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Reaction of Si^+ (^2P) with acetylene and with ethylene. Examination of the potential energy surfaces for adducts $SiC_2H_2^+$ and $SiC_2H_4^+$

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Abstract

Ab initio molecular orbital calculations have been performed at levels of theory up to, and including, QCISD(T)(full)/6-311+ + G(2df,p) on structural isomers associated with the adducts of $Si^+(^2P)$ with acetylene and of $Si^+(^2P)$ with ethylene. Critical points on each surface have been characterised by harmonic frequency calculations at the UHF/6-31G(d,p) level of theory. There are many similarities between the minima on the $SiC_2H_2^+$ surface and those on the analogous neutral surface, whereas significant topological differences were observed to exist between the $SiC_2H_4^+$ surface and its neutral analogue. The inclusion of electron correlation in post-Hartree–Fock calculations to second-order Møller–Plesset perturbational theory was observed to affect significantly the topologies of the two cationic surfaces. The global minimum on each of the cationic surfaces, as calculated at the MP2 level of theory, is a three-membered cyclic species ($^2B_2$ state), and represents the products of the symmetry-allowed additions of $Si^+(^2P)$, with its unpaired electron in $3p_y$, to acetylene and to ethylene respectively. By contrast, the formation of cyclic species with electronic states $^2A_1$ and $^2B_1$, structures which are excited states of the respective global minima, from the addition of $Si^+(^2P)$ to the appropriate hydrocarbon, are both symmetry-forbidden processes. The existence of significant barriers (> 20 kcal mol^{-1}) to the interconversion of three minima on the $SiC_2H_2^+$ and five minima on the $SiC_2H_4^+$ surfaces suggests the probable existence of several isomers of each formula as stable species in the gas phase. The formation of adducts from $Si^+ + HC{\equiv}CH$ and from $Si^+ + H_2C{=}CH_2$ is strongly exothermic; reactions which result in hydrogen elimination from these adducts are weakly exothermic or are thermoneutral.

1. Introduction

Silicon and carbon are both abundant elements, but relatively few stable molecules containing these two elements bonded together are known. The discovery of SiC_2, then, in the circumstellar envelope of IRC + 10216 stimulated considerable interest in organosilicon compounds [1]. Much of this interest has been in ab initio molecular orbital studies, where substitution of silicon for carbon in an organic molecule is a trivial procedure [2]. This work has led to the recognition that, unlike carbon, silicon frequently is divalent and that, wherever possible, silicon avoids multiple bonds to carbon [2(a),3].

Silicon is more electropositive and more polarisable than carbon and consequently is more effective at stabilising a positive charge. Molecular orbital calculations have verified these properties

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but surprisingly few silyl cations are sufficiently stable to be characterised in solution [4].

Many organosilicon cations have been found in the gas phase. Following Lampe's early tandem mass spectrometry experiments [5] one of us has used the SIFT [6] method to examine the reactions of $Si^+(^2P)$ with acetylene and with ethylene [7]. These reactions appear to follow similar reaction pathways; formation of adducts $SiC_2H_2^+$ and $SiC_2H_4^+$ and formation of ions SiC_2H^+ and $SiC_2H_3^+$, both accompanied by the loss of one hydrogen atom (Eqs. (1) and (2)).

$$Si^+ + HC{\equiv}CH \rightarrow SiC_2H_2^+ \quad (1a)$$

$$\rightarrow SiC_2H^+ + H \quad (1b)$$

$$Si^+ + H_2C{=}CH_2 \rightarrow SiC_2H_4^+ \quad (2a)$$

$$\rightarrow SiC_2H_3^+ + H \quad (2b)$$

Preliminary ab initio molecular orbital calculations at UMP2/6-31G(d,p)//UHF/6-31G(d,p) were reported for the adduct ions [7]. The cyclic $SiC_2H_2^+$ ion in which Si bridges the acetylene in a structure reminiscent of the vinyl cation [8] with C_{2v} symmetry was found to be a transition structure between two unsymmetrically bridged structures (C_s symmetry). Inclusion of electron correlation reversed the relative stabilities with the symmetrically bridged ion now being a minimum. This ion then provides another example of the already well-established phenomenon of neglect of electron correlation favouring open or classical structures over cyclic, non-classical structures. With this type of structural problem in mind, and recognising that open shell molecules are often difficult to handle at the UHF level due to spin contamination [9], we have re-examined these ions at higher levels of theory.

Here we report extensive studies of both the $SiC_2H_2^+$ and $SiC_2H_4^+$ energy hypersurfaces in which electron correlation has been included in structure optimisations. For isomers on the $SiC_2H_2^+$ surface, structures were optimised at UMP2(FULL)/6-311G(d,p) while for the larger and more numerous structures on the $SiC_2H_4^+$ surface the UMP2(FULL)/6-31G(d,p) level of theory was used. Finally we have used those optimised structures for single-point calculations at higher levels of theory [MP4SDTQ/6-311++G(2df,p) and QCISD(T)/6-311++G(2df,p)] to establish the thermochemistry of the reactions in Eqs. (1) and (2).

2. Computational methods

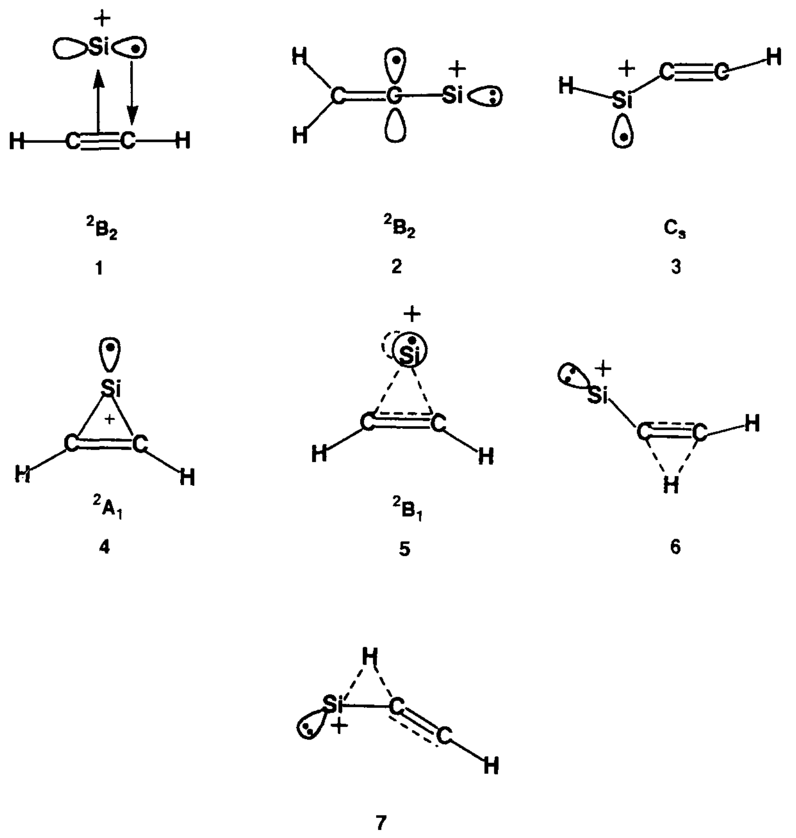
Ab initio molecular orbital calculations were carried out with the GAUSSIAN suite of programs [10]. Structure optimisations employed gradient techniques [11] and were performed with the standard 6-31G(d,p) [12] and 6-311G(d,p) [12(d),13] basis sets at UHF and UMP2(FULL). Transition structures were crudely located using point-by-point procedures and were then optimised using either the CALCALL algorithm [10] or the EF method [14]. The optimised structures were characterised by harmonic frequency calculations (one imaginary frequency) and each was established to be the desired transition structure by using the IRC method [15]. Single-point calculations at the MP4(valence)SDTQ [16] and QCI(FULL)SD(T) [17] levels of theory used the 6-311++G(2df,p) basis set [12(d),18]. Spin contamination was projected out of the UMP4 level calculations using Schlegel's procedure [19]. These calculations are denoted as PMP4/6-311++G(2df,p).

