Q



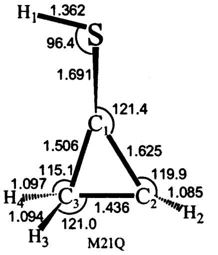
M7Q



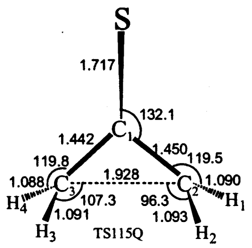
< $H_3C_3SC_2$ = 98.5
M14Q



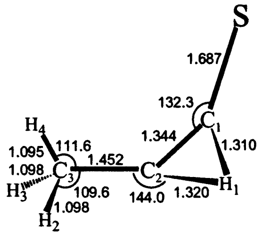
< $H_2C_2C_1S$ = 117.0
< $H_4C_3C_2C_1$ = 114.5
M20Q



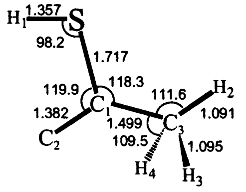
M21Q



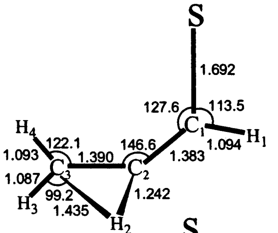
TS115Q



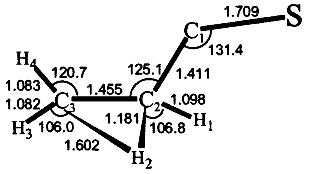
< $C_2C_3H_3$ = 109.6
TS35Q



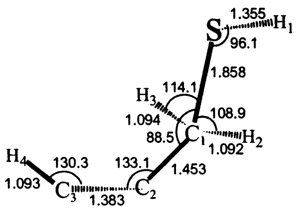
< $SC_1C_3H_3$ = 121.3
M22Q



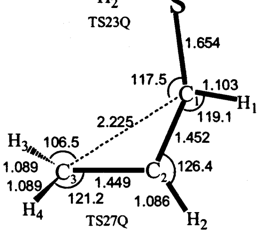
TS23Q



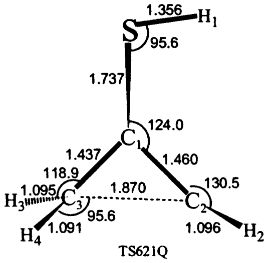
TS519Q



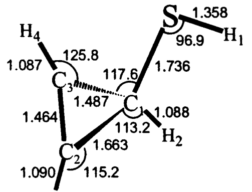
M23Q



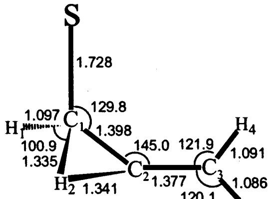
TS27Q



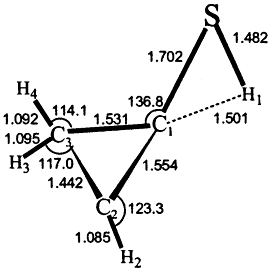
TS621Q



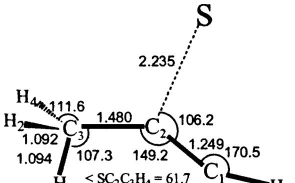
M24Q



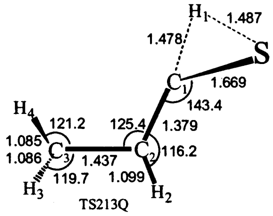
TS29Q



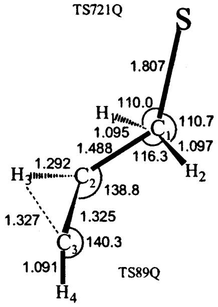
TS721Q



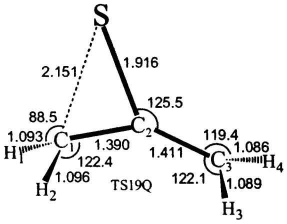
< $SC_2C_3H_4$ = 61.7
TS4SQ



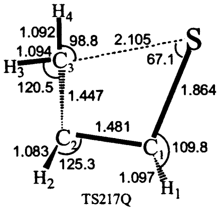
TS213Q



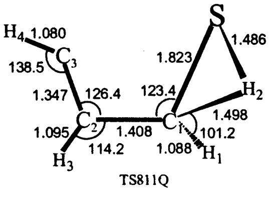
TS89Q



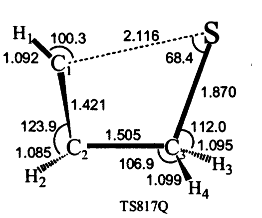
TS19Q



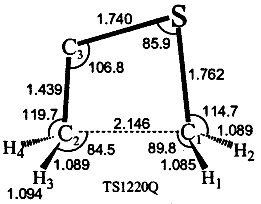
TS217Q



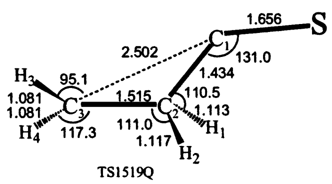
TS811Q



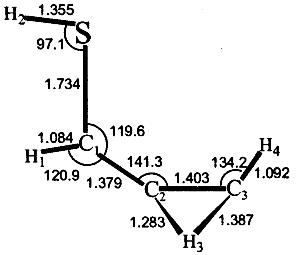
TS817Q



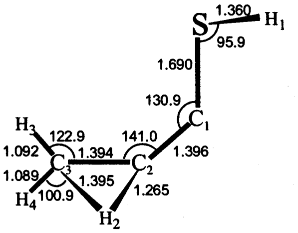
TS1220Q



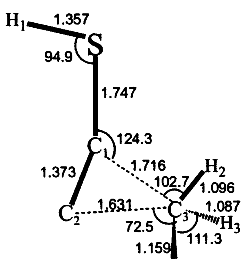
TS1519Q



TS1011Q



TS1316Q



TS1622Q

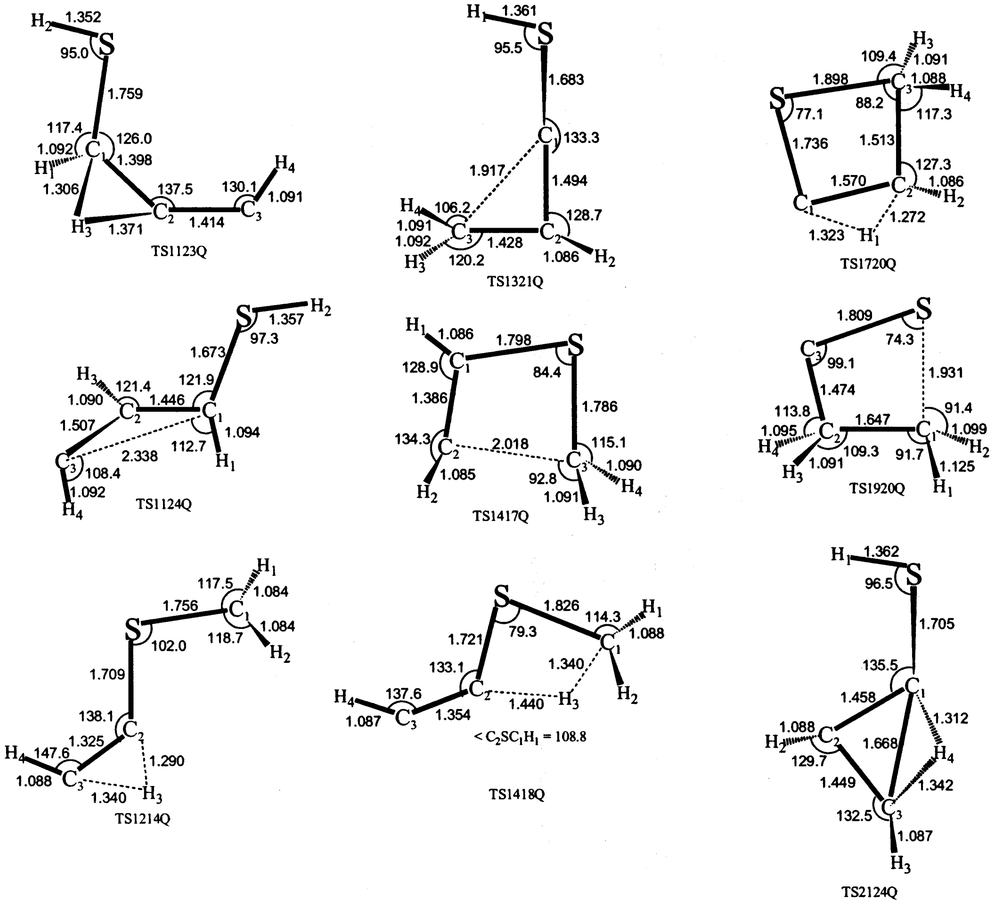


Figure 2. B3LYP/6-311G** optimized geometries (angstroms and degrees) of the most-relevant minima and saddle points of the doublet PES of the $SC_3H_4^+$ system.

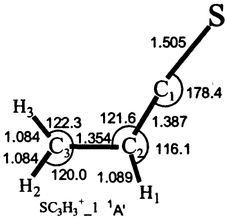
and C1−C2 bonds are average between double and single, and the unpaired electron is divided between S and C2. M2 may isomerize into a similar form, M10. M10 has a C_{2v} structure with a $^2A_2$ electronic state corresponding to a leading [...$10a_1^2$-$3b_1^2 5b_2^2 1a_2^1$] electron configuration. The unpaired electron is divided between C1 and C3. M10 may evolve into the bicyclic form M12. The latter species has a nonplanar structure of C_s symmetry with a $^2A'$ state corresponding to a leading electron configuration of [...$13a'^2 5a''^2 14a'^1$]. It has single C1−C2 or C2−C3 bonds and a C1−C3 bond that is almost single (the AIM bond order is 0.83). The unpaired electron is divided between S, which has most of the spin density, and both C1 and C3.

M2 may isomerize into two other cyclic forms that are relatively high in energy, namely, M18 and M19. M18 has a $^2A'$ electronic state and a [...$14a'^2 4a''^2 15a'^1$] electron configuration. The wave function analysis reveals an almost double S−C1 bond, which is quite polar; the unpaired electron is localized on C1. M19 presents a $^2A'$ electronic state with a [...$12a'^2 6a''^2 13a'^1$] electron configuration. This structure consists of single bonds, although those between the carbon atoms have an AIM bond order of 1.24 and the S−C1 or S−C3 bonds have an order of 0.86. The unpaired electron mostly resides on C2. Note that M19 may convert into the methylenethiirane cation by a ring-opening process.

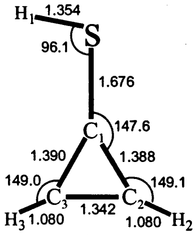
M2 may also isomerize into a four-membered cyclic thiol, M13. Its electronic state is $^2A''$ with the leading electron configuration [...$13a'^2 5a''^2 6a''^1$]. The C−C bonds are average between single and double, and the unpaired electron is divided between C1 and C3.

The cyclic intermediates may lead to a number of other species by means of ring-opening processes. For instance, M2 may produce M24, M23, and M11; in the latter case, a hydrogen shift from C2 to C3 occurs at the same time as ring opening.

