J. Phys. Chem. A **1999,** *103,* 9125−9131

Theoretical Study of the Reaction of S^+ with C_3H_2

Pilar Redondo, Elena Calleja, Carmen Barrientos, and Antonio Largo*

Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received: June 21, 1999; In Final Form: September 2, 1999

A theoretical study of the $(SC_3H_2)^+$ species has been carried out. Two different models, complete MP4 at MP2 geometries and QCISD(T) at B3LYP geometries, have been employed. Our calculations predict that the global minimum is $SCCCH_2{}^+(^2B_2)$, although a doublet cyclic isomer lies only about 5 kcal/mol higher in energy. The lowest-lying quartet is also $SCCCH_2{}^+(^4B_2)$, followed by a nonplanar three-membered ring isomer. These theoretical results allow the development of thermodynamic arguments about the reaction pathways of the process $S^+ + C_3H_2$. For the reaction of S^+ with cyclopropenylidene (c-C_3H_2) production of cyclic SC_3H^+ is slightly endothermic and proceeds through a significant energy barrier. On the other hand, production of the linear isomer $SCCCH^+$ is exothermic and there is at least a mechanism leading to this species that is barrier-free. However, the preferred channel seems to be charge transfer, since it is predicted to be more exothermic. In the case of the reaction of S^+ with vinylidenecarbene (l-C_3H_2), charge transfer is not competitive since it is clearly endothermic. Production of cyclic SC_3H^+, although exothermic, seems to involve an energy barrier at the QCISD(T) level. Production of the linear $SCCCH^+$ isomer should be the preferred channel, since it is more exothermic and there are two different mechanisms that are barrier-free. Therefore, it seems that only the linear $SCCCH^+$ isomer can be produced from the reaction of S^+ with both c-C_3H_2 and l-C_3H_2. Consequently, these ion−molecule reactions could be possible sources of precursors of C_3S in space.

Introduction

The interstellar chemistry of second-row elements has been the subject of growing interest in recent years. To date, about 30 molecules containing second-row elements have been detected in space. One of the most interesting classes of interstellar molecules containing these elements is that constituted by binary carbon clusters. Several compounds corresponding to the C_nX formulas have been observed in space. So far, simple binary compounds, CSi, CS, and CP, as well as other more complex compounds, such as C_2Si,[1] C_4Si,[2] C_2S,[3] and C_3S[4] have been detected in space.

In addition to the interest in astrochemistry, the study of binary carbon clusters is interesting on its own, because the properties of the carbon clusters may change by the presence of the heteroatom. Organosulfur clusters of the type C_nS have been the subjects of experimental[5−9] and theoretical[10−14] work. All these studies showed that the C_2S and C_3S compounds, which have been observed in space, have linear ground states. In the case of C_2S, the ground state corresponds to a triplet ($^3\Sigma^-$), whereas for C_3S a singlet ($^1\Sigma^+$) is shown to be the ground state. Theoretical studies[15,16] have also been carried out on the C_3S^+ and SC_3H^+ systems (as well as on the isoelectronic HC_3P[17,18] species).

One of the most interesting questions related to interstellar molecules is how these compounds may be produced in space. Given the physical conditions reigning in the interstellar medium (low density, low temperature), important processes must be exothermic and also must have low (or zero) activation energy. For that reason most of the proposed models[19−21] for the production of binary sulfur−carbon clusters claim that ion−molecule pathways should be the most important ones. In particular, Smith et al.[19] suggest the reactions of S^+ with hydrocarbons as the sources of C_nS compounds in space through the following scheme:

$$S^+ + C_nH_2 \rightarrow HC_nS^+ + H \tag{1}$$

$$HC_nS^+ + e \rightarrow C_nS + H \tag{2}$$

Nevertheless, quite recently Petrie[22] has also suggested alternative radical−neutral pathways to C_nS compounds, involving reactions of C_2H with S or CS:

$$S + C_2H \rightarrow C_2S + H \tag{3}$$

$$CS + C_2H \rightarrow C_3S + H \tag{4}$$

Therefore, to ascertain whether ion−molecule chemistry may play an important role in the interstellar synthesis of C_nS compounds, it would be interesting to study the reactions of S^+ with the appropriate hydrocarbons. In the case of the reaction of S^+ with acetylene, which would be the first step in the production of C_2S, we have previously carried out a theoretical study,[23] and there are also several experimental works[19,24,25] on such processes. Unfortunately, an experimental study in the case of the reaction of S^+ with C_3H_2 (which would be the first step in an ion−molecule pathway to C_3S) is highly unlikely, given the laboratory instability of C_3H_2. Therefore, a theoretical study in this case should be highly valuable. In addition, we must recall that there are two different C_3H_2 isomers that have been detected in the interstellar medium: cyclopropenylidene, c-C_3H_2, which is one of the most abundant hydrocarbons in interstellar space,[26] and propadienylidene (singlet vinylidenecarbene), l-C_3H_2, with a linear carbon backbone and two hydrogens bonded to an end carbon.[27] Theoretical studies[28,29] predict singlet cyclopropenylidene to lie lower in energy (about 14 kcal/mol) than propadienylidene.

---

* To whom correspondence should be addressed.

10.1021/jp992042j CCC: $18.00

In previous works[30,31] we have carried out theoretical studies of the reactions of P^+ and Si^+ with C_3H_2, concluding that both processes are feasible under interstellar conditions and may lead to precursors of the corresponding carbon clusters C_3P and C_3-Si. The aim of the present work is to provide a theoretical study of the reaction of S^+ with both isomers of C_3H_2, cyclic and linear, determining its energetics as well as the possible energy barriers associated with the different channels. In this way the different reaction pathways for the process $S^+ + C_3H_2$ can be analyzed by employing thermodynamic arguments. A comparison with the results obtained for phosphorus and silicon will be made. Since S^+ would be primarily formed from photoionization of the neutral atom, the reaction should proceed in principle on the quartet $(H_2C_3S)^+$ surface. Nevertheless, given the lack of information about the structure and stability of $(H_2C_3S)^+$ species, we will previously study the stable structures on both the doublet and quartet surfaces.