3. Results and discussion

Preliminary optimisation studies at SCF/6-31G(d,p) produced many minima on both the $SiC_2H_2^+$ and $SiC_2H_4^+$ surfaces. Several of these minima disappeared when electron correlation was included. Other minima were significantly higher in energy than the gas phase reactants of Si^+ plus acetylene or ethylene and frequently had large amounts of spin contamination. As our main interest lies in the chemistries of the Si^+ adducts we decided to restrict our higher level studies only to isomers which are lower in energy than the reactants, Si^+ plus hydrocarbon.

3.1. Details of the $SiC_2H_2^+$ surface

We have located five isomers, structures **1**, **2**, **3**,



Scheme 1.

4, and 5 which are at minima lower in energy than the reactants $Si^+ + HC\equiv CH$ (see Scheme 1). There are close similarities between the $SiC_2H_2^+$ surface and that previously reported for the SiC_2H_2 neutral isomers [2e,f]. On the neutral surface, silacyclopropenylidene is the global minimum and ions **1**, **4** and **5** have the same electronic structure as silacyclopropenylidene but with one electron removed from molecular orbitals with symmetries $4b_2$, $8a_1$ and $2b_1$ respectively. Neutrals 1-silapropadienylidene and 1-silapropargylene are both approximately 20 kcal mol^{-1} higher in energy than silacyclopropenylidene [2e], and removal of one electron from each of these isomers yields ions **2** and **3** respectively. On the ion surface at the UHF/6-31G(d,p) level of theory **2** is the global minimum, but when electron correlation is included the cyclic ion, **1**, has the lowest energy (Table 1).

At UHF/6-31G(d,p), optimisation of ion **1** resulted in an unsymmetrical structure, with the symmetrically bridged ion being a transition structure. When electron correlation was included in the wavefunction at both MP2/6-31G(d,p) and MP2/6-311G(d,p) the symmetrical ion (C_{2v} symmetry) was the only critical point for ion **1**. This large structural change and the change in the relative energies of isomers **1** to **5**, show that inclusion of electron correlation is essential for an adequate description of this surface.

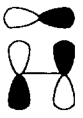
The structures of ions **1** to **5** are given in Fig. 1. Ion **1** has molecular orbital occupancies $1a_1$ $2a_1$ $1b_2$ $3a_1$ $1b_1$ $4a_1$ $2b_2$ $5a_1$ $3b_2$ $6a_1$ $7a_1$ $2b_1$ $8a_1$ $4b_2$, with all orbitals doubly filled except $4b_2$ which contains the

Table 1
Total energies (hartrees) for isomers of $SiC_2H_2^+$ [a]

Molecule	UHF/6-31G(d,p)	$\langle S^2 \rangle$	UMP2/6-31G(d,p)	UMP2/6-311G(d,p)	ZPE[b] (kcal mol^{-1})	UMP2/6-311G(d,p) energies relative to structure **1**[c] (kcal mol^{-1})
1	−365.43666[d]	0.76	−365.76967	−365.95556	15.8	0
2	−365.45378	0.94	−365.75706	−365.94177	16.6	9.4
3	−365.42364	0.85	(−365.74455)[e]	(−365.91046)[e]	14.8	(27.3)
4	−365.42671	0.77	−365.75931	−365.94449	17.8	8.9
5	−365.38352	0.76	−365.68247	−365.86729	18.1	57.7
6	−365.38842	0.77	−365.70263	−365.88872	14.5	40.6
7	−365.37830	0.94	−365.68804	−365.87702	12.2	45.7
$Si^+ + HC{\equiv}CH$	−365.37313	0.76	−365.68719	−365.87823	15.4	48.1

[a] Structures were fully optimised at each level of theory.
[b] Zero-point energy from UHF/6-31G(d,p), scaled by a factor of 0.89.
[c] Relative energies in kcal mol^{-1} at 0 K using zero-point energies from SCF level calculations.
[d] Transition structure at the SCF level.
[e] Optimisation not quite complete at UMP2/6-31G(d,p) and UMP2/6-311G(d,p).

unpaired electron. It is interesting to compare the structure of this ion with that of silacyclopropenylidene which has the same electronic configuration but has an additional electron in $4b_2$. The major contributors to the $4b_2$ orbital are the $3p_y$ orbital on the silicon and the π^* orbital from the in-plane π-system of the acetylene. Removal of an electron from this molecular orbital depletes the bonding between the carbon and silicon atoms and removes antibonding from between the carbon atoms. The net result is lengthening of the C–Si bond (to 1.983 Å from 1.809 Å at SCF/6-31G(d,p)) and shortening of the C–C bond (to 1.247 Å from 1.336 Å). Ion **1** is best described as a π-complex in which there is π-donation from acetylene to the vacant $3p_z$-orbital on silicon and weak donation to π^* of acetylene from the unpaired electron in the $3p_y$-orbital of silicon.



$4b_2$

Cyclic ion **4**, obtained by removing one electron from an a_1-type molecular orbital of silacyclopropenylidene, is at a minimum at all levels of theory. As with structure **1**, inclusion of electron correlation results in slight increases in all bond lengths. Ion **4** has C–Si distances of 1.742 Å and C–C 1.377 Å, both close to standard double bond lengths. The unpaired electron is located on silicon and molecular orbitals $7a_1$ and $4b_2$, both doubly occupied, account for the majority of the bonding between silicon and carbon, i.e., there is $\pi \rightarrow Si^+$ donation and Si lone-pair to π^* back donation. This ion then fits Dewar's criteria [20] to be described as a three-membered ring and not a π-complex.

Ion **5**, the third cyclic ion, is obtained by removing one electron from a b_1-type molecular orbital of silacyclopropenylidene. This ion has a long C–C bond, due to the unpaired electron being located mainly on the two carbon atoms. The lack of π-delocalisation results in an elongation of the Si–C bond (to 1.93 Å at UHF/6-31G(d,p)). Ion **5** is the highest of the five minima, but at UHF/6-31G(d,p) it is lower in energy than the reactants, $Si^+ + HC{\equiv}CH$, by 3.8 kcal mol^{-1} (when zero-point energy is included). Unlike the other cyclic ions, **5** is destabilised by inclusion of electron correlation and, at the higher levels of theory, formation of **5** from the reactants is endothermic. Furthermore, characterisation by frequency calculations showed **5** to be a minimum at UHF/6-31G(d,p) but to be a transition structure at UMP2/6-311G(d,p).