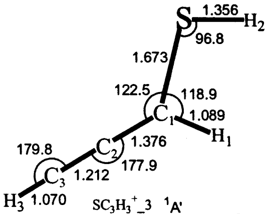
The wave function analysis of M24 reveals that the C1−C2 bond is very weak because it has a rather small AIM bond order (0.79) that is consistent with a large bond distance. The C2−C3 bond is a double bond, and the unpaired electron is localized on the sulfur atom. This species can also be originated from M5 by hydrogen migration from C3 to C2, which entails ring opening. M11 and M23 are thioethers with open structures. M11, the methylthioethyne cation, presents a $^2A''$ electronic state with a leading [...$15a'^2 3a''^2 4a''^1$] electron configuration. The C2−C1 bond is average between double and triple whereas the S−C2 bond is average between single and double and is also rather polar. The unpaired electron is divided between S and C1. M23 presents almost double S−C3 and C1−C2 bonds. The unpaired electron is localized on C1, and sulfur retains the positive charge; this fact causes the S−C3 bond to be very polar. It is interesting that M11 and M23 are connected by a saddle point. The corresponding process is a hydrogen migration from C3 to C2. Note also that M11 may be obtained from M4 by means of a migration of the methyl group from C2 to sulfur with a simultaneous breaking of the S−C1 bond. M18 may also originate a species similar to M11 or M23 by ring opening, namely, M15. The latter species can also be originated from M23 by hydrogen migration. M15 has a complex electronic structure corresponding to a $^2A'$ electronic state and to a [...$15a'^2$ $3a''^2 16a'^1$] electron configuration. The C2−C1 and S−C2 bonds are almost double in character, especially the first one. But S−C3 has an AIM bond order higher than single (1.37). C3 holds most of the spin density, and the rest resides on C2. Sulfur



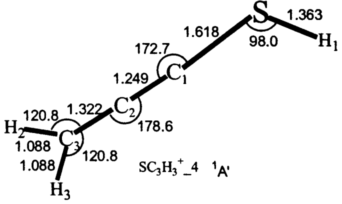
$SC_3H_3^+$_1 $^1A'$



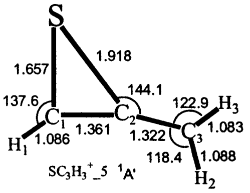
$SC_3H_3^+$_2 $^1A'$



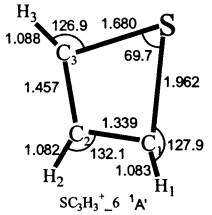
$SC_3H_3^+$_3 $^1A'$



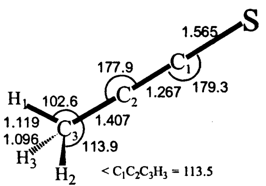
$SC_3H_3^+$_4 $^1A'$



$SC_3H_3^+$_5 $^1A'$

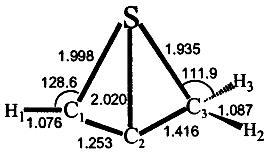


$SC_3H_3^+$_6 $^1A'$



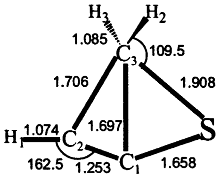
$< C_1C_2C_3H_3 = 113.5$

$SC_3H_3^+$_7 $^1A'$



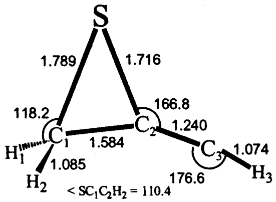
$< SC_2C_3H_2 = 105.9$

$SC_3H_3^+$_8 $^1A'$



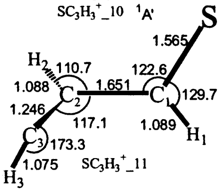
$< SC_3C_2H_2 = 113.4$

$SC_3H_3^+$_9 $^1A'$

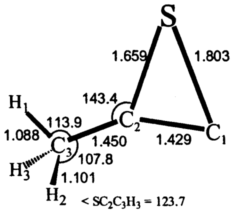


$< SC_1C_2H_2 = 110.4$

$SC_3H_3^+$_10 $^1A'$

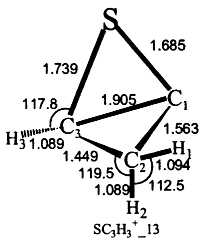


$SC_3H_3^+$_11

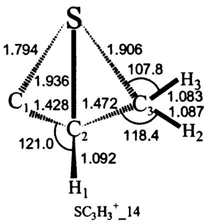


$< SC_2C_3H_3 = 123.7$

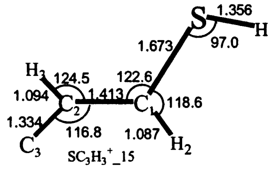
$SC_3H_3^+$_12 $^1A'$



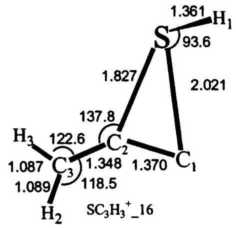
$SC_3H_3^+$_13



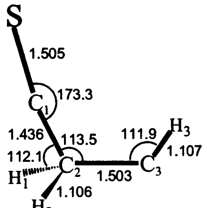
$SC_3H_3^+$_14



$SC_3H_3^+$_15

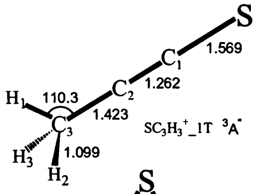


$SC_3H_3^+$_16

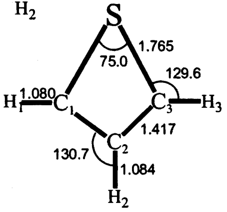


$< C_1C_2C_3H_2 = 124.9$

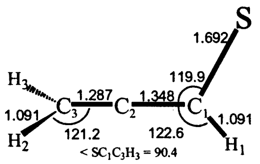
$SC_3H_3^+$_17 $^1A'$



$SC_3H_3^+$_1T $^3A''$

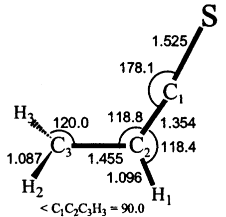


$SC_3H_3^+$_2T $^3B_2$



$< SC_1C_2H_3 = 90.4$

$SC_3H_3^+$_3T $^3A''$



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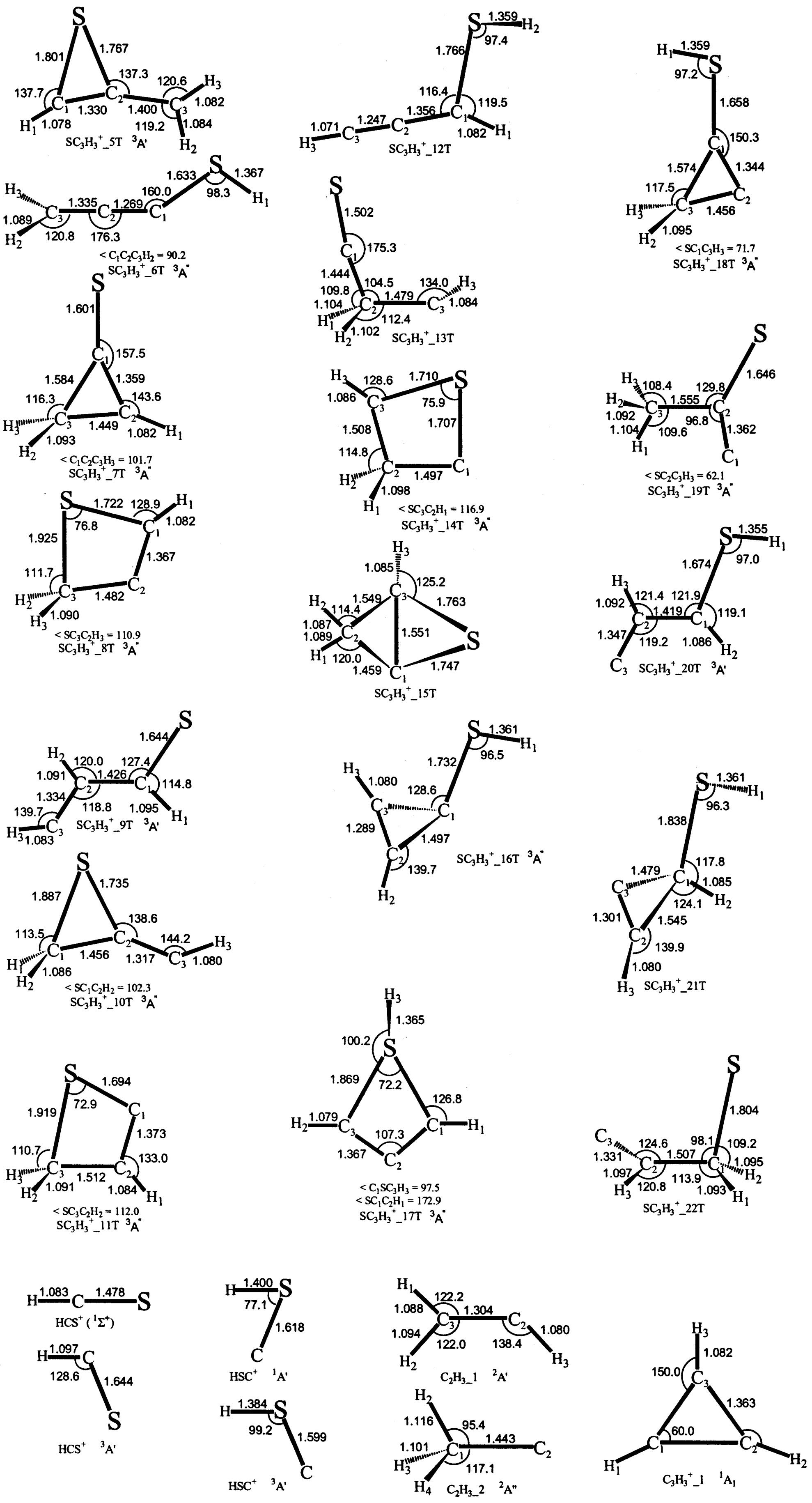
$SC_3H_3^+$_4T $^3A''$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1.767
137.3
120.6
H3
137.7
C1
C2
1.330
1.400
C3
1.082
H1
1.078
119.2
1.084
H2
SC3H3+_5T 3A'
S
1.359
H2
97.4
1.766
116.4
1.356
119.5
1.071
1.247
C3
C2
C1
H3
1.082
H1
SC3H3+_12T
H1
1.359
S
97.2
1.658
C1
150.3
1.574
1.344
117.5
C2
H3
C3
1.456
1.095
H2
< SC1C3H3 = 71.7
SC3H3+_18T 3A"
H3
1.335
C3
C2
1.269
160.0
1.633
S
1.367
C1
98.3
H1
1.089
H2
120.8
176.3
< C1C2C3H2 = 90.2
SC3H3+_6T 3A"
S
1.502
C1
175.3
1.444
104.5
134.0
H3
109.8
1.479
1.104
C2
C3
1.084
H1
112.4
H2
1.102
SC3H3+_13T
S
1.601
C1
157.5
1.584
1.359
116.3
143.6
H3
C3
C2
1.449
1.093
1.082
H1
H2
< C1C2C3H3 = 101.7
SC3H3+_7T 3A"
H3
128.6
1.710
S
1.086
C3
75.9
1.508
1.707
114.8
H2
C2
1.497
C1
1.098
H1
< SC3C2H1 = 116.9
SC3H3+_14T 3A"
S
H3
108.4
129.8
1.646
H2
1.555
1.092
C3
96.8
C2
1.104
109.6
1.362
H1
C1
< SC2C3H3 = 62.1
SC3H3+_19T 3A"
S
1.722
128.9
H1
76.8
C1
1.082
1.925
1.367
111.7
C2
H2
C3
1.482
1.090
H3
< SC3C2H3 = 110.9
SC3H3+_8T 3A"
H3
1.085
125.2
H2
1.549
C3
1.763
114.4
1.087
C2
1.551
1.089
S
H1
120.0
1.459
C1
1.747
SC3H3+_15T
S
1.355
H1
1.674
97.0
H3
121.4
121.9
1.092
C2
1.419
C1
119.1
1.347
119.2
1.086
H2
C3
SC3H3+_20T 3A'
S
1.644
H2
120.0
127.4
1.091
C2
1.426
C1
114.8
1.334
118.8
1.095
139.7
H1
H3
C3
1.083
SC3H3+_9T 3A'
S
1.361
H1
96.5
1.732
H3
1.080
128.6
C3
C1
1.289
1.497
C2
139.7
H2
SC3H3+_16T 3A"
S
1.361
H1
96.3
1.838
117.8
1.479
C1
1.085
C3
124.1
H2
1.301
1.545
C2
139.9
1.080
H3
SC3H3+_21T
S
1.735
1.887
138.6
113.5
C2
144.2
H3
H1
C1
1.456
1.317
C3
1.080
H2
1.086
< SC1C2H2 = 102.3
SC3H3+_10T 3A"
H3
1.365
100.2
S
1.869
72.2
126.8
H2
1.079
C3
C1
H1
107.3
1.367
C2
< C1SC3H3 = 97.5
< SC1C2H1 = 172.9
SC3H3+_17T 3A"
S
1.694
1.919
72.9
C1
1.373
110.7
133.0
H3
C3
1.512
C2
H2
1.091
1.084
H1
< SC3C2H2 = 112.0
SC3H3+_11T 3A"
S
1.804
C3
124.6
98.1
109.2
1.331
C2
1.507
C1
1.095
1.097
H2
H3
120.8
113.9
1.093
H1
SC3H3+_22T
H
1.083
C
1.478
S
HCS+ (1Σ+)
H
1.097
C
128.6
1.644
S
HCS+ 3A'
H
1.400
S
77.1
1.618
C
HSC+ 1A'
H
1.384
S
99.2
1.599
C
HSC+ 3A'
H1
122.2
1.088
C3
1.304
C2
1.080
1.094
122.0
138.4
H2
H3
C2H3_1 2A'
H2
1.116
95.4
1.443
C1
C2
1.101
H3
117.1
H4
C2H3_2 2A"
H3
1.082
150.0
C3
1.363
60.0
C1
C2
H1
H2
C3H3+_1 1A1