Computational Methods. The present work employs the same methods used in our previous studies on the reactions of P^+ and Si^+ with C_3H_2.[30,31] The geometries of all species studied in this work were obtained at the second-order Møller−Plesset (MP2) level with the split-valence plus polarization 6-31G* basis set,[32] including all electrons in the calculation. In addition, for comparative purposes, density functional theory (DFT) was also employed for obtaining optimized geometries. In the DFT calculations we used the B3LYP exchange-correlation functional,[33] and the 6-311G** basis set[34] for carbon and hydrogen atoms and the McLean and Chandler basis set[35] (supplemented with a set of d functions) for sulfur. Harmonic vibrational frequencies were also computed on each optimized structure at its corresponding level of theory, and these values were employed to estimate zero-point vibrational energies (ZPVE). These computations also allow an assessment of the nature of stationary points. We must point out that we have made tests with larger basis sets (in particular 6-311G** for MP2 calculations and cc-pVTZ[36,37] for B3LYP). The results obtained were very similar to those provided by the smaller basis sets.

On the MP2(full)/6-31G* geometries, single-point calculations at the fourth-order Møller−Plesset (MP4) level[38,39] were carried with the 6-311G** basis set. In these calculations inner-shell molecular orbitals were not included for computing electron correlation energies (frozen-core approximation). Spin contamination may affect the convergence of the MP series. For this reason, in addition to the MP4 energies, we will report the projected fourth-order Møller−Plesset values (PMP4).[40,41] On the B3LYP geometries we performed QCISD(T) calculations,[42] that is quadratic CI calculations with singles and doubles substitutions followed by a perturbative treatment of triple substitutions, with the 6-311G** basis set. The theoretically determined relative heats of formation are employed for the prediction of reaction enthalpies and energy barriers for the reaction of $S^+ + C_3H_2$.

All calculations were carried out with the Gaussian-94 program package.[43]

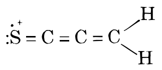
Results and Discussion

$(SC_3H_2)^+$ Isomers. The optimized geometries for the different $(SC_3H_2)^+$ structures are shown in Figure 1, the corresponding harmonic vibrational frequencies and IR intensities being available upon request.

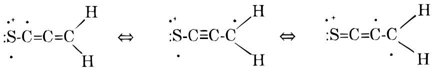
Isomer **1** corresponds to a linear carbon backbone with sulfur in a terminal position and the two hydrogen atoms bonded to the end carbon atom. Its lowest-lying electronic state is $^2B_2$, corresponding to the following electronic configuration:

$$\{\text{core}\}\ 7a_1^{\,2}\ 8a_1^{\,2}\ 9a_1^{\,2}\ 10a_1^{\,2}\ 11a_1^{\,2}\ 2b_2^{\,2}\ 2b_1^{\,2}\ 3b_2^{\,2}\ 3b_1^{\,2}\ 4b_2^{\,1} \qquad \text{(I)}$$

This structure can be represented by the following valence-bond description, which basically agrees with the geometrical parameters shown in Figure 1 (a relatively short S−C bond distance and two similar C−C bond distances slightly shorter than a normal carbon−carbon double bond).



Excitation of an electron from the $3b_1$ orbital to the $12a_1$ orbital in electronic configuration (I) would result in a $^4A_2$ state that correlates with ground-state $S^+(^4S) + l\text{-}C_3H_2(^1A_1)$, whose optimized geometry is also given in Figure 1. This structure in fact can be viewed as an ion−molecule complex, with a very long S−C distance. However, this structure is not a true minimum on the quartet $(H_2C_3S)^+$ surface, since it has an imaginary vibrational frequency at both MP2 and B3LYP levels (26i and 159i cm^{-1}, respectively), associated with a b_1 normal mode corresponding to out-of-plane bending. This suggests that there should be a nonplanar structure with lower energy. We made optimizations, following this mode, obtaining a $^4A''$ state that finally collapses into another C_{2v}-symmetric state ($^4B_2$) with an electronic configuration that can be obtained from (I) upon $3b_1 \rightarrow 4b_1$ excitation. The $^4B_2$ state is a true minimum (all its frequencies are real) and can be represented by the following dominant valence-bond structures: that explain why the C_1−C_2 distance is shorter than the C_2−C_3 one.



Both MP2 and B3LYP levels predict that the IR spectrum of the $^4B_2$ state should be dominated by a C−C stretching (2100 cm^{-1} at the scaled MP2 level and 2058 cm^{-1} at the B3LYP level). In the case of the $^2B_2$ state, C−C stretching at 1942 cm^{-1} is also predicted to be the most intense line in the IR spectrum at the B3LYP level, whereas MP2 predicts two different frequencies to have very similar intensities: C−C stretching at 1432 cm^{-1} and C−H symmetric stretching at 2986 cm^{-1} (both values are scaled MP2).

Isomer **2** has also an open-chain carbon backbone and a sulfur in a terminal position, but now the hydrogen atoms are bonded to different carbon atoms. We only were able to obtain this isomer on the quartet surface (the lowest-lying state corresponding to $^4A'$), since all attempts to obtain a doublet state led to the cyclic **3**($^2B_2$) state (see below). The geometrical parameters obtained for the **2**($^4A'$) species at both levels of theory, MP2 and B3LYP, are quite close. The C_1−C_2 and C_2−C_3 bond distances are considerably longer than the corresponding values for isomer **1**. The most intense line in the IR spectrum of **2**($^4A'$) is predicted to be a C−C stretching at 1543 cm^{-1} (scaled MP2) or 1680 cm^{-1} (B3LYP).