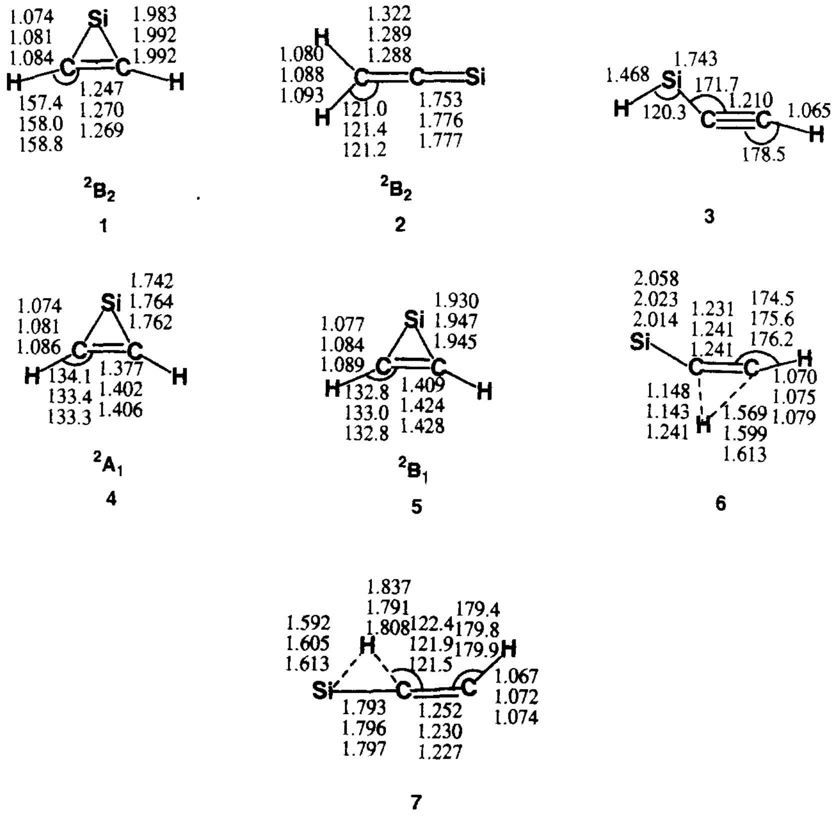


Fig. 1. Geometric parameters for isomers and transition structures on the $SiC_2H_2^+$ surface. The uppermost numbers are from UHF/6-31G(d,p) the central numbers from UMP2/6-31G(d,p) and the lowest from UMP2/6-311G(d,p). All bond lengths are in ångstroms and bond angles are in degrees.

In terms of the initial adduct formed by bringing Si^+ up to the centre of the triple bond of acetylene, the $^2B_2$ state (ion **1**) has the correct orbital symmetry to be formed from an Si^+ ion which has its unpaired electron in the $3p_y$-orbital. However, if the unpaired electron is in the $3p_z$ or $3p_x$ orbital of silicon, then the $^2A_1$ and $^2B_1$ states formed have different occupancies than ions **4** and **5** (one fewer molecular orbital of b_2 symmetry occupied). Hence formation of **4** and **5** from the reactants is symmetry forbidden. At UHF/6-31G(d,p) we have located the symmetry allowed $^2B_1$ structure but this is a high excited state, 121 kcal mol^{-1} above **2**. This structure was not examined at higher levels of theory.

1-Silapropadienylidene has a C–Si distance of 1.684 Å [1e] but the electron removed to create ion **2** comes from the highest occupied orbital of b_2 symmetry, an orbital which principally describes the C–Si double bond. Consequently the C–Si distance in the ion is 1.753 Å, a value which is much longer than that in the neutral molecule. All other geometric parameters in the ion and neutral molecule are similar. The ion, **2**, has most of its unpaired spin density on the carbon atom and the charge is located on the silicon as described in the structure in Scheme 1.

For ion **3**, the cation derived by ionisation of 1-silapropargylene, we have only structural data from UHF/6-31G(d,p). Attempts to optimise a structure for this ion at UMP2 were unsuccessful, despite numerous attempts. The energies recorded for the correlated wavefunctions then are our best energies and represent an upper limit. Comparison of our structure for **3** with that for neutral 1-silapropargylene show two major changes on ionisation. In the neutral molecule ∠ HSiC is 94.9°, but removal of an electron, formally from the lone pair of the silene, resulted in this angle increasing to 120.3°. The change in hybridisation and the increase in charge on silicon also produced a decrease in the C–Si distance to 1.743 Å from 1.853 Å [1e].

Structures **1**–**5** were characterised by harmonic frequency calculations and, as indicated above, all were found to be minima (i.e. no imaginary frequencies). The frequencies calculated for these ions are given in Table 2. The UMP2/6-311G(d,p) level frequencies were scaled by a factor of 0.94 [21] and the UHF/6-31G(d,p) frequency for **3** was scaled by a factor of 0.89 [22]. The initial long-range interaction between Si^+ and HC≡CH is likely to be between a vacant p-orbital on Si^+ and the π-orbitals of acetylene, with formation of the symmetry allowed product, ion **1**. It is important to know whether there is sufficient energy available from the initial reaction to permit formation of other isomers on the surface. We have therefore calculated the transition structures for the barriers to rearrangement of **1** into **2** and **3**. The geometric parameters of the transition structures for these reactions are given in Fig. 1 and the reaction profiles are given in Fig. 2. Both transition structures have been fully characterised by frequency calculations (and each was found to have one imaginary frequency associated mainly with the migrating hydrogen). Curiously we have been able to locate transition structure **7**, for the transformation of **1** into **3**, at UMP2/6-311G(d,p), although we were unable to locate the minimum for **3** at this level of theory. Transition structures **6** and **7** are 40.6 kcal mol^{-1} and 45.7 kcal mol^{-1} respectively above structure **1**, but both are slightly lower in energy than the reactants, Si^+ + HC≡CH (48.1 kcal mol^{-1} above **1**). Ions **1**, **2** and **3** then are all accessible from the reactants, but removal by collisions of a small amount of the excess energy generated in the initial formation of **1** will preclude formation of **2** and **3**. Conversely if ions **2** and/or **3** are formed by some other gas phase process, then these ions have appreciable barriers to rearrangement to **1** (25.8 kcal mol^{-1} for **3** at UHF/6-31G(d,p) and 31.2 kcal mol^{-1} for **2** at UMP2/6-311G(d,p)) and it should be possible to characterise their individual reactivities experimentally.

3.2. Details of the $SiC_2H_4^+$ surface

On the $SiC_2H_4^+$ surface we have optimised structures for eleven isomers, all of which have energies lower than that of the reactants, $Si^+ + H_2C{=}CH_2$. Two of these isomers are excited states of the global minimum, the cyclic ion, **8**. After considerable computational effort we have located the eight transition structures required to interconnect the remaining nine minima. In view of the complexity of the surface we were forced to economise by optimising only at the UHF/6-31G(d,p) and UMP2/6-31G(d,p) levels. Structural details are given in Fig. 3. Single-point calculations were then performed at UMP2/6-311G(d,p) using the UMP2/6-31G(d,p) optimised structures. The relative energies recorded in Table 3 are from these single-point calculations and include corrections for contributions from zero-point energies. Our experience with the $SiC_2H_2^+$ surface, where energy differences using both UMP2/6-31G(d,p) and UMP2/6-311G(d,p) optimised structures are almost identical, suggests that this procedure will sacrifice very little accuracy.