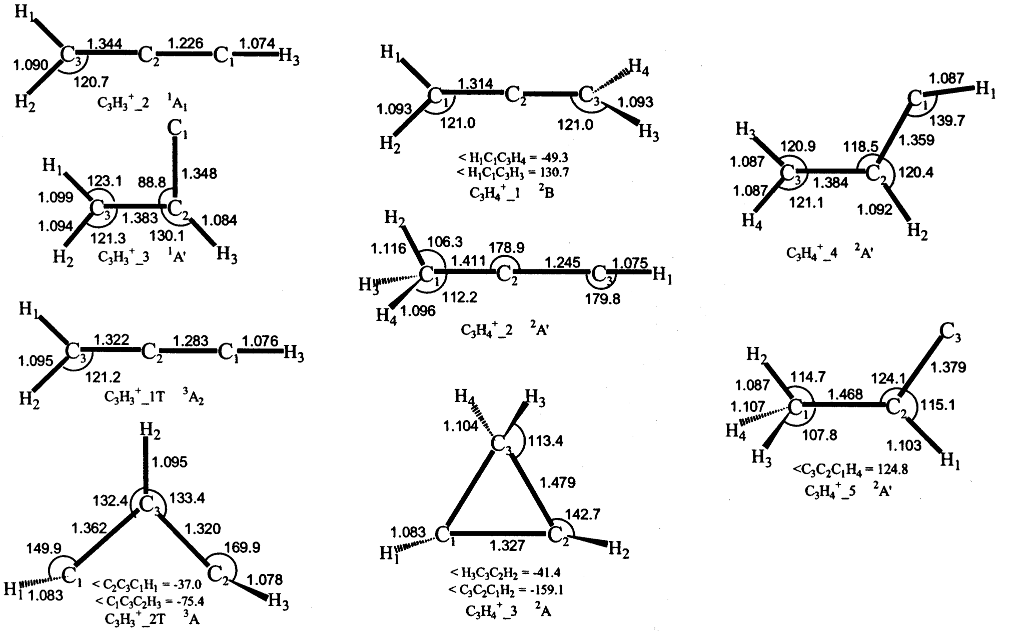


Figure 3. B3LYP/6-311G** optimized geometries (angstroms and degrees) of the fragmentation products of the $SC_3H_4^+$ system that can be formed in the $S^+ + CH_3CCH$ reaction.

retains the positive charge, making the S−C2 bond a very polar one (Q(S) = 0.97, Q(C2) = −0.69).

The rest of the intermediates are thiols. M8, M21, and M25 can be obtained directly from M4. Note that in all cases the process of hydrogen migration to sulfur entails the opening of the thiirene ring of M4. M8, which has the structure of 1-propynylium, 1-mercapto, presents a C2−C1 bond that is average between double and triple whereas the S−C1 bond is average between double and single and it is quite polar because sulfur holds most of the positive charge (Q(S) = 0.86, Q(C1) = −0.40). The unpaired electron is divided between sulfur and C2. M21 is originated from M4 by the insertion of sulfur into one of the C−H bonds of the methyl group. It presents a $^2A''$ electronic state with a [...$15a'^2 3a''^2 4a''^1$] leading configuration. The wave function analysis indicates that the C2−C3 bond is average between double and triple and that the unpaired electron is mostly localized on sulfur, C3 retaining most of the rest of the spin density. M25 can be reached from M4 by the migration of one of the hydrogen atoms of the methyl group to the sulfur atom. It presents a $^2A'$ electronic state with a [...$15a'^2 3a''^2 16a'^1$] electron configuration The C−C bonds are average between single and double, the unpaired electron is mostly localized on C2, and the positive charge is very much divided, with sulfur retaining only 0.31. M8 may isomerize into 1-propynylium, 2-mercapto noted as M26. The latter species has a nonplanar structure of C_s symmetry. It presents a $^2A''$ electronic state with a [...$15a'^2 3a''^2 4a''^1$] electron configuration. The S−C1 and C1−C2 bonds are average between double and single, and the unpaired electron is divided between S and C2.

The thioacrolein cation (M3) may isomerize into M14, which has the structure as 2-propenylium,1-mercapto. M14 presents a $^2A'$ electronic state corresponding to a [...$15a'^2 3a''^2 16a'^1$] electron configuration. The S−C1 bond is almost double and is very polar whereas both C−C bonds are average between single and double. The unpaired electron is mostly localized on sulfur.

The methylenethiirane cation (M5) may also transform into a thiol, namely, M7, the marcaptoallene cation, which can also be obtained from M14 by a hydrogen shift process. M7 has a nonplanar structure of C_s symmetry with a $^2A''$ electronic state corresponding to a [...$15a'^2 3a''^2 4a''^1$] electron configuration. The C2−C3 bond is almost double whereas the C1−C2 and S−C1 bonds are average between single and double. Both the positive charge and the unpaired electron are divided between S and C2, the former atom having the larger share in both cases.

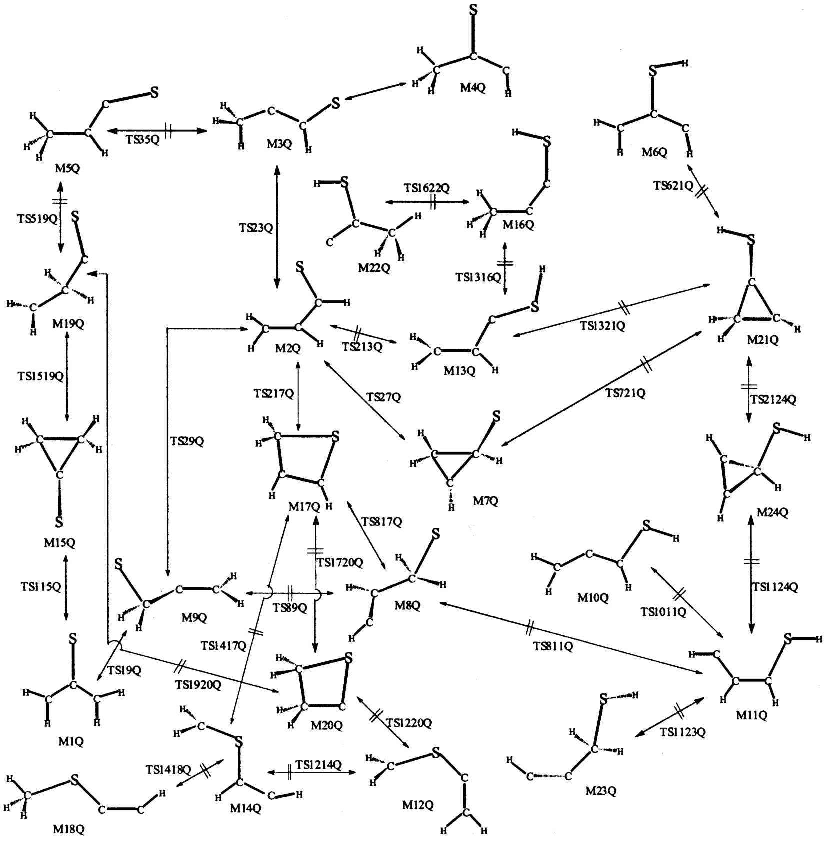
M7 may originate M16 by hydrogen migration, although the latter species may also be formed by the ring opening of M13. M16 presents a $^2A'$ electronic state with a [...$15a'^2 3a''^2 16a'^1$] leading configuration. The C2−C3 and S−C1 bonds are close to double (AIM bond order is 1.71 in both cases). The unpaired electron is neatly localized on C3. M16 may originate M20 by the closure of a C_3 ring. M20 has a nonplanar structure of C_s symmetry and presents a $^2A''$ electronic state corresponding to a [...$14a'^2 4a''^2 5a''^1$] electron configuration. The C2−C3 bond is a double bond, and the S−C1 bond is somewhat stronger than a single bond. The unpaired electron is mostly localized on sulfur, but C1 has a nonnegligible contribution to the spin density (0.17e). There is another thiol with a C_3 cycle, namely, M17, which can be formed from M14 or M25 by ring-closure processes. M17 has a nonplanar structure of C_s symmetry. Its electronic state is $^2A''$ corresponding to a [...$15a'^2 3a''^2 4a''^1$] electron configuration. The S−C1 and C1−C2 bonds are average between single and double. The unpaired electron is divided between S and C2, the latter atom having the higher share (0.56 vs 0.35).