Isomer **3** has a cyclic C_3 unit with the sulfur atom bonded through an apex. The lowest-lying electronic state is also $^2B_2$, corresponding to the following electronic configuration

$$\{\text{core}\}\ 6a_1^{\,2}\ 7a_1^{\,2}\ 3b_2^{\,2}\ 8a_1^{\,2}\ 9a_1^{\,2}\ 4b_2^{\,2}\ 2b_1^{\,2}\ 10a_1^{\,2}\ 3b_1^{\,2}\ 5b_2^{\,1} \qquad \text{(II)}$$

The C_1−C_2 and C_2−C_3 bond lengths are very similar to those found for c-C_3H_2, whereas the S−C_1 distance suggests a true formal bond.

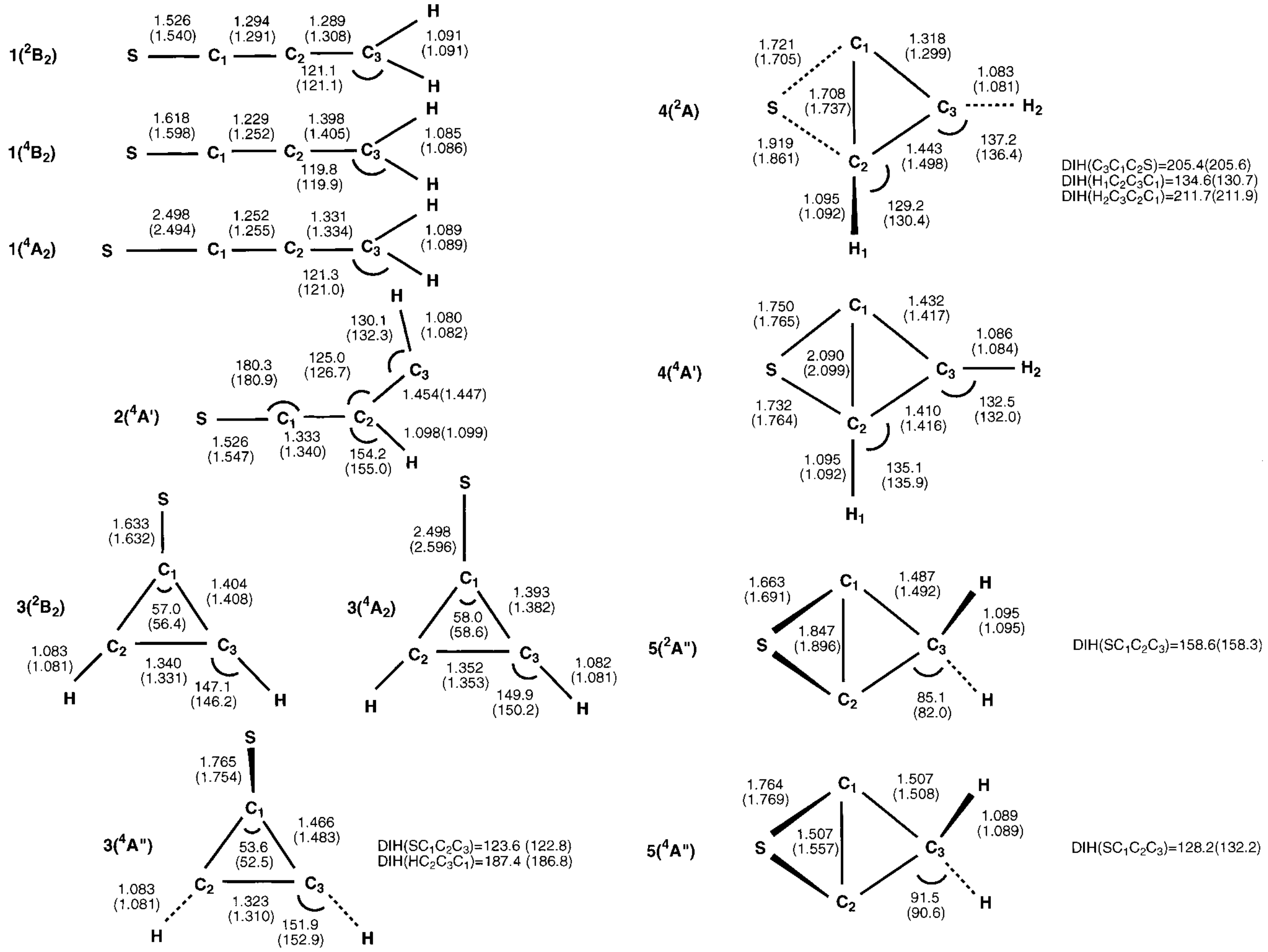


Figure 1. MP2/6-31G* and B3LYP/6-311G** (in parentheses) optimized geometries for the different $SC_3H_2^+$. Distances are given in angstroms, and angles, in degrees.

Upon $3b_1 \rightarrow 11a_1$ excitation, a $^4A_2$ state is obtained, which correlates with ground-state $S^+(^4S)$ + c-$C_3H_2(^1A_1)$. In this case the S−C_1 bond distance is very long, suggesting that in fact **3**($^4A_2$) is an ion−molecule complex. The geometrical parameters of the C_3H_2 unit are only slightly modified with respect to cyclopropenylidene. A cyclic structure with a short bond length on the quartet surface has also been found, corresponding to a nonplanar $^4A''$ state. It is interesting to point out that this state also correlates with $S^+(^4S)$ + c-$C_3H_2(^1A_1)$. All these cyclic states are true minima on the respective doublet and quartet surfaces, since all their vibrational frequencies are real. For both $^2B_2$ and $^4A_2$ a C−C stretching (near 1283 and 1358 cm^{-1}, respectively, at the B3LYP level) is predicted to dominate the IR spectrum. In the case of **3**($^4A''$) the most intense line is predicted to be a C−H stretching at 3224 cm^{-1}.