There are many similarities and some dramatic differences between the $SiC_2H_2^+$ and $SiC_2H_4^+$ surfaces. On each surface the global minimum is a cyclic ion, ions **1** and **8**, with electronic state $^2B_2$, and is the π-complex formed by the symmetry-allowed addition of Si^+ (^2P) to the π-bond of acetylene or ethylene. On the $SiC_2H_4^+$ surface there are two low-lying excited states of **8**. The electronic configuration of **12**, with eight a_1-type orbitals doubly occupied, one of a_2-type, three of b_2-type and two of b_1-type, and with the unpaired electron in a b_1-type orbital, has the correct occupancy to be formed from $Si^+(^2P)+H_2C{=}CH_2$. This ion is only 15.5 kcal mol^{-1} above **8**; by contrast on the $SiC_2H_2^+$ surface the ion with the equivalent occupancy was about 121 kcal mol^{-1} above **1** and another $^2B_1$ state, ion **5**, with a different orbital occupancy, was considerably lower in energy.

Ion **12** has an extremely long C–Si distance

Table 2
Harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) from UMP2/6-311G(d,p) calculations[a]

1			**2**			**3**[b]			**4**			**5**		
Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry
3118.3	66.6	a_1	3023.3	49.3	b_2	3158.8	107.4	a′	3065.0	42.3	a_1	3039.2	50.9	a_1
3051.2	204.0	b_2	2939.0	45.5	a_1	2122.4	18.6	a′	3055.7	22.0	b_2	3024.9	34.8	b_2
1645.0	0.3	a_1	1789.5	469.4	a_1	1752.7	377.8	a′	1257.3	130.6	b_2	1222.9	0.9	a_1
881.8	68.7	b_2	1289.3	73.3	a_1	830.0	18.6	a″	1231.1	46.9	a_1	1055.0	48.3	b_2
783.0	12.8	a_1	1077.6	21.9	b_1	727.9	45.0	a′	927.5	0.0	a_2	883.6	4.5	a_1
693.3	96.0	b_1	804.0	0.2	b_2	703.9	115.6	a′	883.8	55.0	a_1	733.2	1.45	b_1
679.2	0.0	a_2	652.3	30.0	a_1	664.4	45.3	a′	810.5	1.3	a_1	621.0	49.5	a_1
532.7	0.4	b_2	259.7	18.6	b_2	196.6	28.4	a′	759.6	32.9	b_2	531.4	60.7	b_2
519.9	31.3	a_1	231.5	24.1	b_1	188.1	33.5	a″	691.4	105.0	b_1	1116.3i	–	a_2
Zero-point energies	17.0			17.2			14.8			18.1				

[a] All frequencies and zero-point energies are scaled by a factor of 0.94.

[b] UHF/6-31G(d,p) frequencies, scaled by a factor of 0.89.

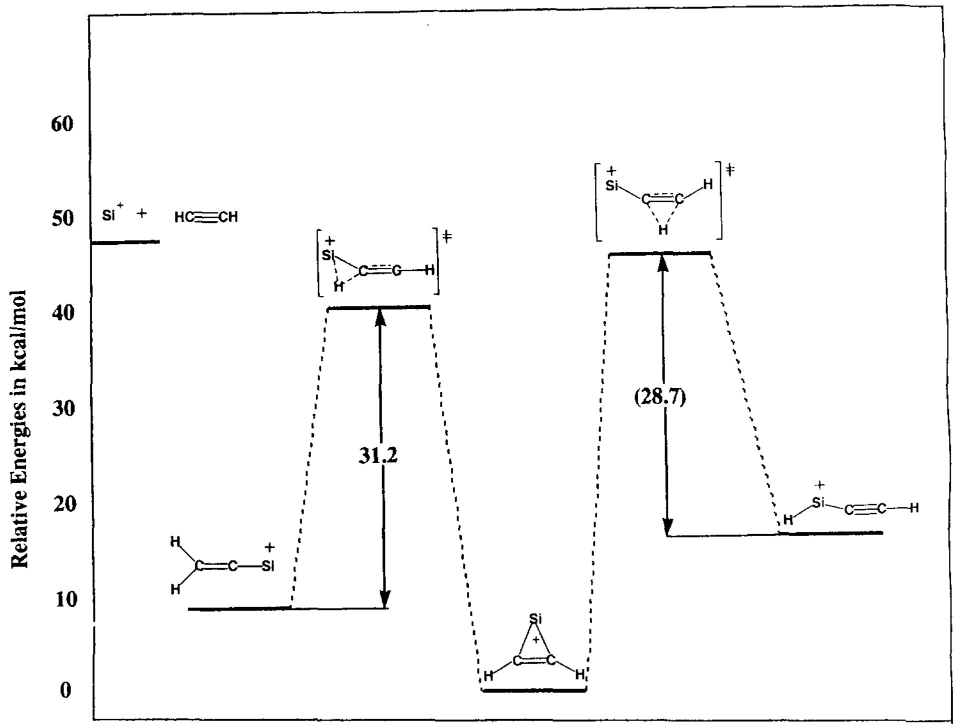


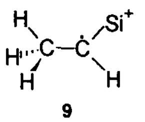
Fig. 2. Energy surface for $SiC_2H_2^+$ as calculated at UMP2/6-311G(d,p). The number in parentheses is the barrier height as calculated at UHF/6-31G(d,p).

(2.556 Å) and a short C–C distance (1.356 Å), consistent with little π-donation and no back-donation (the $4b_2$ orbital, not occupied in this ion, is responsible for back-donation in other cyclic ions). Ion **12** then is best considered to be a solvated ion or possibly a weak π-complex.

Ion **14**, the third cyclic ion, lies 15.0 kcal mol^{-1} above **8**. It has a long C–C distance (1.651 Å) and short C–Si distances (1.822 Å) and the structure differences between **14** and **8** are very similar to those between **4** and **1**. **14** has the wrong orbital symmetry (one too few occupied orbitals of a_1-type and one too many of b_2-type) to be formed directly from ground state Si^+ and ethylene. In this respect **14** also then resembles ion **4**.

Ab initio calculations on silacyclopropylidene gave optimised bond lengths of 1.935 Å and 1.521 Å for Si–C and C–C respectively [2a]. Ions **8** and **14** are formed by removal of an electron from molecular orbitals $4b_2$ and $8a_1$ of silacyclopropylidene. By comparison with silacyclopropylidene the C–C distance in **8** is shorter and C–Si is longer, while the converse is true for **14**. Similar structural differences were observed for **1** and **4** relative to silacyclopropenylidene on the $SiC_2H_2^+$ surface.

Ion **9** lies only 5.1 kcal mol^{-1} above **8**. It has C–C and C–Si distances of 1.486 Å and 1.817 Å respectively, both slightly shorter than normal single bond lengths [9]. The C–Si bond eclipses a C–H bond, and the structure is planar at the three-coordinate carbon. The unpaired electron is in an a''-type orbital and is almost entirely localised on the central carbon atom. The charge is located on silicon and the ion is well represented by the following valence bond structure:



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Ion **10** also is 5.1 kcal mol^{-1} above **8**. The C–C distance of 1.346 Å is characteristic of a double bond and the lowest energy rotamer has the hydrogen atom on the silicon eclipsing the double bond as in propene [23]. The charge and spin are both localised on the silicon and the ion is well represented by structure **10**.

Rotamer **11** is only 0.3 kcal mol^{-1} above **10**, and the barrier to rotation via transition structure **13** is 8.8 kcal mol^{-1} above **10**.