As one would expect, many of the species have one or more isomers; the particular form described here is the most stable one. We have been able to locate other isomeric forms for M3, M7, M14, M16, M17, and M24. Normally, the energy differences between the isomeric forms of the same species are very small, and the saddle points connecting them lie very close to the minima. For this reason, one does not need to take into account all those additional isomers in order to discuss the dynamics of the $SC_3H_4^+$ system under conditions of high excitation energy.

It must be pointed out that all of the minima and all of the saddle points we have studied lie below ground-state $S^+ + CH_3CCH$.

It may be interesting to compare the present relative energy data with those of the MNDO computations for the neutral system by Bock et al.[1] They found that the most stable species

SCHEME 2: Evolution of the $SC_3H_4^+$ System on the PES of the Lowest Quartet Electronic State



is thioacrolein but that methylthioketene and 1-propynethiol are only 1.4 and 5.6 kcal/mol higher in energy. Perhaps the most relevant difference between neutral and cationic forms is the fact that the thiete structures M2 and M12, which lie only 6.5 and 26.3 kcal/mol above the ground state, are very much higher in energy in the neutral system; the corresponding energy gaps are 16.3 and 69.4 kcal/mol, respectively.

B. Quartet States of the $SC_3H_4^+$ System. Scheme 2 shows the possible evolution pathways of the $SC_3H_4^+$ system along the quartet PES. Figure 2 presents the B3LYP/6-311G** optimized geometries of the local minima and the transition states.

We start with the description of the M4Q species, which is formed by the bonding of the sulfur cation with the central carbon of propyne. It presents a $^4A''$ state corresponding to a $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. It is only 40.6 kcal/mol lower in energy than the reactants. The S−C2 bonds and C1−C2 bonds are average between single and double. The spin density is split evenly between the S and C1 atoms. As a general rule, in the quartet intermediates, the positive charge is mainly localized on sulfur with much smaller contributions of the hydrogen atoms.

Structure M3Q can also be formed by bonding the sulfur cation to the terminal carbon of propyne. This species, which lies only 7.2 kcal/mol lower than M4Q, has a $^4A''$ electronic state, and its electron configuration is $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$. The S−C1 and C1−C2 bonds are average between single and double. C2 holds an unpaired electron, and sulfur has the major part of the rest of the spin density. We could not find any minima on the doublet PESs, which were analogous to M3Q and M4Q, although there is a related structure with a S−C−C ring, namely, M4. M4 is much more stable than M3Q or M4Q; it is 51.8 and 59.0 kcal/mol lower in energy, respectively. For the M3Q ↔ M4Q isomerization to take place, a S−C bond-breaking process must occur; the latter process has a saddle point in the case of M4Q (TS4SQ), which can also be viewed, to some extent, as the saddle point corresponding to the M3Q ↔ M4Q isomerization.

M3Q may produce M2Q by the migration of a hydrogen atom of the methyl group to the central carbon; this process involves transition state TS23Q, which is 36.4 kcal/mol higher in energy than M3Q. M3Q may also give M5Q by means of hydrogen migration from the carbon atom bonded to sulfur to the central carbon. The corresponding transition state, TS35Q, is 49.1 kcal/mol higher in energy than M3Q; this implies that it lies in fact 1.3 kcal/mol above the reactants, so isomerization between M3Q and M5Q can hardly take place.

M2Q has a $^4A'$ electronic state and a $[...15a'^2 2a''^2 16a'^1 3a''^1 4a''^1]$ electron configuration. The S−C1, C1−C2, and C2−C3 bonds are average between single and double. Sulfur and, to a lesser extent, C3 have the highest shares of the spin density. The analogous minimum on the doublet PES, M3, is much lower in energy, namely, by 52.7 kcal/mol.

M5Q presents a $^4A''$ state with a $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ dominant electron configuration. The S−C1 and C1−C2 bonds are average between single and double. There is an unpaired electron localized on C1, and the rest of the spin density mostly belongs to the sulfur atom. The analogous minimum of the doublet PES is the absolute minimum, M1, and lies as much as 77.7 below M5Q. M2Q may generate, apart from M3Q, four species. The first possibility is the formation of a four-membered ring involving the heavy atoms, M17Q. This process involves the transition structure TS217Q, which lies 43.0 kcal/mol above M2Q. M17Q is only 8.7 kcal/mol more stable than the reactants. Alternatively, M2Q may undergo a C−C−C ring-closure process giving M7Q, which lies 19.5 kcal/mol above M2Q. The corresponding saddle point is 25.2 kcal/mol higher in energy than M2Q. The third possibility involves hydrogen migration from C1 to the sulfur atom, which gives M13Q. This thiol lies 27.5 kcal/mol above M2Q; however, the corresponding saddle point lies 0.9 kcal/mol above the reactants, so the process might not be feasible. Finally, M2Q may originate M9Q by a hydrogen migration process from C2 to C1; the corresponding saddle point lies 46.6 kcal/mol above M2Q. M9Q is a relatively high-lying species because it is 21.1 kcal/mol higher in energy than M2Q.

M17Q presents no symmetry; its electron distribution features unpaired electrons localized on C1, C2, and S. M7Q presents a S−C1 bond that is average between single and double; there is an unpaired electron localized on C2, and the rest of the spin density mostly belongs to sulfur. M13Q presents S−C1 and C1−C2 bonds that are average between single and double; there are two unpaired electrons localized on C1 and C3, respectively, and the rest of the spin density is shared by S and C2. As in many other cases, the corresponding doublet structure, M14, is much lower in energy, namely, 57.8 kcal/mol. M9Q also appears to have no symmetry. The salient features of its electron distribution are an almost double C2−C3 bond, an unpaired electron localized on C2, and the rest of the spin density corresponding mostly to the sulfur atom. We could not locate an analogous minimum on the doublet PES, but there is a similar structure with a S−C−C cycle (the allene episulfide cation) named M5, which is 66.2 kcal/mol lower in energy than M9Q.

M17Q may generate M8Q by ring opening; the latter species is 20.1 kcal/mol lower in energy. The corresponding transition state is only 3.0 kcal/mol higher in energy than M17Q. M8Q has an almost double C2−C3 bond and the spin density is shared by S and C3, but it is somewhat lower in the latter atom. The analogous doublet species, M24, is only 19.2 kcal/mol more stable.

In principle, M8Q might generate M9Q by hydrogen migration; M9Q is only 0.3 kcal/mol higher in energy and has already been described. However, the corresponding saddle point is 48.5 kcal/mol higher in energy than M8Q and as much as 19.7 kcal/mol higher in energy than the reactants, so this process cannot take place in the $S^+ + CH_3CCH$ reaction. M8Q may generate M11Q by hydrogen migration from C1 to S. M11Q is slightly higher in energy than M8Q (5.4 kcal/mol), but the corresponding transition state is 35.0 kcal/mol higher in energy than M8Q. M11Q presents a $^4A'$ electronic state with a $[\ldots 15a'^2 2a''^2 16a'^1 3a''^1 4a''^1]$ electron configuration. Its three bonds between heavy atoms are somehow average between single and double. The spin density is divided between S, C1, and C2, with sulfur having the largest share. M11Q relates to species M16 of the doublet surface, which lies 51.0 kcal/mol below the former species.

M11Q can be connected to several structures. One of them is M23Q, but this species is 10.9 kcal/mol above the reactants. M23Q has an unpaired electron localized on C2, and C3 retains most of the rest of the spin density. The C2−C3 bond is average between double and single. There is an analogous minimum on the doublet PES, M21, which is 79.7 kcal/mol lower in energy. If M11Q undergoes hydrogen migration from C2 to C3, then we get species M10Q; the latter state is only 0.3 kcal/mol more stable than M11Q. M10Q has a $^4A'$ electronic state arising from the following configuration: $[\ldots 15a'^2 2a''^2 16a'^1 3a''^1 4a''^1]$. The three bonds of the chain S−C1, C1−C2, and C2−C3 are average between single and double. There is an unpaired electron residing on C2, and the rest of the spin density is split between S and C3, the latter atom having a somewhat higher share. The corresponding minimum of the doublet PES, M7, is 68.3 kcal/mol lower in energy. Finally, M11Q might undergo a closure of the C_3 ring such that structure M24Q is generated, but the latter species lies 12.4 kcal/mol above the reactants. It has a weak C1−C2 bond, there is an unpaired electron localized on C3, and the rest of the spin density is divided between C2 and S, residing mostly on C2. M24Q is the highest-lying minimum, and it is only 0.4 kcal/mol lower in energy than TS1124Q. This fact suggests that M24Q could be a spurious minimum (more sophisticated levels of theory than the ones employed here would be necessary to assess this point). However, even if it were a true minimum, its influence on the reaction dynamics should be negligible. There is a similar species on the doublet PES, M20, that is more stable than M24Q by 81.4 kcal/mol.

M24Q may be connected with M21Q, which is also higher in energy than the reactants, although by only 0.7 kcal/mol. The C1−C2 bond is a weak one whereas the S−C1 bond is average between double and single. There is an unpaired electron localized on C1, and the rest of the spin density is divided between C2 and S, but C2 retains the major part. The analogous doublet species is M17, which lies 74.5 kcal/mol below.

M21Q is connected to M7Q by a saddle point that lies 20.9 kcal/mol above the reactants. The same is true for M6Q; the saddle point for the M6Q ↔ M19Q isomerization lies above the reactants. M6Q has a $^4A'$ state corresponding to the electron configuration $[\ldots 15a'^2 2a''^2 16a'^1 3a''^1 4a''^1]$. The S−C1, C1−C2, and C1−C3 bonds are all average between single and double. About half of the spin density is localized on the C2 atom, and the rest is divided between C3 and S. There is a corresponding structure on the doublet PES, M25, that is only 15.3 kcal/mol lower in energy. Finally, M21Q is connected to M13Q; the corresponding saddle point is also above the reactants. M13Q is connected to M16Q; the latter species is 13.0 kcal/mol higher in energy. The corresponding saddle point is 17.2 kcal/mol higher in energy than the reactants. M16Q presents a $^4A''$ state with a $[\ldots 14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. The S−C1 and C1−C2 bonds are average between single and double, C1 has an unpaired electron, and the rest of the spin density corresponds to C2 and S, the former atom having the higher share. The doublet M8 species is similar to M16Q and lies 80.6 kcal/mol lower in energy. M16Q connects with M22Q through a very high-lying saddle point (57.4 kcal/mol above the reactants). M22Q is also above the reactants (0.9 kcal/mol). It has a nonplanar C_s-symmetric structure with a $^4A''$ electronic state arising from a $[\ldots 14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. The S−C1 and C1−C2 bonds are average between single and double. C2 holds two unpaired electrons, and sulfur draws most of the rest of the spin density. The analogous form of the doublet PES, M26, is also very high lying but still 37.8 kcal/mol lower than M22Q.