Two different isomers, numbered **4** and **5**, with a four-membered ring have been found on both doublet and quartet surfaces. In isomer **4** the two hydrogen atoms are bonded to different carbons, whereas in **5** they are bonded to the same carbon atom. In the case of the **4**(^2A) structure quite different peripheral C−C bond distances are found. The transannular C_1−C_2 length is much shorter for the doublet state than for the **4**($^4A'$) state. However none of them are indicative of a true C_1−C_2 bonding. In fact, the only four-membered ring structure with a formal transannular C−C bond is the quartet state of isomer **5**. In that case peripheral and transannular C−C bond distances are all quite similar and close to typical C−C single bond distances. In fact, **5**($^4A''$) should be best described as a bicyclic structure with two three-membered rings.

TABLE 1: Relative Energies (kcal/mol) for the $(SC_3H_2)^+$ Species at Different Levels of Theory with the 6-311G Basis Set**[a]

	MP4	PMP4	B3LYP	QCISD(T)
1 ($^2B_2$)	0.0	0.0	0.0	0.0
1 ($^4B_2$)	55.3	64.6	61.1	60.0
1 ($^4A_2$)	94.8	103.7	108.7	98.2
2 ($^4A'$)	79.2	89.4	90.3	84.6
3 ($^2B_2$)	−6.6	5.6	9.2	4.7
3 ($^4A_2$)	78.8	91.2	98.4	90.1
3 ($^4A''$)	67.0	79.3	84.7	77.3
4 (^2A)	44.0	54.7	61.6	52.3
4 ($^4A'$)	74.0	86.1	91.1	82.1
5 ($^2A''$)	66.5	74.2	85.6	69.3
5 ($^4A''$)	117.5	130.2	137.4	126.1

[a] Zero-point vibrational energy differences have been included.

The relative energies at different levels of theory of the $(SC_3H_2)^+$ species are presented in Table 1. It is readily seen that all levels of theory, except MP4, predict that the lowest-lying species is **1**($^2B_2$). **3**($^2B_2$) is also predicted to lie the lowest in energy at the MP2/6-31G* level, about 13.9 kcal/mol below **1**($^2B_2$). Therefore, higher correlation levels seem to favor the open-chain structure (the energy difference between both structures is reduced to 6.6 kcal/mol at the MP4 level). Furthermore, since spin contamination may affect the convergence of the MP series for open-shell systems, PMP4 and QCISD(T) should be the most reliable levels of theory, and both predict that **3**($^2B_2$) lies higher in energy than **1**($^2B_2$). Consequently, it seems that the global minimum of $(SC_3H_2)^+$ is an open-chain structure. On the other hand, we should remember that c-C_3H_2 is lower in energy than l-C_3H_2 (about 12.4 kcal/mol at the MP4 level). Nevertheless, the predicted energy difference between **1**($^2B_2$) and **3**($^2B_2$) is rather small, nearly 5 kcal/mol, and therefore both could be accessible to experimental detection. The four-membered ring doublets, **4**(^2A) and **5**($^2A''$), lie much higher in energy.

The lowest-lying quartet species is also the open-chain structure **1**($^4B_2$), followed by the nonplanar three-membered ring isomer. In this case, structures **2**($^4A'$) and **4**($^4A'$) are even more stable than the planar cyclic isomer **3**($^4A_2$), which lies nearly 30 kcal/mol higher in energy than the lowest-lying quartet state. Again, isomer **5** is the less stable structure on the quartet surface. It is also interesting to note that, as a general trend, B3LYP performs not too badly in the prediction of relative energies compared with QCISD(T).

The relative stability of $(SC_3H_2)^+$ species is similar to that found for the silicon analogue system. In the case of $(SiC_3H_2)^+$, we found that an open-chain structure similar to **1** is the predicted ground state,[27] with the three-membered cyclic isomer lying about 9 kcal/mol higher in energy. On the other hand, in the case of triplet $(PC_3H_2)^+$, the cyclic isomer is predicted to lie below the linear one by 9 kcal/mol,[26] and therefore retains the stability order found for the hydrocarbon, C_3H_2.

Reaction of S^+ with C_3H_2. We will discuss in this section the reaction of sulfur ions with either cyclopropenylidene or vinylidenecarbene, to produce possible precursors of C_3S in space. Thermodynamic arguments about the reaction pathways employing theoretically calculated relative heats of formation will be developed. In addition to the production of SC_3H^+ there are two other possible channels: production of C_3S^+ and charge transfer. Therefore, we should consider the following possibilities

$$\begin{aligned} &\rightarrow SC_3H^+ + H\,(^2S)\\ S^+(^4S) + C_3H_2(^1A_1) &\rightarrow C_3S^+ + H_2(^1\Sigma_g{}^+)\\ &\rightarrow S(^3P) + C_3H_2{}^+(^2A_1)\end{aligned}$$

Given the multiplicity of the reactants, only triplet states for SC_3H^+ and quartets for C_3S^+ should be in principle taken into account. Calculations on C_3S^+ [15] and SC_3H^+ [15,16] have been reported. In these works only linear (or quasi-linear) structures were reported on the doublet (ionized C_3S) and singlet (protonated C_3S) surfaces. Therefore, we have characterized the stable structures of the required multiplicity for each system. In the case of C_3S^+ a linear (l-C_3S^+) and a three-membered ring isomer with sulfur in the exocyclic position (c-C_3S^+) were obtained on the quartet surface. For SC_3H^+ five species were obtained on the triplet surface, and they are shown in Figure 2. Details on the structure and properties (optimized geometries at both MP2 and B3LYP levels, vibrational frequencies, and IR intensities) of these species can be obtained from the authors upon request.