Ion **15**, a cyclic ion with two hydrogens on silicon and one on each carbon atom, has C_{2v} symmetry and lies 14.5 kcal mol^{-1} above **8**. The C–C distance of 1.271 Å is intermediate between a double and a triple bond and C–Si of 1.960 Å is longer than the single bond in silaethane (1.867 Å) [9]. The unpaired electron is in an orbital of b_2-type symmetry and the unpaired spin is approximately 50% on silicon and 25% on each carbon. The orbital occupancy, eight doubly occupied orbitals

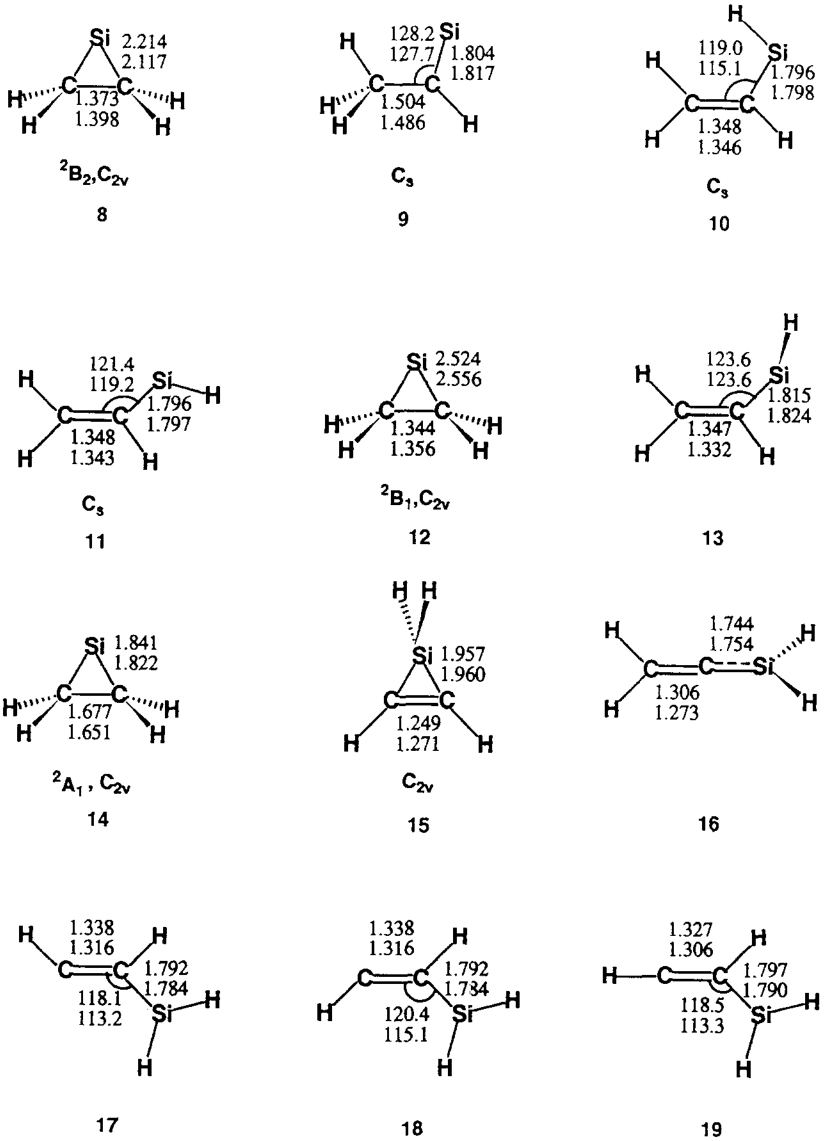


Fig. 3. Continued overleaf.

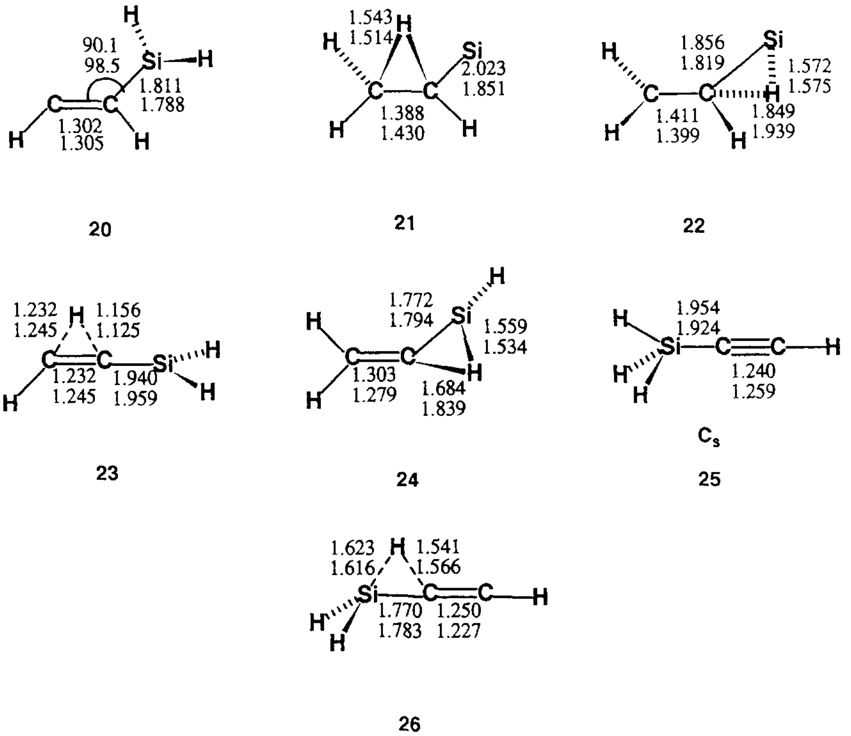
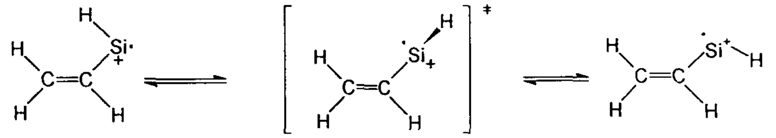
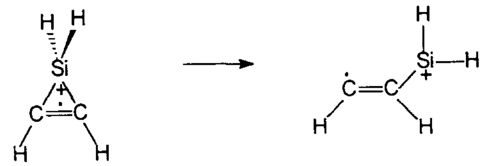


Fig. 3. Fig. 3. Geometric parameters for isomers and transition structures on the $SiC_2H_4^+$ surface. The upper numbers are from UHF/6-31G(d,p) and the lower ones from UMP2/6-31G(d,p). Bond lengths are in ångstroms and angles in degrees. For clarity, only the parameters involving two heavy atoms are included.



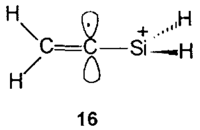
10 **13** **11**

of a_1-type, three of b_1-type, and three and a half of b_2-type correlates with acetylene combining with the excited state of SiH_2^+ in which the unpaired electron is in the π-orbital on silicon.



15 **17**

Ion **17** is 13.6 kcal mol^{-1} above **15**, but the barrier to rearrangement to **15** via **20** is only 0.5 kcal mol^{-1}.