M5Q is connected to M19Q, which is 29.2 kcal/mol higher in energy. The corresponding transition structure lies 38.8 kcal/mol above M5Q and 6.7 kcal/mol above the reactants. Concerning the electron distribution of M19Q, the S−C1 bond appears to be almost double, and S, C1, and C3 all hold an unpaired electron. The corresponding doublet species is M9, which lies 86.5 kcal/mol below M19Q. M19Q gives M15Q by the formation of a C1−C3 bond; this process entails ring closure. The corresponding saddle point, however, is only 1.1 kcal/mol higher in energy than M19Q, so this species must be considered, at the most, to be a very unstable one (it might not be a true minimum at higher levels of computation). M15Q has a $^4A''$ electronic state and a $[\ldots 12a'^2 5a''^2 13a'^1 14a'^1 6a''^1]$ electron configuration. The S−C1 bond is average between single and double. One of the unpaired electrons is localized on C1, and sulfur retains most of the rest of the spin density. The analogous doublet species is M6, which is 74.7 kcal/mol more stable than M15Q. M15Q may transform into M1Q by means of a C2−C3 bond-breaking process that entails ring opening. The corresponding transition state is only 10.9 kcal/mol higher in energy than M15Q but lies as much as 52.3 kcal/mol above M1Q. M1Q has C_{2v} symmetry and presents a $^4A_1$ state and a $[...10a_1^2 2b_1^2 5b_2^2 1a_2^1 3b_1^1 6b_2^1]$ electron configuration. The S−C1 bond and the C−C bonds are average between single and double. Sulfur holds most of the spin density, and C2 and C3 share the rest. The analogous doublet species, M22, is rather high lying, but even in this case it is lower in energy (by 8.9 kcal/mol) than the quartet species. M1Q may isomerize to M9Q by sulfur migration; the corresponding transition state is also quite high in energy with respect to M1Q (45.1 kcal/mol) but clearly lower than the reactants (by −13.7 kcal/mol).

The quartet thiete cation M17Q is connected to another four-membered cycle M20Q and also to species M14Q by ring opening; the corresponding transition states are well above the reactants by 33.7 and 17.4 kcal/mol, respectively. M20Q has a $^4A'$ electronic state with a $[...14a'^2 3a''^2 15a'^1 4a''^1 5a''^1]$ electron configuration. There is an unpaired electron localized on S whereas C1 holds most of the rest of the spin density. M20Q relates to species M18 of the doublet PES; the latter state is as much as 68.9 kcal/mol lower in energy. M14Q is a C_s-symmetric species that presents a $^4A''$ electronic state arising from a $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. C3 has an unpaired electron whereas the rest of the spin density is divided between C1, which holds the major part, and sulfur. The three bonds between heavy atoms are average between single and double, but C2−C1 is almost a double bone whereas S−C3 is almost single. The corresponding doublet species, M23, is 28.2 kcal/mol lower in energy. M14Q is connected to M18Q by a saddle point that lies 20.7 kcal/mol above the reactants; the corresponding process entails hydrogen migration between the carbon atoms bonded to sulfur. M18Q is a nonplanar species with C_s symmetry that presents a $^4A''$ electronic state with a $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. The S−C2 and C2−C1 bonds are average between single and double, although the former is quite close to being double (the AIM bond order is 1.75). C1 holds about half of the spin density, and the rest is divided between C2 and S, C2 having the major part of it. The corresponding doublet species M11 is 77.9 kcal/mol lower in energy.

M12Q is connected to M20Q by ring opening and to M14Q by hydrogen migration. M12Q has a nonplanar structure of C_s symmetry with a $^4A''$ electronic state corresponding to a $[...14a'^2 3a''^2 15a'^1 16a'^1 4a''^1]$ electron configuration. C3 has an unpaired electron, and the rest of the spin density is divided between the other heavy atoms, C2 having the largest share. The equivalent species of the doublet PES is M15, which lies 54.0 kcal/mol lower in energy.

As in the case of the doublet intermediates, some of the species have other isomeric forms that lie very close in energy to the most stable one, which is the one described here. Those species are M3Q, M5Q, M8Q, M10Q, M11Q, M12Q, and M13Q.

C. Products of the $S^+ + CH_3CCH$ Reaction. C.1. $SC_3H_3^+$ System. In this section, the most-relevant minima of both the singlet and triplet PESs of the $SC_3H_3^+$ system are described. We are going to start with the singlet species and follow an order based on increasing energy for both singlet and triplet states. The triplet species are marked with a T. Atomic charges and spin densities have been computed using the AIM method in combination with the B3LYP/6-311G** level. The optimized geometries are shown in Figure 3. The absolute and relative energies are presented in Table 2.

$SC_3H_3^+$_1 presents the structure of 2-propenylium, 1-thioxo and has a $^1A'$ electronic state corresponding to a $[...15a'^2 3a''^2]$ electron configuration. Perhaps the main feature of its electronic structure is a S−C1 bond that is average between double and triple and is very polar (the atomic charges are $Q(S) = 1.15$ and $Q(C1) = -0.76$). Both C−C bonds are average between single and double. In the $SC_3H_3^+$ species, no matter whether they are singlet or triplet, sulfur holds most of the positive charge, but quite often $Q(S) < 0.70$, and the rest of the charge is very much divided between many atoms, with very significant contributions of the hydrogen atoms. In this respect, $SC_3H_3^+$_1 is an exception, the result being the strong polarization of the S−C bond. Recall that the absolute minimum of the $SC_3H_4^+$ system is also a ketene cation—the methyl thioketene cation.

$SC_3H_3^+$_2, which has the structure of 2-cyclopren-1-ylium, 1-mercapto, presents a $^1A'$ state arising from a $[...15a'^2 3a''^2]$ electron configuration and lies 15.7 kcal/mol above the previous species. The S−C1 bond as well as the three C−C bonds are average between double and single.

$SC_3H_3^+$_3 is a thiol with an open structure. It has a $^1A'$ state corresponding to a $[...15a'^2 3a''^2]$ electron configuration and lies 11.0 kcal/mol higher than the previous species. The S−C1 and C1−C2 bonds are average between double and single whereas the C2−C3 bond is average between double and triple.

$SC_3H_3^+$_4 presents a $^1A'$ state with a $[...15a'^2 3a''^2]$ electron configuration and lies only 0.4 kcal/mol above the preceding species. The S−C1 and C2−C3 bonds are average between single and double whereas the C1−C2 bond has some triple character. The positive charge is localized on sulfur, making the S−C1 bond strongly polar (the atomic charges are $Q(S) = 0.87$ and $Q(C1) = -0.47$).

$SC_3H_3^+$_5 (the methylenethiirene cation) has a S−C−C ring and is 5.4 kcal/mol higher in energy than the latter species. The electronic state is $^1A'$ arising from the $[...15a'^2 3a''^2]$ electron configuration. The S−C2 bond is very weak (the corresponding Mulliken overlap population is 0.22 at the B3LYP/6-311G** level, and the S−C overlap population of methylthiol is 0.51). The S−C1 and C1−C2 bonds are average between single and double whereas the C2−C3 bond is almost double.

$SC_3H_3^+$_6 is a four-membered cycle (the thietium cation) that lies only 3.6 kcal/mol above the preceding structure. It has a $^1A'$ electronic state and a $[...15a'^2 3a''^2]$ electron configuration. The S−C3 and C1−C2 bonds are average between single and double.

$SC_3H_3^+$_7 has the structure of 1-propynylium,1-thioxo. Its electronic state is $^1A'$ and arises from a $[...14a'^2 4a''^2]$ electron configuration. The S−C bond is strongly polar (the atomic charges are $Q(S) = 1.00$ and $Q(C1) = -0.51$). It is 15.7 kcal/mol higher in energy than $SC_3H_3^+$_6.

$SC_3H_3^+$_8 is a four-membered cyclic species with a very weak linkage in the ring, namely, S−C2. The S−C1 and S−C3 bonds are also rather weak, but the bonds involving the carbon atoms are quite strong; in particular, C1−C2 is average between single and double. It has a plane of symmetry and presents a $^1A'$ state corresponding to a $[...14a'^2 4a''^2]$ electron configuration. It is only 1.3 kcal/mol higher in energy than the preceding species.

The next structure $SC_3H_3^+$_9 is also a four-membered cycle, but in this case, the internal bond involves two carbon atoms. It presents a $^1A'$ state with a $[...14a'^2 4a''^2]$ electron configuration.

TABLE 2: Energies (hartrees) and Relative Energies (kcal/mol) for the Possible Products of the $S^+ + CH_3CCH$ Reaction[a]

species	QCISD(T)/ 6-311G(2df,p)	ZPVE B3LYP/6-311G**	G2(QCI) type	G2(QCI) relative energy
$S^+(^4S) + CH_3CCH$	−513.69054	0.05548	−513.69266	0.0
H + $SC_3H_3^+$_1	−513.77600	0.04818	−513.79092	−61.7
H + $SC_3H_3^+$_2	−513.74860	0.04570	−513.76591	−46.0
H + $SC_3H_3^+$_3	−513.73034	0.04493	−513.74841	−35.0
H + $SC_3H_3^+$_4	−513.72895	0.04414	−513.74778	−34.6
H + $SC_3H_3^+$_5	−513.72243	0.04621	−513.73925	−29.2
H + $SC_3H_3^+$_6	−513.71774	0.04740	−513.73342	−25.6
H + $SC_3H_3^+$_7	−513.69007	0.04467	−513.70838	−9.9
H + $SC_3H_3^+$_8	−513.68991	0.04659	−513.70636	−8.6
H + $SC_3H_3^+$_9	−513.68732	0.04656	−513.70381	−7.0
H + $SC_3H_3^+$_10	−513.68077	0.04543	−513.69835	−3.6
H + $SC_3H_3^+$_11	−513.67667	0.04353	−513.69608	−2.1
H + $SC_3H_3^+$_12	−513.67040	0.04550	−513.68791	3.0
H + $SC_3H_3^+$_13	−513.66821	0.04686	−513.68441	5.2
H + $SC_3H_3^+$_14	−513.65796	0.04683	−513.67418	11.6
H + $SC_3H_3^+$_15	−513.65147	0.04328	−513.67113	13.5
H + $SC_3H_3^+$_16	−513.63763	0.04284	−513.65771	21.9
H + $SC_3H_3^+$_17	−513.63442	0.04307	−513.65428	24.1
$SH(^2\Pi) + C_3H_3^+$_1	−513.76887	0.05111	−513.78096	−55.4
$SH(^2\Pi) + C_3H_3^+$_2	−513.72435	0.04873	−513.73874	−28.9
$SH(^2\Pi) + C_3H_3^+$_3	−513.65609	0.04780	−513.67138	13.4
$HCS^+(^1\Sigma^+) + C_2H_3$_1	−513.73262	0.04890	−513.74685	−34.0
$HCS^+(^1\Sigma^+) + C_2H_3$_2	−513.65427	0.04759	−513.66976	14.4
$HSC^+(^1A') + C_2H_3$_1	−513.61206	0.04532	−513.62975	39.5
$HSC^+(^1A') + C_2H_3$_2	−513.53371	0.04401	−513.55266	87.9
H + $SC_3H_3^+$_1T	−513.71699	0.04574	−513.72853	−22.5
H + $SC_3H_3^+$_2T	−513.69751	0.04640	−513.70841	−9.9
H + $SC_3H_3^+$_3T	−513.69312	0.04486	−513.70550	−8.1
H + $SC_3H_3^+$_4T	−513.68410	0.04320	−513.69809	−3.4
H + $SC_3H_3^+$_5T	−513.68033	0.04399	−513.69356	−0.6
H + $SC_3H_3^+$_6T	−513.66979	0.04183	−513.68510	4.7
H + $SC_3H_3^+$_7T	−513.67229	0.04474	−513.68479	4.9
H + $SC_3H_3^+$_8T	−513.66717	0.04762	−513.67688	9.9
H + $SC_3H_3^+$_9T	−513.66189	0.04501	−513.67413	11.6
H + $SC_3H_3^+$_10T	−513.65452	0.04500	−513.66677	16.2
H + $SC_3H_3^+$_11T	−513.65623	0.04698	−513.66656	16.4
H + $SC_3H_3^+$_12T	−513.64237	0.04074	−513.65874	21.3
H + $SC_3H_3^+$_13T	−513.64491	0.04409	−513.65804	21.7
H + $SC_3H_3^+$_14T	−513.63610	0.04575	−513.64762	28.3
H + $SC_3H_3^+$_15T	−513.63113	0.04640	−513.64202	31.8
H + $SC_3H_3^+$_16T	−513.62401	0.04157	−513.63957	33.3
H+$SC_3H_3^+$_17T	−513.61933	0.04257	−513.63392	36.9
H+$SC_3H_3^+$_18T	−513.61299	0.04331	−513.62687	41.3
H+$SC_3H_3^+$_19T	−513.60064	0.04420	−513.61366	49.6
H+$SC_3H_3^+$_20T	−513.59096	0.04403	−513.60415	55.5
H+$SC_3H_3^+$_21T	−513.58830	0.04223	−513.60322	56.1
H+$SC_3H_3^+$_22T	−513.58200	0.04382	−513.59539	61.0
$S(^3P) + C_3H_4^+$_1	−513.70522	0.05235	−513.71036	−11.1
$S(^3P) + C_3H_4^+$_2	−513.68222	0.05197	−513.68773	3.1
$S(^3P) + C_3H_4^+$_3	−513.66926	0.05162	−513.67511	11.0
$S(^3P) + C_3H_4^+$_4	−513.67130	0.05411	−513.67475	11.2
$S(^3P) + C_3H_4^+$_5	−513.60108	0.05034	−513.60817	53.0
$SH(^2\Pi) + C_3H_3^+$_1T	−513.65467	0.04423	−513.66765	15.7
$SH(^2\Pi) + C_3H_3^+$_2T	−513.61435	0.04304	−513.62849	40.3
$HCS^+(^3A') + C_2H_3$_1	−513.59669	0.04761	−513.60641	54.1
$HCS^+(^3A') + C_2H_3$_2	−513.51834	0.04631	−513.52933	102.5
$HSC^+(^3A') + C_2H_3$_1	−513.55531	0.04629	−513.56631	79.3
$HSC^+(^3A') + C_2H_3$_2	−513.47697	0.04499	−513.48923	127.7