The relative energies of the different possible products for the reactions of S^+ with c-C_3H_2 and l-C_3H_2 are given in Tables 2 and 3, respectively. It can be readily seen that the B3LYP level overestimates the reaction enthalpy for several processes and, compared with PMP4 and QCISD(T) methods, does not seem reliable for the prediction of reaction enthalpies. On the other hand, the PMP4 and QCISD(T) levels are generally in rather good agreement, with the exception of formation of l-C_3S^+, where a discrepancy of about 16 kcal/mol is observed. The relative good agreement between these two methods perhaps makes them more reliable than the B3LYP method.

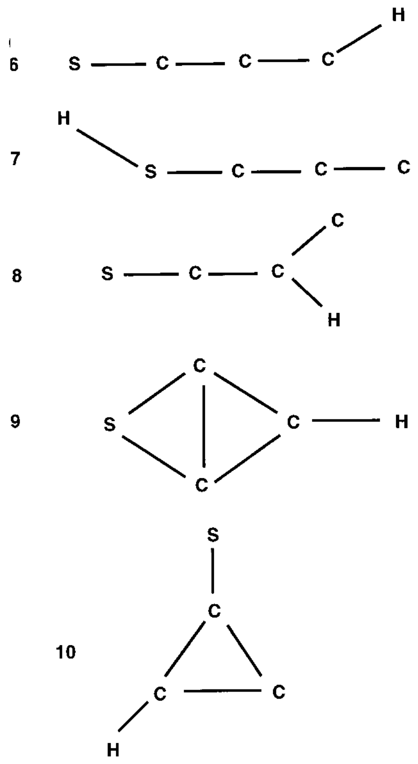


Figure 2. Schematic representation of the different SC_3H^+ species.

TABLE 2: Relative Energies (kcal/mol) for the Different Possible Products of the Reaction of S^+ with c-C_3H_2

	$SC_3H^+ + H$					$C_3S^+ + H_2$		$S +$
	6	7	8	9	10	l-C_3S^+	c-C_3S^+	c-$C_3H_2^+$
MP4	3.2	47.6	29.9	36.7	4.9	44.8	51.0	−13.6
PMP4	−1.5	35.4	22.0	33.8	3.3	38.4	48.4	−14.7
B3LYP	−27.9	16.3	7.1	17.8	−13.9	3.0	31.6	−33.4
QCISD(T)	−7.5	33.2	16.3	25.5	2.3	21.2	42.8	−15.0

TABLE 3: Relative Energies (kcal/mol) for the Different Possible Products of the Reaction of S^+ with l-C_3H_2

	$SC_3H^+ + H$					$C_3S^+ + H_2$		$S +$
	6	7	8	9	10	l-C_3S^+	c-C_3S^+	l-$C_3H_2^+$
MP4	−9.3	35.1	17.4	24.1	−7.6	32.3	38.5	29.8
PMP4	−14.0	22.9	9.5	21.3	−9.2	25.8	35.9	19.0
B3LYP	−39.0	5.2	−4.0	6.7	−25.0	−8.1	20.5	−6.9
QCISD(T)	−19.3	21.4	4.5	13.8	−9.5	9.4	31.1	12.9

In both cases, reaction of S^+ with c-C_3H_2 and l-C_3H_2, production of C_3S^+ seems to be endothermic. Only for the production of linear C_3S^+ from l-C_3H_2 does the B3LYP result predict an exothermic process. Nevertheless, both PMP4 and QCISD(T) levels agree in that these processes should be discarded. Concerning the production of SC_3H^+ from c-C_3H_2, only production of the quasi-linear isomer **6** is clearly exothermic, whereas formation of the cyclic isomer **10** is only slightly endothermic at both PMP4 (3.3 kcal/mol) and QCISD(T) (2.3 kcal/mol) levels. In the case of the reaction $S^+ +$ l-C_3H_2 there are two processes that are clearly exothermic, production of isomers **6** and **10**, whereas formation of **8** is predicted to be slightly endothermic (4.5 kcal/mol at the QCISD(T) level). Another important result from Tables 2 and 3 is that charge transfer is exothermic by nearly 15 kcal/mol in the case of the reaction of $S^+ +$ c-C_3H_2, and therefore it should be a competitive process in that case. On the other hand, both PMP4 and QCISD-

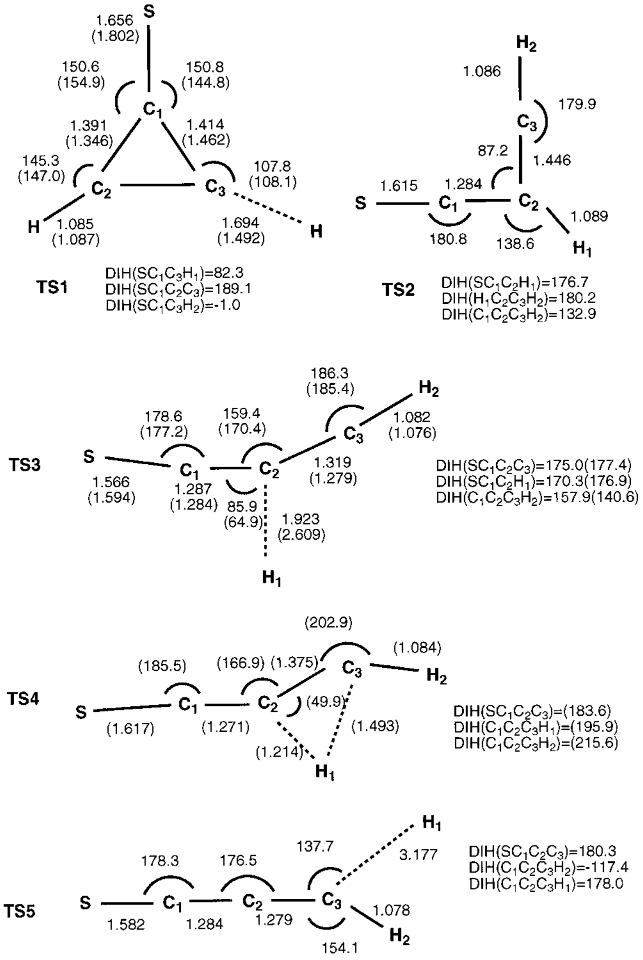


Figure 3. MP2/6-31G* and B3LYP/6-311G** (in parentheses) optimized geometries for the relevant transition states involved in the reaction of S^+ with C_3H_2. Distances are given in angstroms, and angles, in degrees.