16

Ion **16**, derived by removing an electron from 1-silaallene, has a short C–C distance (1.273 Å) and a Si–C distance (1.759 Å) intermediate between a single and a double bond. The charge is calculated to be on silicon and the unpaired electron is located almost entirely on the central carbon atom. The ion

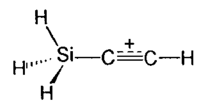
Table 3
Total energies (hartrees) for isomers of $SiC_2H_4^+$ [a]

Molecule	UHF/6-31G(d,p)	$\langle S^2 \rangle$	ZPE (kcal mol^{-1})	UMP2/6-31G(d,p)	UMP2/6-311G(d,p)	UMP2/6-311G(d,p) Energies relative to structure **8** (kcal mol^{-1})
8	−366.64412	0.76	31.2	−366.99479	−367.18081[b]	0
9	−366.64678	0.76	30.5	−366.98469	−367.17151	5.1
10	−366.64184	0.79	29.5	−366.98208	−367.16990	5.1
11	−366.64228	0.80	29.4	−366.98167	−367.16933	5.4
12	−366.63246	0.76	31.4	−366.97192	−367.15650	15.5
13	−366.62956	0.87	28.3	−366.96569	−367.15408	13.9
14	−366.61261	0.81	28.9	−366.96556	−367.15327	15.0
15	−366.60591	0.76	25.8	−366.95906	−367.14915	14.5
16	−366.62866	0.89	26.6	−366.95613	−367.14505	17.8
17	−366.61726	0.92	26.6	−366.93884	−367.12865	28.1
18	−366.61469	0.93	26.7	−366.93695	−367.12659	29.5
19	−366.60605	0.91	25.4	−366.93011	−367.12109	31.7
20	−366.60490	0.87	25.7	−366.93646	−367.12643	28.6
21	−366.59229	0.77	29.2	−366.93305	−367.12070	35.7
22	−366.59264	0.81	26.8	−366.92504	−367.11360	37.7
23	−366.58033	0.78	24.1	−366.91670	−367.10692	39.2
24	−366.58044	0.85	25.5	−366.91437	−367.10384	42.6
25	−366.58904	0.76	25.2	−366.90934	−367.09821	45.8
26	−366.56218	0.81	23.1	−366.89522	−367.08857	49.7
$Si^+ + H_2C{=}CH_2$	−366.59014	0.76	30.4	−366.92317	−367.11197	42.4
$SiH_3^+ + HC{\equiv}CH$	−366.53517	0.75	22.8	−366.87355	−367.06947	61.4

[a] Structures were fully optimised at UHF/6-31G(d,p) and at UMP2/6-31G(d,p). The UMP2/6-311G(d,p) calculations are at UMP2/6-31G(d,p) optimised structures.
[b] Optimised at UMP2/6-311G(d,p).

then is best represented by a valence bond structure containing a vinyl radical and a silyl cation, **16**.

The three lowest ions on the $SiC_2H_4^+$ surface (Fig. 4) all are best represented by valence bond structures in which the positive charge is formally located on the silicon. Two of these structures, **8** and **9** have all the hydrogen atoms attached to carbon, and the third, **10**, has only one hydrogen attached to silicon. Higher energy structures on the surface are all either electronically excited states of **8**, or have two or three hydrogens attached to silicon. Curiously, the highest minimum which we have located, ion **25**, is formed by removal of an electron from 3-silapropyne, the molecule which is the global minimum on the neutral SiC_2H_4 surface [2a]. Ion **25** undergoes rearrangement to ion **17** and the barrier to rearrangement is low (3.9 kcal mol^{-1} at UMP2/6-311G(d,p). It should be noted that, on inclusion of spin projection [19] at the same level of theory, this barrier disappears completely.



25

From the profile of the surface in Fig. 4 it is apparent that five ions, **8**, **9**, **10**, **15**, and **16** are in deep potential wells and each of these therefore could be stable in interstellar clouds or even in the gas phase in the laboratory. The calculated harmonic vibrational frequencies for these five ions as calculated with the UHF/6-31G(d,p) level of theory are given in Table 4.

Rearrangement of the cyclic ion, **15**, appears to have the most complicated pathway to rearrangement. Ring opening of **15** forms ion **17**, and this is followed by inversion to **18**. A 1,2-hydrogen shift then converts **18** into the 1-silaallene cation, **16**. This overall pathway has a barrier of 24.7 kcal mol^{-1} above **15** and is endothermic by 3.3 kcal mol^{-1}. However, rearrangement via

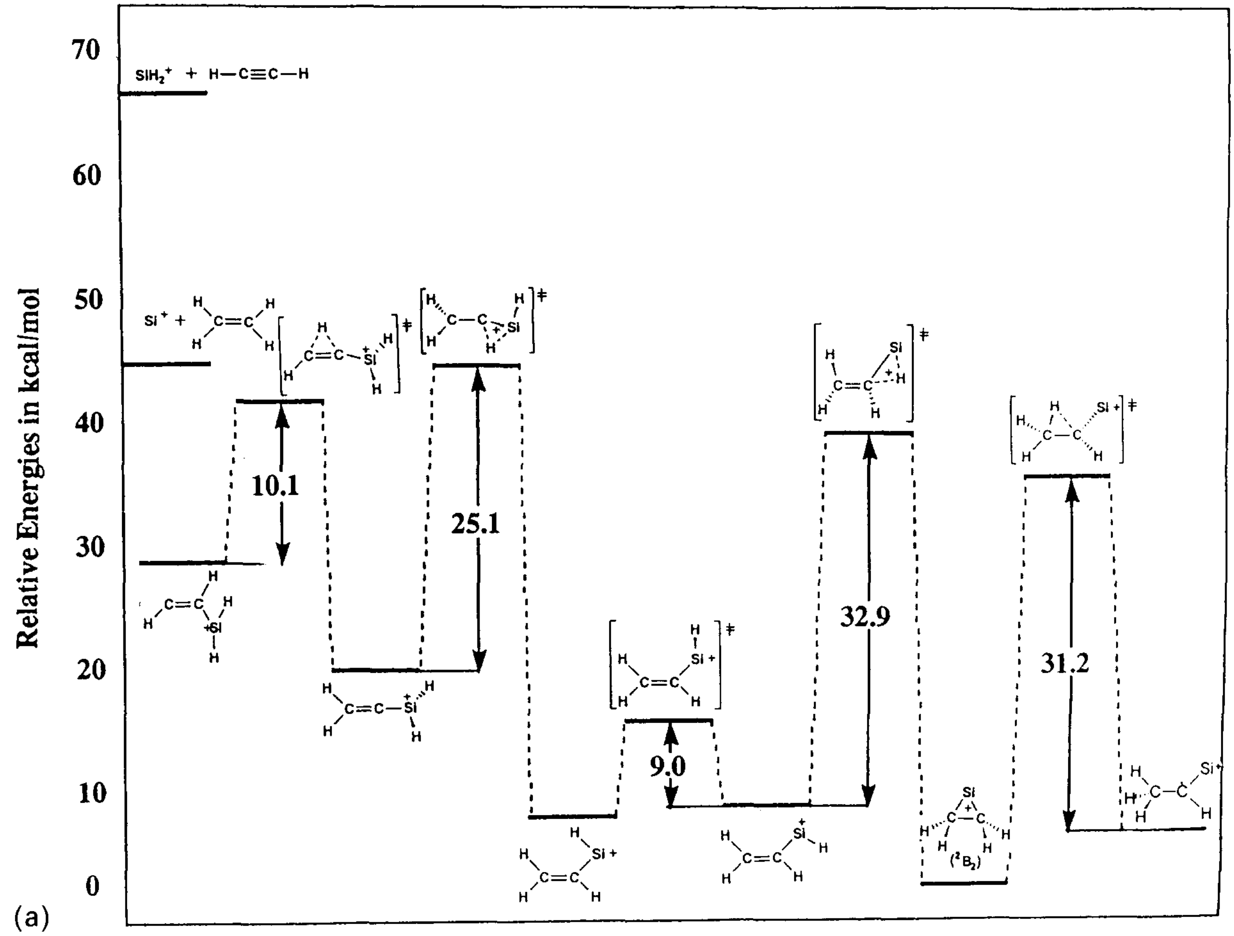
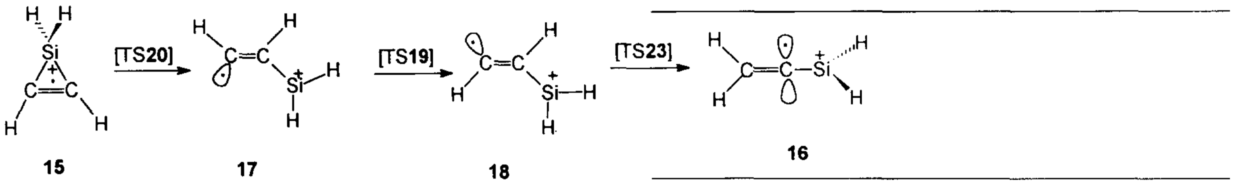