[a] Some products are marked with T if they are in the triplet electronic state.

There is a very weak linkage between C1 and C3, but the S−C1 and C1−C2 bonds are close to double. It is very close in energy to the preceding species; the difference is only 1.6 kcal/mol.

$SC_3H_3^+$_10 is similar to $SC_3H_3^+$_5 but with the S−C−C ring in the other segment of the carbon chain. It has a plane of symmetry and presents a $^1A'$ state corresponding to a [...$14a'^2 4a''^2$] electron configuration. The C1−C2 linkage is rather weak, but the C2−C3 bond is stronger than a double bond. It is also close to the last species, the difference being 3.4 kcal/mol.

$SC_3H_3^+$_11 has a structure similar to that of the thioacrolein cation but with a hydrogen atom eliminated from the terminal carbon atom. As in the case of the thioxo compounds ($SC_3H_3^+$_1 and $SC_3H_3^+$_7), the S−C bond is very polar ($Q(S) = 0.86$ and $Q(C1) = -0.57$). Again, it is very close in energy to the former species, the difference being 1.5 kcal/mol.

$SC_3H_3^+$_12 is quite similar to $SC_3H_3^+$_5, which has a thiirene cycle. Its electronic state is $^1A'$, and its electron configuration is [...$15a'^2 3a''^2$]. The S−C2 bond is average between single and double. It is 5.1 kcal/mol higher in energy than the former species. This is the last singlet $SC_3H_3^+$ state for which the $S^+ + CH_3CCH \rightarrow SC_3H_3^+ + H$ reaction is exothermic.

$SC_3H_3^+$_13 and $SC_3H_3^+$_14 are four-membered cycles; the former is related to $SC_3H_3^+$_9, and the latter is similar $SC_3H_3^+$_8. It is interesting that the AIM analysis points to the existence of a weak C1−C3 bond with a covalent bond order of 0.76 in the case of $SC_3H_3^+$_13.

$SC_3H_3^+$_15 and $SC_3H_3^+$_16 are very-high-lying thiols. The former species is symmetric and has a $^1A'$ state with a [...$15a'^2 3a''^2$] electron configuration.

Finally, $SC_3H_3^+$_17 has a $^1A'$ state with a [...$15a'^2 3a''^2$] electron configuration. It presents a highly polar S−C bond ($Q(S) = 1.14$, $Q(C1) = -0.77$), as do the other thioxo compounds.

The lowest-lying triple state is $SC_3H_3^+$_1T, where sulfur is bonded to a propynyl group. It presents C_{3v} geometry and a $^3A''$ state corresponding to a [...$14a'^2 3a''^2$ $15a'^1$ $4a''^1$] electron configuration. The wave function analysis indicates that the S−C1 and C1−C2 bonds are basically double in character. As in the case of the singlet thioxo species, the S−C1 bond is very polar (with atomic charges $Q(S) = 1.04$, $Q(C1) = -0.53$). The unpaired electrons are localized on the S and C2 atoms. The analogous singlet species is $SC_3H_3^+$_7, which lies 12.6 kcal/mol lower in energy.

The next structure, $SC_3H_3^+$_2T, is a four-membered cyclic species of C_{2v} symmetry that presents a $^3B_2$ electronic state and a [...$10a_1^2 2b_1^2 5b_2^2 1a_2^1 3b_1^1$] electron configuration. The four bonds of the cycle are somehow average between single and double. The spin density is divided almost equally among S, C1, and C3; C2 has a very small contribution. There is not an analogous singlet species.

$SC_3H_3^+$_3T has C_s symmetry and presents a $^3A''$ state arising from a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration. The C2−C3 bond is a double bond whereas the C2−C1 and S−C1 bonds are average between single and double. Sulfur holds the major part of the spin density whereas C2 retains most of the rest. We could not find a similar structure on the singlet PES.

$SC_3H_3^+$_4T (2-propenylium, 1 thioxo) has C_s symmetry and presents a $^3A''$ state corresponding to a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration. The S−C1 bond is average between double and triple whereas the C1−C2 bond is average between single and double. As in the case of $SC_3H_3^+$_1T, the S−C bond is strongly polar ($Q(S) = 1.11$, $Q(C1) = -0.75$). One of the unpaired electrons is localized on C3, and S and C2 share the other. The corresponding singlet species, $SC_3H_3^+$_1, is 58.3 kcal/mol lower in energy.

$SC_3H_3^+$_5T (methylenethiirene cation) has a $^3A'$ state with a [...$15a'^2 2a''^2 3a''^1 4a''^1$] electron configuration. The C−C bonds are average between single and double. Most of the spin density is divided between S and C3; the rest goes to C1. The corresponding singlet species, $SC_3H_3^+$_5, is 28.6 kcal/mol lower in energy.

The first thiol is $SC_3H_3^+$_6T, which has a $^3A''$ state arising from a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration. The C1−C2 bond is a double bond whereas the S−C1 and C2−C3 bonds are average between single and double bonds. The S−C1 bond is considerably polar (atomic charges $Q(S) = 0.86$, $Q(C1) = -0.39$). The spin density is delocalized along the S−C−C−C frame. The analogous singlet structure, $SC_3H_3^+$_4, is 39.3 kcal/mol lower in energy. The generation of $SC_3H_3^+$_6T in the $S^+ + CH_3CCH$ reaction is already an endothermic process, so the rest of the triplet species are somewhat less important for the present purposes.

$SC_3H_3^+$_7T (the 1-cyclopropenethione cation) has a $^3A''$ state coming from a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration. The S−C1 bond is a double bond whereas C1−C2 is average between single and double. The spin density is mostly localized on the sulfur atom; C2 has a small share.

$SC_3H_3^+$_8T, $SC_3H_3^+$_11T, $SC_3H_3^+$_14T, and $SC_3H_3^+$_15T are all four-membered thietiumlike structures. The first three all have C_s symmetry and $^3A''$ states corresponding to a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration. One unpaired electron resides on the carbon atom that is not bonded to hydrogen, and sulfur has an important share of the rest of the spin density. The S−C3 bonds of $SC_3H_3^+$_8T and $SC_3H_3^+$_11T are quite weak whereas both S−C bonds of $SC_3H_3^+$_14T are average between single and double. $SC_3H_3^+$_15T has no symmetry and should be better viewed as a consisting of condensed cycles because the C1−C3 bond is not very weak—its AIM bond order is 0.93, which is coincident with the C2−C3 bond order and slightly lower than the C1−C2 bond order (1.13). C1 and C3 together hold an unpaired electron (C1 having the higher share) whereas the rest of the spin density is mostly localized on sulfur.

There are a number of high-lying thioxo compounds, namely, $SC_3H_3^+$_9T, $SC_3H_3^+$_13T, $SC_3H_3^+$_19T, and $SC_3H_3^+$_22T. The first species has a $^3A'$ electronic state with a [...$14a'^2 3a''^2 15a'^1 16a'^1$] electron configuration. $SC_3H_3^+$_19T has a $^3A''$ state corresponding to a [...$14a'^2 3a''^2 15a'^1 4a''^1$] electron configuration, and the other two have no symmetry. In all cases, especially for $SC_3H_3^+$_13T, the S−C bond is highly polar, and the sulfur atom holds a sizable positive charge. The unpaired electrons are localized on S and C3 (9T), on C3 (13T), on S and C1 (19T), and on S (22T).

$SC_3H_3^+$_10T (methylidynethiirane cation) presents a $^3A''$ state with a [...$14a'^2 3a''^2 15a'^1 4a''^1$] configuration. S and C3 have the unpaired electrons, and the C2−C3 bond is a double bond.

$SC_3H_3^+$_12T, $SC_3H_3^+$_16T, $SC_3H_3^+$_17T, $SC_3H_3^+$_18T, $SC_3H_3^+$_20T, and $SC_3H_3^+$_21T are thiols with very different structures. $SC_3H_3^+$_12T and $SC_3H_3^+$_20T have open carbon chains; the former species presents no symmetry whereas the latter has a $^3A'$ state corresponding to a [...$14a'^2 3a''^2 15a'^1 16a'^1$] electron configuration. In the 12T species, the spin density is delocalized along the S−C−C−C frame whereas in the 20T form it is localized on the terminal carbon; the C−C bond orders are consistent with the corresponding distances and somehow explain why 12T is much lower in energy than 20T.

$SC_3H_3^+$_16T, $SC_3H_3^+$_18T, and $SC_3H_3^+$_21T all have three-membered carbon rings. The first and second species each present C_s symmetry and have a $^3A''$ electronic state but different electron configurations, namely, [...$13a'^2 4a''^2 14a'^1 5a''^1$] (16T) and [...$14a'^2 3a''^2 15a'^1 4a''^1$] (18T). 16T and 21T have the unpaired electrons localized on two atoms; one of them is sulfur, and the other is C1 in the former structure and C3 in the latter. In $SC_3H_3^+$_18T, the C2 atom retains one unpaired electron, but the rest of the spin density is divided between S and C1; the S−C1 bond may be considered to be average between single and double and appears to be very polar ($Q(S) = 0.71$, $Q(C1) = -0.39$).