(T) levels predict relatively high endothermicities for charge transfer in the reaction $S^+ + l\text{-}C_3H_2$, which suggest that in this case charge transfer would not compete with production of SC_3H^+.

We will only consider in what follows the possible reaction mechanisms leading to exothermic (or close to thermoneutrality) products. The relevant transition states are shown in Figure 3, whereas the energy profiles for the reactions of S^+ with $c\text{-}C_3H_2$ and $l\text{-}C_3H_2$ are given in Figures 4 and 5, respectively, at the QCISD(T) and PMP4 levels.

For the reaction of S^+ with $c\text{-}C_3H_2$ the first step is formation of isomer **3**. Then hydrogen atom elimination through transition state TS1 would lead to the cyclic product **10**.

$$S^+ + c\text{-}C_3H_2 \rightarrow SC_3H_2^+\,(\mathbf{3}) \xrightarrow{TS1} SC_3H^+\,(\mathbf{10}) + H \qquad (a)$$

We have seen that this channel is slightly endothermic. In addition, TS1 lies above the reactants by 44 kcal/mol (QCISD(T)) or 11 kcal/mol (PMP4). This is the only transition state for which both levels of theory predict very different relative energies (in part because of the different geometries employed; the B3LYP level predicts a planar transition state, whereas a nonplanar structure is obtained at the MP2 level). In any case, both levels agree in that there is a significant energy barrier, which together with the small endothermicity of this process, quite likely would prevent formation of the cyclic SC_3H^+ isomer in space.

Another possibility is isomerization of cyclic $SC_3H_2^+$ into an open-chain isomer (**2**), through transition state TS2 (whose imaginary frequency is associated with ring opening). The

$$SC_3H_2^+\,(\mathbf{3}) \xrightarrow{TS2} SCCHCH^+\,(\mathbf{2}) \xrightarrow{TS3} SCCCH^+\,(\mathbf{6}) + H \qquad (b)$$

intermediate formed in this way, with the hydrogen atoms bonded to different carbon atoms, may undergo hydrogen atom elimination leading to the quasi-linear $SCCCH^+$ isomer. This process involves transition state TS3.

Alternatively, $SCCHCH^+$ (**2**) may suffer isomerization into the lowest-lying $SCCCH_2^+$ (**1**) isomer with both hydrogen atoms bonded to terminal carbon. Then the final product $SCCCH^+$

$$SCCHCH^+\,(\mathbf{2}) \xrightarrow{TS4} SCCCH_2^+\,(\mathbf{1}) \xrightarrow{TS5} SCCCH^+\,(\mathbf{6}) + H \qquad (c)$$

(**6**) may be formed through hydrogen atom elimination. This path involves transition states TS4 and TS5.

We were able to obtain these two transition states only at the B3LYP level. All attempts to search for TS4 at the MP2 level led to TS3 (hydrogen atom elimination), whereas in the case of TS5, elimination of the hydrogen atom takes place directly without any barrier at the MP2 level. We carried out a scan for this process, performing optimizations at different C−H distances and found no sign of transition state. In any case we have computed the PMP4 energy at the B3LYP geometry to obtain an estimate of the possible energy barriers for both processes involved in path c.

As can be seen in Figure 4, path b implies a small energy barrier (4 kcal/mol) at the PMP4 level, although the QCISD(T) level predicts that TS3 lies slightly below reactants (−3.7 kcal/mol). In any case it seems that path (c), which proceeds through the most stable $SC_3H_2^+$ isomer, should be favored, since both TS4 and TS5 lie well below reactants at all levels of theory. Therefore, there is at least a mechanism for the reaction of S^+ with $c\text{-}C_3H_2$ which is exothermic and barrier-free for the production of $SCCCH^+$. However, we must remember that charge transfer is competitive in this case, since it is predicted to be more exothermic.

For the reaction of S^+ with vinylidenecarbene, the first step is formation of $SC_3H_2^+$ (**1**). Then three different channels may be devised. One of them is direct hydrogen elimination to give the open-chain product $SCCCH^+$.

$$S^+ + l\text{-}C_3H_2 \rightarrow SCCCH_2^+\,(\mathbf{1}) \xrightarrow{TS5} SCCCH^+\,(\mathbf{6}) + H \qquad (d)$$

Another process involves migration of a hydrogen atom followed by hydrogen elimination:

$$SCCCH_2^+\,(\mathbf{1}) \xrightarrow{TS4} SCCHCH^+\,(\mathbf{2}) \xrightarrow{TS3} SCCCH^+\,(\mathbf{6}) + H \qquad (e)$$

Finally, cyclation may occur, leading to the cyclic $SC_3H_2^+$ (**3**) isomer.

$$SCCCH_2^+\,(\mathbf{1}) \xrightarrow{TS4} SCCHCH^+\,(\mathbf{2}) \xrightarrow{TS2} SC_3H_2^+\,(\mathbf{3}) \xrightarrow{TS1} SC_3H^+\,(\mathbf{10}) + H \qquad (f)$$

The energy profile for this reaction is shown in Figure 5. As can be seen, only TS1 is found to lie above the reactants at the QCISD(T) level, suggesting that production of cyclic SC_3H^+ from the reaction of $S^+ + l\text{-}C_3H_2$ should be precluded in the interstellar medium. On the other hand all transition states