Fig. 4. Continued facing page.

16 is essential if lower energy isomers are to be formed.



15 **17** **18** **16**

Ion **16** undergoes a 1,2-hydrogen atom shift from silicon to carbon to form ion **10**. The barrier to this rearrangement is 24.8 kcal mol^{-1} above **16**. Ion **10** rearranges through transition structure **13** to its rotamer **11**, which then undergoes a 1,2-hydrogen shift from silicon to carbon involving transition structure **22** to form the global minimum, ion **8**. Transition structure **22** is 32.6 kcal mol^{-1} above **10**, but is lower than **24** by 4.9 kcal mol^{-1}. Transition structure **24** then is the highest barrier that has to be overcome in order to convert **15** and **16** (and other higher energy ions like **25**) into the global minimum.

Finally ion **9** is converted into **8** by a 1,2-hydrogen shift between carbon atoms accompanied by

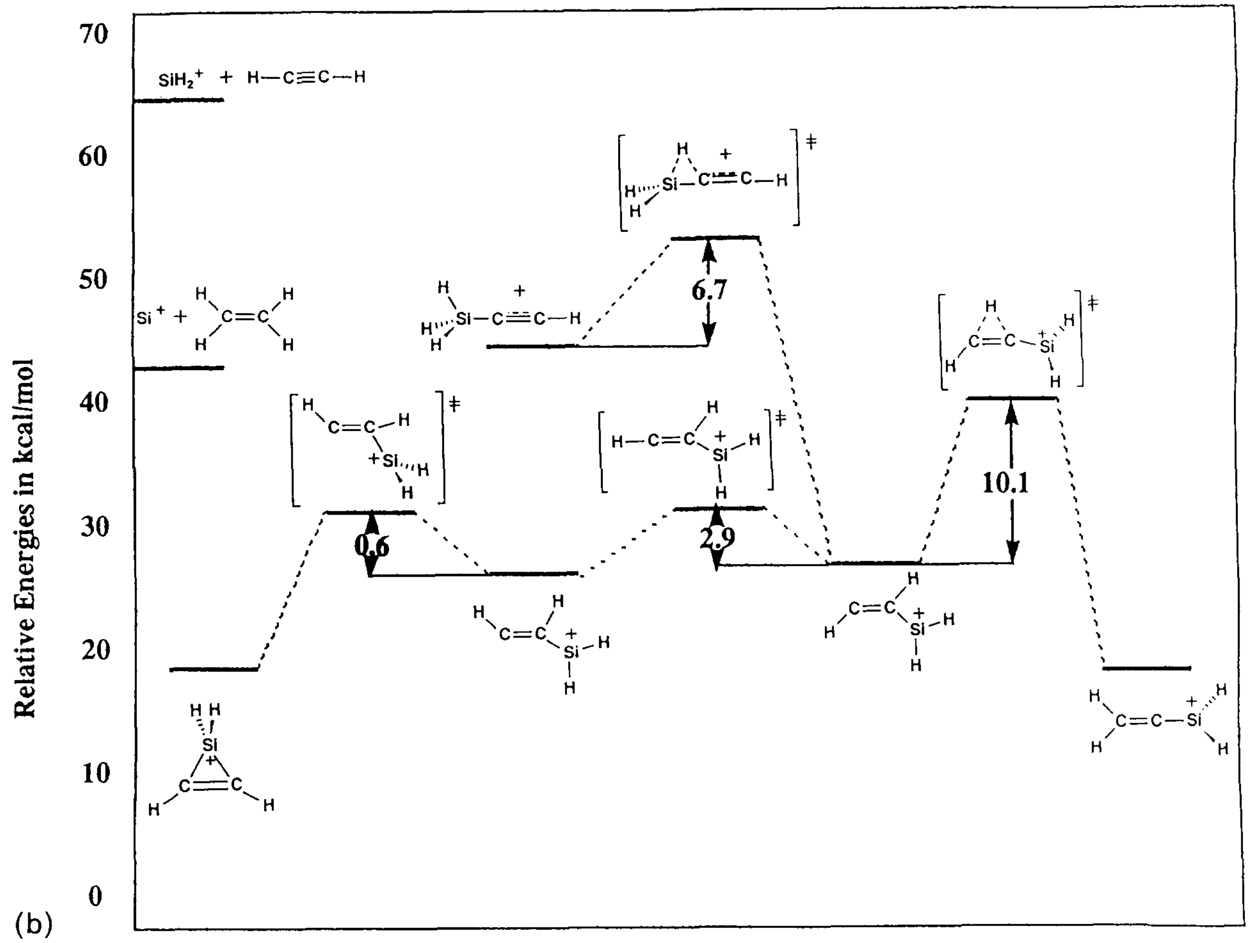
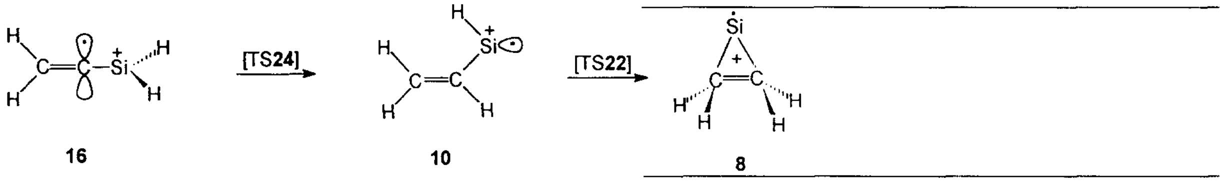
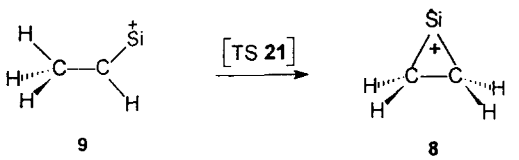


Fig. 4. Energy surface for $SiC_2H_4^+$ as calculated at UMP2/6-31G(d,p). (a) The lowest energy isomers and (b) the higher energy ones. For continuity the three levels on the left-hand side of (a) are also included on the right-hand side of (b).



ring closure. The transition structure, **21**, for this reaction is 34.3 kcal mol^{-1} above **9**.