$SC_3H_3^+$_17T is a nonplanar four-membered cycle that presents C_s symmetry. The electronic state is $^3A''$, and the dominant electron configuration is [...$12a'^2 5a''^2 13a'^1 6a''^1$]. The C−C bonds are average between single and double, and the spin density is delocalized along the C3 frame. This structure differs from that of $SC_3H_3^+$_2T in the fact that there is a S−H bond instead of a C2−H bond. The energy difference between these two bonds and the loss of the lone pair that sulfur has in the 2T species justify why 17T is so much higher in energy.

C.2. $C_3H_4^+$ System. We have made a preliminary study of the lowest-lying states of the $C_3H_4^+$ system to determine which ones may be important in the present context.

The most stable structure is the allene cation $C_3H_4^+$_1, which has C_2 symmetry and presents a ^2B electronic state (see Figure 3). The next species in order of increasing energy ($C_3H_4^+$_2) has basically the same structure as propyne, but the geometry relaxes to C_s symmetry; the electronic state is $^2A'$ although there is an almost-degenerate $^2A''$ Jahn−Teller component. The measured ionization energy of propyne is 10.36 ± 0.01 eV,[41] which is coincident with our computed value, provided we employ $C_3H_4^+$_2 as the ionic form in the computation. The latter species is 14.2 kcal/mol higher in energy than the ground state. $C_3H_4^+$_3 results from the ionization of cyclopropene. It presents C_2 symmetry and a ^2A electronic state. It is 7.9 kcal/mol higher in energy than the preceding species. $C_3H_4^+$_4 can be generated from the preceding structure by ring opening. It is a planar structure with a $^2A'$ electronic state, which is virtually equal in energy to the cyclic form because it lies only 0.2 kcal/mol above. Finally, we could locate a very-high-lying local minimum $C_3H_4^+$_5 (1-propenylidene cation) that lies 41.8 kcal/mol above the preceding species and has nonplanar C_s geometry and a $^2A'$ electronic state.

C.3. $C_3H_3^+$ System. We have studied some of the lowest-lying states of the $C_3H_3^+$ system, both singlet and triplet. The ground state, $C_3H_3^+$_1, is a cyclic structure of C_{3h} symmetry with a $^1A_1$ electronic state. The next species in order of increasing energy ($C_3H_3^+$_2) is the propargyl cation, which lies as much as 26.5 kcal/mol above the ground-state according to our G2-type computations. Li et al.[42] have obtained a similar energy difference, 27.6 kcal/mol, at the MP4/6-31G**//MP2/6-31G* + ZPVE(HF/4-31G) level. Wong and Radom[43] have obtained a somewhat smaller energy gap, namely, 24.7 kcal/mol, at the MP4/6-311G (2d,2p)//MP2/6-31G* + ZPVE(HF/6-31G*) level. Maclagan[44] has computed the G1 value (26.3 kcal/mol), which, not surprisingly, turns out to be almost coincident with our result.

The next species (2-propen-1-ylium-1-ylidene) has a planar structure and presents a $^1A'$ electronic state. It lies 42.3 kcal/mol above the propargyl cation. This value is almost coincident with the one computed by Li and co-workers,[42] namely, 42.5 kcal/mol.

We have also studied a few relatively low-lying triplet states. $C_3H_3^+$_1T is the lowest-lying triplet state of the propargyl cation ($^3A_2$); it lies 44.6 kcal/mol above the corresponding singlet state. $C_3H_3^+$_2T can be viewed as the lowest triplet state of the $C_3H_3^+$_1 structure; however, it is an open structure of C_2 symmetry. It lies as much as 95.7 kcal/mol above $C_3H_3^+$_1. We have been able to locate other triplet minima, but they are very much higher in energy and will not be described here.

C.4. C_2H_3 System. We have studied the two lowest-lying forms of C_2H_3. The ethenyl radical (C_2H_3_1) is the ground state ($^2A'$), and methyl carbene lies 48.4 kcal/mol above the ground state. The latter species presents a nearly degenerate Jahn−Teller component of $^2A'$ symmetry.

C.5. HCS^+ System. We have studied the HSC^+ and HCS^+ conformations in both the lowest singlet and triplet states. HCS^+($^1\Sigma^+$) is the ground state. The lowest triplet state HCS^+($^3A'$) is as much as 88.1 kcal/mol higher in energy. The lowest singlet state also has a minimum for the HSC conformation at the B3LYP/6-311G** level, but it is an angular one; it presents a $^1A'$ state, and lies 73.5 kcal/mol above HCS^+($^1\Sigma^+$). The saddle point for the isomerization is only 0.7 kcal/mol higher in energy than HSC^+($^1A'$), so the latter structure could be a spurious minimum; this conclusion would be in agreement with the ab initio results of Peyerimhoff et al.[45] The lowest triplet state also has a HSC minimum lying 39.8 kcal/mol above the corresponding singlet form.

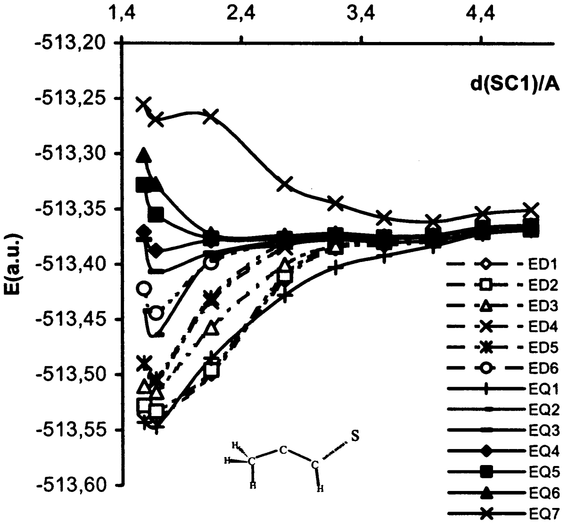


Figure 4. MRCISD/6-311G* energy profiles for the elimination of sulfur from M3Q. Solid lines correspond to the quartet states.

Fragmentation of $SC_3H_4^+$: Dynamics of the $S^+ + CH_3CCH$ Reaction. We have verified that the interaction of the sulfur cation with propyne is attractive in nature if it involves the carbon atoms of the triple bond. To do this, we have performed multireference configuration interaction[39] calculations with single and double excitations (MRCISD) for seven quartet states and six doublet states correlating with some of the lowest-lying states of both $S^+ + CH_3CCH$ and $S + CH_3CCH^+$. The reference wave function is a multiconfiguration self-consistent (MCSCF) wave function of the complete active space type (CASSCF)[46] defined for a state that is an average of the lowest six doublet and seven quartet states. The geometries of the two reaction coordinates we have employed have no symmetry, and the active space consists of [9a−20a] orbitals with 21 electrons. The basis set employed is 6-311G*. There are two quartet intermediates resulting from the bonding of S^+ to propyne, namely, M4Q, where the bond is with the central carbon, and M3Q, where the bond is with the terminal carbon of the acetylene group. We have found a transition state for the elimination of the sulfur cation from M4Q (TS4SQ), but there is no saddle point for M3Q. We have obtained a reaction coordinate at the B3LYP/6-311G** level that starts from M4Q and goes through TS4SQ and then the sulfur atom leans somewhat to the terminal (acetylenic) carbon and finally moves away from propyne. As we have pointed out above, TS4SQ can be viewed to some extent as the transition state for the M3Q ↔ M4Q isomerization, but it must be understood that this process entails the breaking of the S−C1 bond and the subsequent formation of the S−C2 bond. Unfortunately, it has not been possible to make the MRCI computations converge for the whole set of states at some points on the reaction coordinate (when sulfur tilts to the terminal carbon). For this reason, we have employed two reaction coordinates; the first one starts from M4Q and shortly passes TS4SQ, and the second starts from M3Q and reaches a large S−C distance (see Scheme 2). The results are shown in Figures 4 and 5.

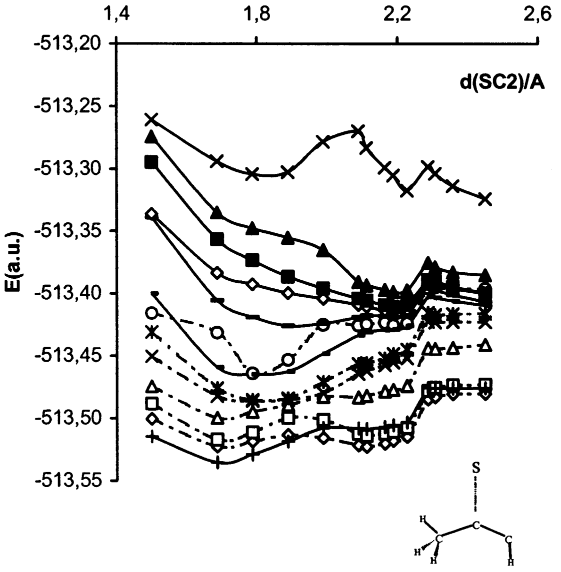


Figure 5. MRCISD/6-311G* energy profiles for the elimination of sulfur from M4Q. The states are noted as in Figure 4.

It is readily seen in Figure 4 that the lowest four quartet states are attractive. However, the highest quartet state correlates with $S^+(^4S)$ + CH_3CCH at large S−C distances (i.e., with the reactants) whereas the other states correlate with S + CH_3CCH^+ (i.e., with the electron-transfer products). In other words, the state correlating with the reactants is repulsive, so from a Born−Oppenheimer point of view, there must be a mechanism for the system to undergo surface hopping to the lowest attractive electronic states. Figure 4 shows no conspicuous avoided crossing between the highest quartet state and any other quartet state; such a crossing would be related to a Landau−Zener mechanism.[47] However, the energy profiles of the highest quartet state and the other quartet states are basically parallel at long S−C distances and start diverging at short distances. This pattern is compatible with a nonadiabatic transition of the Rosen−Zener−Demkov type.[47] Moreover, the energy gap between the highest quartet state and the other quartet states is probably not as wide as Figure 4 suggests because, as we will mention below, the experimental value for the energy of the electron-transfer reaction is 0.00 eV.[41,48] This near-degeneracy would increase the probability of a Rosen−Zener−Demkov transition into the group of quartet states correlating with S + $CH3CCH^+$. Another very important point is that the near-degeneracy between the doublet states and all of the quartet states except the highest one is maintained up to quite short distances. This near-degeneracy is also encountered in Figure 5. In fact, there are some doublet−quartet crossings. Note that the lowest doublet state lies below the lowest quartet in the region of the TS4SQ saddle point (see also Figure 2). These facts point to the occurrence of an intersystem crossing (ISC) process. It must also be noted that the near-degeneracy of doublet and quartet states in the M3Q and M4Q minima disappears with the relatively modest geometrical changes that would bring the conformations of M3Q or M4Q into line with that of M4. An MRCISD/6-311G* computation (including Davidson's correction and employing the same active space as in the calculation of the energy profiles) on the optimal geometry of M4 gives an energy gap between the electronic ground state (which is a doublet) and the lowest quartet state of 155.8 kcal/mol. For this reason, we will assume that a high percentage of the reaction flux will end up on the doublet PES by means of ISC processes taking place in the region of the M4 local minimum.