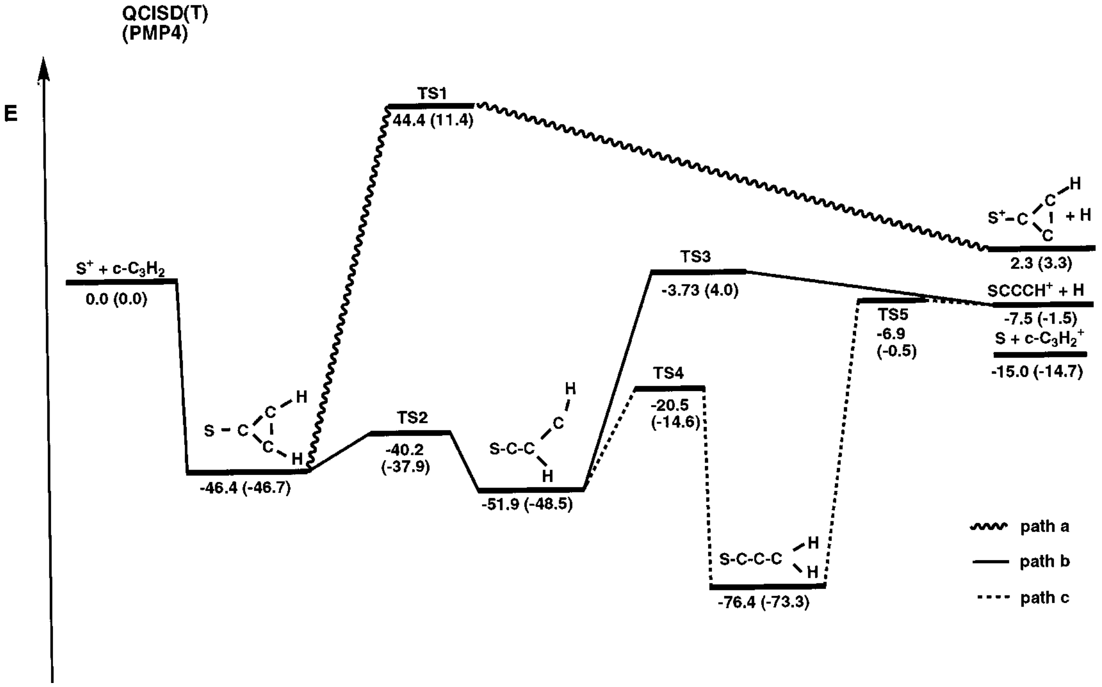


Figure 4. Energy profile, in kcal/mol, for the reaction of S^+ with c-C_3H_2 at the QCISD(T) and PMP4 (in parentheses) levels. ΔZPVE corrections have been included at the B3LYP/6-311G** and MP2/6-31G* levels, respectively.

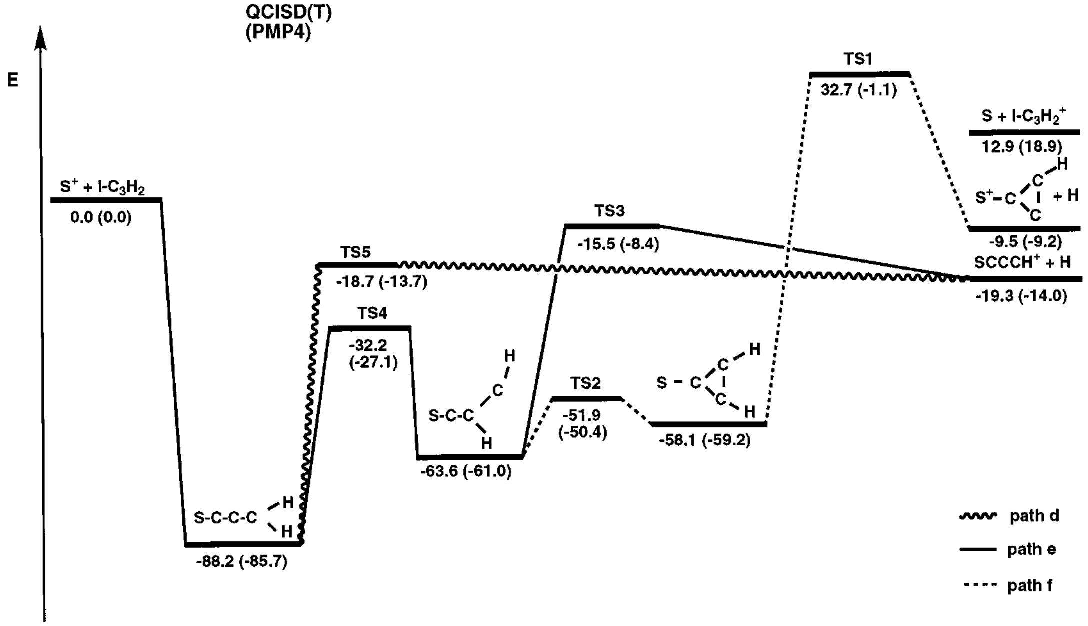


Figure 5. Energy profile, in kcal/mol, for the reaction of S^+ with l-C_3H_2 at the QCISD(T) and PMP4 (in parentheses) levels. ΔZPVE corrections have been included at the B3LYP/6-311G** and MP2/6-31G* levels, respectively.

involved in processes e and f lie well below the reactants and therefore are feasible under interstellar conditions. Furthermore, in this case charge transfer should not compete, since it is clearly endothermic.