Transition structure **24** is calculated at UMP2/6-311G(d,p) to be 0.2 kcal mol^{-1} higher in energy than $Si^+ + H_2C{=}CH_2$, but when spin contamination is projected out of the wavefunction [19] at PMP2/6-311G(d,p), then **24** is 1.3 kcal mol^{-1} lower in energy than the reactants. Transition structures **21**, **22**, **23**, and **24** then all have lower energies than $Si^+ + H_2C{=}CH_2$, and there is, in principle, sufficient energy available to form all five adduct ions

Table 4
Harmonic vibrational frequencies (cm^{-1}) and intensities ($km\ mol^{-1}$) from UHF/6-31G(d,p)[a]

8			**9**			**10**			**16**			**15**		
Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry
3026.6	18.5	b_1	2928.0	12.8	a'	3035.5	5.0	a'	2996.2	20.7	b_2	2979.3	92.4	a_1
3007.4	0.0	a_2	2892.0	8.9	a'	2990.5	9.9	a'	2910.0	50.5	a_1	2921.6	206.1	b_2
2934.9	10.4	a_1	2890.0	1.1	a''	2946.9	0.4	a'	2249.7	15.7	b_2	2216.6	12.7	b_2
2925.6	15.5	b_2	2829.2	5.6	a'	2128.8	25.0	a'	2210.7	7.6	a_1	2165.1	4.4	a_1
1511.5	0.0	a_1	1432.1	38.1	a'	1516.4	58.6	a'	1538.9	26.7	a_1	1584.5	8.3	a_1
1407.4	19.9	b_2	1410.4	11.0	a''	1334.3	180.7	a'	1336.6	6.3	a_1	879.1	68.7	a_1
1222.2	4.6	a_1	1350.0	9.5	a'	1237.3	5.7	a'	963.5	39.9	b_2	821.1	33.1	b_2
1187.4	0.0	a_2	1232.3	0.4	a'	1073.2	21.5	a''	906.4	114.5	a_1	756.4	15.0	a_1
1001.9	16.4	a_1	1017.4	5.2	a'	990.2	4.8	a'	872.9	0.2	b_1	637.0	164.3	b_1
964.5	25.7	b_2	903.7	10.7	a'	958.1	34.6	a''	655.8	54.0	a_1	630.0	44.8	b_2
927.7	0.0	a_2	892.9	5.8	a''	713.3	45.8	a'	631.3	85.0	b_2	587.3	0.0	a_2
785.7	2.0	b_1	657.3	48.6	a'	679.6	79.1	a'	613.6	56.3	b_1	554.1	6.7	a_1
543.2	4.4	b_1	570.9	4.8	a''	428.0	3.2	a'	274.0	0.0	a_2	546.1	3.5	b_1
214.2	0.7	a_1	193.6	1.8	a'	323.4	18.4	a''	209.8	15.4	b_1	495.0	6.1	b_2
178.3	4.3	b_2	142.6	1.0	a''	259.5	0.8	a'	209.7	16.7	b_2	318.9	0.0	a_2

[a] All frequencies were scaled by a factor of 0.89.

(**8**, **9**, **10**, **15**, and **16**) in this ion–molecule gas phase reaction.

3.3. Thermochemistry for addition of Si^+ (^2P) to acetylene and ethylene

The global minimum on both the $SiC_2H_2^+$ and $SiC_2H_4^+$ surfaces are cyclic ions with electronic states $^2B_2$. These ions are formed by direct combination of $Si^+(^2P)$ with the hydrocarbons in symmetry-allowed processes. We have extended the level of theory in order to determine more accurately the exothermicities of the adduct-forming reactions, assuming formation of cyclic ions **1** and **8**.

We have also calculated the thermochemistry of the second reaction observed experimentally, loss of a hydrogen atom from each of the adducts (the reactions described by Eqs. (1b) and (2b)). For reaction 1 all three levels of theory, UMP4/6-311++G(2df,p), PMP4/6-311++G(2df,p) and QCISD(T)/6-311++G(2df,p) gave formation of $SiC_2H_2^+(^2B_2)$ to be exothermic by 52.5 kcal mol^{-1} at 0 K (Table 5). This compares with a value of 48.1 kcal mol^{-1} obtained from the lower level UMP2(FULL)/6-311G(d,p) calculations. The other observed products, $SiC_2H^+ + H$, are slightly lower in energy than the reactants, with the energy difference being only 2.4 kcal mol^{-1} at QCISD(T)/6-311++G(2df,p). Hydrogen loss is one of the major channels observed experimentally and must therefore occur with little or no activation barrier.

The exothermicity of the reaction between Si^+ and $H_2C{=}CH_2$ is also calculated to be greater at MP4/6-311++G(2df,p) than at UMP2(FULL)/6-311G (d,p) (46.0 kcal mol^{-1} compared with 42.4 kcal mol^{-1}). Formation of the dissociation products, $SiC_2H_3^+ + H$, is slightly exothermic (by 0.6 kcal mol^{-1}) at UMP4/6-311++G(2df,p), but when spin projection is included the reaction is calculated to be thermoneutral.

4. Conclusions

In the addition of $Si^+(^2P)$ to acetylene and to ethylene the symmetrically bridged adducts with electronic state $^2B_2$ (ions **1** and **8**) are formed without barrier. On each surface these isomers have the lowest energy, i.e. are the global minima. The reactions to produce the other experimentally observed reaction channels, leading to the adduct ions minus a hydrogen atom, are calculated to be almost thermoneutral and, since major amounts of these ions are formed, there clearly is little or no barrier to this dissociation reaction.

On both the $SiC_2H_2^+$ and $SiC_2H_4^+$ surfaces the high exothermicities of the adduct-forming reactions provide sufficient energy for several other isomers to be accessible, i.e. the transition structures are lower in energy than the reactants. The initially formed cyclic ions then can undergo unimolecular rearrangement prior to stabilisation by collisions. When isomeric ions are formed in this manner and become collisionally stabilised they may coexist since many of the barriers to rearrangement are high. Conversely, if one of the low energy isomers, **1**, **2**, and **3** on the $SiC_2H_2^+$ surface and **8**, **9**, **10**, **15**, and **16** on the $SiC_2H_4^+$ surface, is formed by a low energy gas phase

Table 5
Energies (hartrees) of reactants and observed products for reaction of $Si^+(^2P)$ with acetylene and with ethylene[a]

Molecule	UMP4/6-311++G(2df,p)		PMP4/6-311++G(2df,p)		QCISD(T)/6-311++G(2df,p)	
1	−365.89380	(0)	−365.89475	(0)	−366.07327	(0)
$SiC_2H^+ + H$	−365.80868	(48.6)	−365.80868	(49.2)	−365.98571	(50.1)
$Si^+ + HC{\equiv}CH$	−365.8095	(52.5)	−365.81042	(52.5)	−365.98900	(52.5)
8	−367.12672	(0)	−367.12773	(0)	–	
$SiC_2H_3^+ + H$	−367.04395	(45.4)	−367.04395	(46.0)	–	
$Si^+ + H_2C{=}CH_2$	−367.0522	(46.0)	−367.05312	(46.0)	–	

[a] Energies (kcal mol^{-1}) relative to the global minimum on each surface are given in parentheses.

process, then it should be possible to design experiments to characterise this isomer independently.

Finally, we have provided harmonic frequencies in the hope that they may be of assistance in identifying some of these ions spectroscopically. A note of caution should be added here, since it has been found that in some molecules spin contamination can cause significant errors in the calculated vibrational frequencies [24].

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