To discuss the reaction mechanisms, we distinguish between trajectories not affected by an ISC process, which will be described by the quartet PES, and those undergoing an ISC process, which will evolve on the doublet PES.

A. Evolution on the Quartet PES. The evolution on the quartet surface is very much constrained by the fact that many saddle points and local minima lie above the reactants S^+ + CH_3CCH, so the system will normally not have enough energy to reach those points (see Scheme 2). Considering the energy of the many saddle points, we have identified the following processes as the most important:

$$S^+ + CH_3CCH \rightarrow M4Q,\ M3Q$$

$$M3Q{-}TS23Q \rightarrow M2Q \rightarrow SC_3H_3^+\_1T + H$$

M2Q may also transform into M9Q, which in turn may give S + $C_3H_4^+$_1 or $SC_3H_3^+$_3T + H or isomerize into M1Q, which may produce S + $C_3H_4^+$_1.

B. Evolution on the Doublet PES. The evolution on the doublet PES is much more complicated and is preceded by an ISC process:

$$S^+ + CH_3CCH \rightarrow M3Q,\ M4Q{-}ISC \rightarrow M4$$

In this case, there are very few forbidden processes because most of the saddle points and reaction intermediates lie below the reactants (see Scheme 1). We have identified a number of processes for the generation of the different products, which according to the energy of the intermediates and the transition states involved with them as well as the nature of those transition states (tight or loose)[49] should be the most important ones.

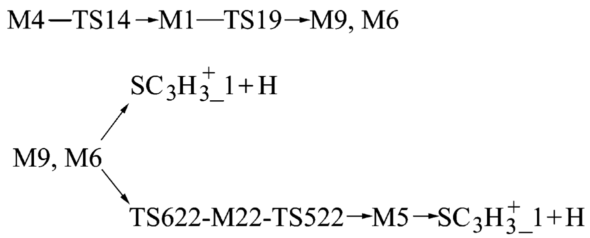
B.1. Formation of $SC_3H_3^+$ + H. These products may be generated in many electronic states, as can be seen in Table 2, by the fragmentation of many intermediates. To keep the discussion simple, we will pay attention to only the most important channels.

M4 may undergo as many as six different isomerization processes (see Scheme 1), all of them involving tight transition states. It may also fragment into $SC_3H_3^+$_5 + H by C−H bond breaking in the methyl group, but this process requires relatively high energy as compared to that required for most of the isomerization channels ($SC_3H_3^+$_5 + H is −29.2 kcal/mol below the reactants). Besides, the collision and the ISC process leading to M4 are not likely to accumulate the excess energy in the methyl group; energy randomization may not be complete at this stage. The process needing less energy is, by far, the generation of the most stable form, M1:

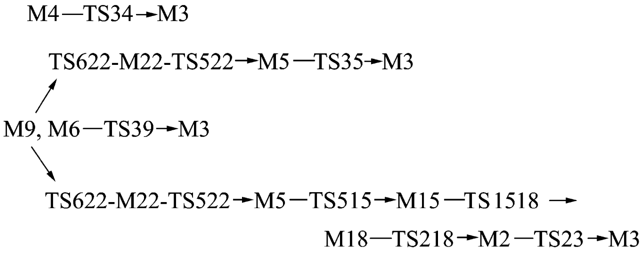
$$M4{-}TS14 \rightarrow M1 \rightarrow SC_3H_3^+\_1 + H$$

M1 has two isomerization channels giving M9−M6 and M4, respectively. The saddle points of these processes lie respectively −63.9 and −69.9 kcal/mol below the reactants. The C−H bond-breaking process of the methyl group has no saddle point (i.e., there is a loose transition state), and the products ($SC_3H_3^+$_1 + H) are only slightly higher in energy (−61.7 kcal/mol). Therefore, one would foresee that product generation may be an important process, although M1 may also undergo isomerization to M4 and, even more importantly, to M9−M6. The latter species may generate $SC_3H_3^+$_1 + H through a process involving no saddle point.

M9−M6 may also isomerize to M3, M5, and M18. The corresponding saddle points lie −63.5 kcal/mol (TS39), −67.9 kcal/mol (TS622 or TS522), and −50.9 kcal/mol (TS918) below the reactants. Only the first two processes, mostly the second one, are likely to be competitive with the generation of $SC_3H_3^+\_1$. M5 has five isomerization possibilities apart from conversion back to M9−M6, but only TS519 lies below $SC_3H_3^+\_1 + H$ (−64.1 kcal/mol vs −61.7 kcal/mol), so we predict that these products will also be produced from M5.



Note that $SC_3H_3^+\_1 + H$ are not only the most stable products (see Table 2) but also may be obtained from several of the most stable intermediates. In fact, they can also be generated from M3, but in this case, there is a saddle point TS3H that lies −54.8 kcal/mol below the reactants. M3 can be reached through several paths:



M3 has six isomerization paths, and the most energetically favorable is, by far, the generation of the four-membered cycle M2 (TS23 has a relative energy of −85.8 kcal/mol with respect to that of the reactants). However, M2 does not have very favorable fragmentation paths ($SC_3H_3^+\_6 + H$ has a relative energy of −25.6 kcal/mol), and the same is true for M10 and M11. These are the only intermediates that can be reached easily from M2, apart from M3. This is an important consideration because it implies that M2 may likely transform back into M3. The four-membered cyclic intermediates—M2, M10, M12, M13, M18, and M19—may be reached from M5 through TS519. These cyclic species may very often end up producing M3, although the process M2−TS213 → M13 certainly provides an "escape route" connecting them to the many thiols encountered in the doublet PES.

B.2. Generation of $HCS^+ + C_2H_3$. The only products of this type that are compatible with an exothermic reaction are $HCS^+(^1\Sigma^+) + C_2H_3\_1$ (their relative energy with respect to the reactants is −34.0 kcal/mol). This result limits their generation possibilities almost to the fragmentation of M3, which does not present a transition state:

$$\mathrm{M3} \rightarrow \mathrm{HCS}^+(^1\Sigma^+) + \mathrm{C_2H_3\_1}$$

B.3. Generation of $C_3H_3^+ + SH$. According to Table 2, the reaction would be exothermic only if $C_3H_3^+\_1$ or $C_3H_3^+\_2$ is formed; the intermediates that may be involved are M20 and M7, respectively. One of the routes is

$$\mathrm{M3{-}TS314} \rightarrow \mathrm{M14{-}TS714} \rightarrow \mathrm{M7}$$

$$\mathrm{M7} \rightarrow \mathrm{C_3H_3^+\_2} + \mathrm{SH}$$

$$\mathrm{M7{-}TS716} \rightarrow \mathrm{M16{-}TS1620} \rightarrow \mathrm{M20} \rightarrow \mathrm{C_3H_3^+\_1} + \mathrm{SH}$$

M14 may easily transform into M17 (TS1417 has a relative energy of −63.7 kcal/mol), but the isomerization of the latter species to M25 is more difficult because the relative energy of TS1725 is −46.2 kcal/mol. The most favorable isomerization process of M7, apart from transformation back into M14, is conversion to M16. The most favorable isomerization of M16 gives precisely M20. Besides, M16 is part of the escape route from the region of the PES corresponding to the four-membered cyclic intermediates that we mentioned above, so one could imagine a process such as

$$\mathrm{M2{-}TS213} \rightarrow \mathrm{M13{-}TS1316} \rightarrow \mathrm{M16{-}TS1620} \rightarrow \mathrm{M20} \rightarrow \mathrm{C_3H_3^+\_1} + \mathrm{SH}$$

Note that M13 may isomerize somewhat faster to M16 than back to M2 because the relative energies of the corresponding transition states are −57.9 and −52.7 kcal/mol, respectively. Note also that conversion to M13 is the most favorable transformation path of M2 apart from isomerization to M3.

Finally, the fragmentation of M20 into $C_3H_3^+\_1 + SH$ (which involves no saddle point, i.e., there is a loose transition state) might have a speed comparable to isomerization back to M16. The reason is that loose transition states are likely to draw more-reactive flux than tight ones if the energies are similar. The latter process (M20 → M16) involves the saddle point TS1620 (a tight transition state), which has a relative energy of −62.8 kcal/mol; this value is not far from the relative energy of $C_3H_3^+\_1 + SH$ (−55.4 kcal/mol). Incidentally, this could be one of the reasons that the branching ratio of $C_3H_3^+ + SH$ is quite high (20%) despite the fact that the reaction mechanisms leading to these products are rather involved.

B.4. Generation of $S + C_3H_4^+$. The experimental value of the energy of the process $S^+(^4S) + CH_3CCH \rightarrow S(^3P) + C_3H_4^+$ is 0.00 eV[41,48] (our computed value, using $C_3H_4^+\_2$, is 0.13 eV, i.e., 3.0 kcal/mol). This result implies that some of the collisions that result in dissociation may lead to $S(^3P) + C_3H_4^+\_2$ rather than to the reactants because the sulfur cation and propyne may have approached close enough for charge transfer to take place. This assumption is supported by the MRCISD study discussed above, which shows that the energy profiles corresponding to some quartet and doublet states interact even at very short distances (the doublet states correlate with $S(^3P) + C_3H_4^+\_2$). There are, of course, other possibilities. For instance, M4 may dissociate into $S(^3P) + C_3H_4^+\_2$, or M5 may dissociate into $S(^3P) + C_3H_4^+\_1$, but even the latter process is a relatively high-energy fragmentation (−11.1 kcal/mol), so they may not be competitive with other more favorable fragmentation processes mentioned above.

Conclusions

We have studied the PES of the $SC_3H_4^+$ system both in the lowest doublet and quartet states as well as the fragmentation products that can be obtained in the $S^+ + CH_3CCH$ reaction. The study of the fragmentation products includes a detailed analysis of the $SC_3H_3^+$ system. We have located a plethora of local minima on both the doublet and quartet PESs. In general, the quartet species of the $SC_3H_4^+$ system are much higher in energy than the doublet species. The absolute minimum is the methylthioketene cation, but the 2H-thiete cation, the thioacrolein cation, and the methylthiirene cation lie very close; all of them are doublet states. The most-stable quartet species, however, is a thioxyallyl cation of C_{2v} symmetry; the next quartet state has the conformation of thioacrolein and is about 9 kcal/mol higher in energy. The most-stable forms of $SC_3H_3^+$ are singlet species. The absolute minimum has the structure of 2-propenylium, 1-thioxo, which lies about 16 kcal/mol below the next state, formally 2-cyclopropen-1-ylium, 1-mercapto. The lowest triplet species has the conformation of ethenylium, methylthioxo and is 39 kcal/mol higher in energy than the ground state.

We have also studied the interaction between S^+ and CH_3CCH through a number of electronic states. The results suggest that an intersystem crossing process may play a key role in the dynamics of the $S^+(^4S) + CH_3CCH(^1A_1)$ reaction. The evolution of the $SC_3H_4^+$ system on the quartet PES is very much limited by the fact that many intermediates and transition states are higher in energy than the reactants. Particularly, we have not found on the quartet PES any reaction path leading to $C_3H_3^+ + SH$, which, according to our results, should be generated by the fragmentation of a doublet intermediate. In fact, the formation of all products can be explained by the fragmentation of the doublet intermediates, although the mechanisms are sometimes rather involved.

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Supporting Information Available: Some details of Figures 1, 2, and 3 such as many of the dihedral angles of complex structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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