Conclusions

A theoretical study of the $(SC_3H_2)^+$ species, on the doublet and quartet surfaces, has been carried out. Geometries and vibrational frequencies for the different isomers have been obtained at the MP2/6-31G* and B3LYP/6-311G** levels. Electronic energies have been computed at the MP4/6-311G**//MP2/6-31G* and QCISD(T)//B3LYP/6-311G** levels. The two most reliable levels of theory employed, PMP4 and QCISD(T), predict that the lowest-lying species is $SCCCH_2^+(^2B_2)$, although a cyclic isomer **3**$(^2B_2)$ lies quite close in energy (only about 5 kcal/mol higher in energy than $SCCCH_2^+$). The lowest-lying quartet is also $SCCCH_2^+(^4B_2)$, followed by a nonplanar three-membered ring isomer. In the case of the reaction of S^+ with c-C_3H_2, production of cyclic SC_3H^+ is slightly endothermic and proceeds through a significant energy barrier. On the other hand, production of the linear isomer $SCCCH^+$ is exothermic and there is at least one mechanism leading to this species that is barrier-free. However, charge transfer is competitive in this case, since it is predicted to be more exothermic.

On the other hand, for the reaction of S^+ with l-C_3H_2 charge transfer is not competitive since it is clearly endothermic.

Production of cyclic SC_3H^+, although exothermic, seems to involve an energy barrier at the QCISD(T) level, which disappears at the PMP4 level. Production of the linear $SCCCH^+$ isomer is not only the most exothermic channel, but there are two different mechanisms that are barrier-free.

Therefore, the main conclusion of the present work is that only the linear $SCCCH^+$ isomer can be produced from the reaction of S^+ with both c-C_3H_2 and l-C_3H_2. It is worth noting that in the case of the similar reactions with silicon[27] or phosphorus,[26] both linear and cyclic isomers could be obtained. $SCCCH^+$ is produced in its triplet state. However, upon dissociative recombination (reaction 2 in the Introduction) finally the singlet ground state of C_3S could be reached. Consequently, these ion−molecule reactions could be possible sources of precursors of C_3S in space, in addition to other neutral−radical processes.[22]

Acknowledgment. This research has been supported by the Ministerio de Educación y Cultura of Spain (DGICYT, Grant PB97-0399-C03-01) and by the Junta de Castilla y León (Grant VA 21/97).

References and Notes

(1) Thaddeus, P.; Cummins, S. E.; Linke, R. A. *Astrophys. J. Lett.* **1984**, *283*, L25.

(2) Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S.; Fujita, Y.; Shiratori, Y.; Irvine, W. H. *Astrophys. J. Lett.* **1989**, *345*, L83.

(3) Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *Astrophys. J.* **1987**, *317*, L115.

(4) Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifu, N.; Suzuki, H.; Ohishi, M. *Astrophys. J.* **1987**, *317*, L119.

(5) Sülzle, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1337.

(6) Sülzle, D.; Schwarz, H. *Chem. Ber.* **1989**, *122*, 1803.

(7) Bohn, R. B.; Hannachi, Y.; Andrews, L. *J. Am. Chem. Soc.* **1992**, *114*, 6452.

(8) Yamamoto, S.; Saito, S.; Kawaguchi, K.; Chikada, Y.; Suzuki, H.; Kaifu, N.; Ishikawa, S.; Ohishi, M. *Astrophys. J.* **1990**, *361*, 318.

(9) Oshima, Y.; Endo, Y. *J. Mol. Spectrosc.* **1992**, *153*, 627.

(10) Peeso, D. J.; Ewing, D. W.; Curtiss, T. T. *Chem. Phys. Lett.* **1990**, *166*, 307.

(11) Murakami, A. *Astrophys. J.* **199**0, *357*, 288.

(12) Xie, Y.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *96*, 3714.

(13) Seeger, S.; Botschwina, P.; Flügge, S.; Reisenauer, H. P.; Maier, G. *J. Mol. Struct. (THEOCHEM)* **1994**, *303*, 213.

(14) Lee, S. *Chem. Phys. Lett.* **1997**, *268*, 69.

(15) Maclagan, R. G. A. R.; Sudkeaw, P. *Chem. Phys. Lett.* **1992**, *194*, 147.

(16) Liu, Z. Y.; Tang, Z. C.; Huang, R. B.; Zhang, Q.; Zheng, L. S. *J. Phys. Chem. A* **1997**, *101*, 4019.

(17) Botschwina, P.; Sebald, P. J. *Mol. Spectrosc.* **1993**, *100*, 1.

(18) Jayasuriya, K. *Int. J. Quantum Chem.* **1992**, *44*, 327.

(19) Smith, D.; Adams, N. G.; Giles, K.; Herbst, E. *Astron. Astrophys.* **1988**, *200*, 191.

(20) Wlodek, S.; Bohme, D. K.; Herbst, E. *Mon. Not. R. Astron. Soc.* **1988**, *235*, 493.

(21) Millar, T. J.; Herbst, E. *Astron. Astrophys.* **1990**, *231*, 466.

(22) Petrie, S. *Mon. Not. R. Astron. Soc.* **1996**, *281*, 666.

(23) Barrientos, C.; Largo, A. *J. Phys. Chem.* **1992**, *96*, 5808.

(24) Anicich, V. G.; Huntress, W. T. *Astrophys. J. Suppl.* **1986**, *62*, 553.

(25) Zakouril, P.; Glosik, J.; Skalsky, V.; Lindinger, W. *J. Phys. Chem.* **1995**, *99*, 15890.

(26) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys. J.* **1985**, *299*, L63.

(27) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, *368*, L39.

(28) DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31.

(29) Jonas, V.; Bohme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640.

(30) del Río, E.; Barrientos, C.; Largo, A. *J. Phys. Chem.* **1996**, *100*, 14643.

(31) Redondo, P.; Sagüillo, A. V.; Barrientos, C.; Largo, A. *J. Phys. Chem. A* **1999**, *103*, 3310.

(32) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; De Frees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(34) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980,** *72*, 650.

(35) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(36) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(37) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(38) Pople, J. A.; Krishnan, R. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(39) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(40) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

(41) Schlegel, H. B. *J. Chem. Phys.* **1988**, *92*, 3075.

(42) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. J.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.