Gas-Phase Reactions of $Si^+(^2P)$ with Small Hydrocarbon Molecules: Formation of Silicon–Carbon Bonds

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Abstract: Reactions of ground-state $Si^+(^2P)$ ions have been investigated with the hydrocarbon molecules CH_4, C_2H_6, C_2H_4, C_2H_2, CH_2CCH_2, CH_3CCH, and C_4H_2 proceeding in a helium bath gas at 0.35 Torr and a temperature of 296 ± 2 K with the selected-ion flow tube (SIFT) technique. A range in the nature and degree of reactivity was observed. Methane reacts slowly to form an adduct ion. Results of quantum chemical calculations performed at the UMP4(SDTQ)/6-31G**// UHF/6-31G** level are presented which provide insight into the possible structure of this adduct ion. Adduct formation also is a strong feature in the reactions of Si^+ with C_2H_2 and C_2H_4 in which it competes with condensation resulting in H atom elimination. The reaction with C_2H_6 predominantly leads to Si–C bond formation in the product ions together with elimination of CH_3, CH_4, or H_2. For these three reaction channels possible mechanisms are proposed involving C–C and C–H bond insertion. The reactions with allene and propyne are rapid and have similar product distributions. Several bimolecular product channels are observed and all lead to Si–C bond formation. The reaction with diacetylene is unique in that it proceeds rapidly only by hydride ion transfer. Higher order reactions leading to more complex silicon–carbide ions have also been characterized. The reactivities of the Si^+ reactions are compared with those available for the analogous reactions with C^+ proceeding under similar conditions of temperature and pressure. Except for the reactions with allene and propyne, the reactions with Si^+ are uniformly slower and less efficient than the corresponding reactions with C^+, and the competition with adduct formation is not apparent for the reactions with C^+ in which charge transfer and H atom elimination are sometimes more predominant. The observation and failure to observe reactions at 296 K is used to provide insight into the standard enthalpies of formation of the silicon-containing hydrocarbon ions $SiCH_2^+$, $SiCH_3^+$, SiC_2H^+, $SiC_2H_3^+$, $SiC_2H_2^+$, $SiC_2H_4^+$, $SiC_2H_6^+$, $SiC_3H_3^+$, $SiC_4H_5^+$, and SiC_4H^+. A brief discussion is presented of the implications of the chemistry observed with Si^+ for the formation of molecules containing Si–C bonds in partially ionized environments containing silicon and carbon, such as the circumstellar envelopes of carbon stars.

Introduction

There is a growing interest in fundamental aspects of the chemical bonding of carbon to silicon. For us this interest has been stimulated in part by the detection of silicon–carbide molecules in circumstellar envelopes which can be penetrated and ionized by interstellar UV photons and a need to understand their chemistry of formation. For example, the silicon–carbide molecules SiC, c-SiC_2, and SiC_4 have recently been identified by radioastronomers in the circumstellar envelope of the carbon star IRC+10216 which is famous in astrochemistry for its wealth of molecular species.[1-3] To begin the exploration of Si/C ion chemistry we have conducted a systematic investigation of ion chemistry initiated by ground-state atomic silicon ions reacting with small saturated and unsaturated hydrocarbon molecules. Here we report the results of measurements taken with a selected-ion flow tube (or SIFT) apparatus of the primary kinetics and product distributions at room temperature (296 ± 2 K) in helium carrier gas at 0.35 Torr for reactions of $Si^+(^2P)$ with methane, ethane, ethylene, allene, acetylene, diacetylene, and propyne. These particular hydrocarbons were chosen as substrates, in part, because of the importance of some in the chemistry of circumstellar envelopes, but also to explore more generally the ability of silicon to bond to carbon in reactions of Si^+ with saturated and unsaturated hydrocarbon molecules. An attempt is also made to track higher order reactions in these gases which lead to growth of more complex silicon-bearing carbonaceous ions and molecules.

Several of the hydrocarbon reactions have been investigated previously with other techniques, but often at nonthermal energies and without state selection of $Si^+(^2P)$, and invariably at low pressures. The reaction with methane which is of interest in C–H activation has been studied by ion cyclotron resonance (or ICR) mass spectrometry[4] and reported not to proceed at low pressures at energies near room temperature. A very recent guided ion-beam mass-spectrometry study has explored in detail the onset of endothermic channels for the reaction of methane with $Si^+(^2P)$ under

Chart I
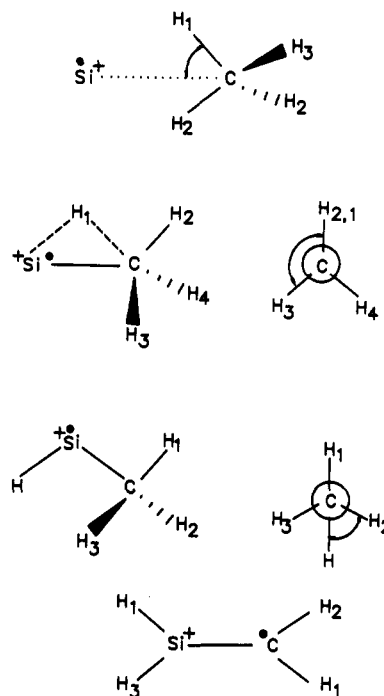
single collision conditions from near-thermal to 14 eV relative kinetic energy.[5] Also, an early tandem mass-spectrometer study

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

(4) Stewart, G. W.; Henis, J. M. S.; Gaspar, P. P. *J. Chem. Phys.* **1972**, *57*, 1990.

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Table I. Rate Constants (10^{-10} cm^3 molecule^{-1} s^{-1}), Product Distributions, and Efficiencies for Reactions of Si$^+$(^{2}P) with Hydrocarbon Molecules at 296 ± 2 K

| neutral reactant	products	product distribution[a]	k_{exp}[b]	k_{exp}/k_c[c]
CH$_4$	SiCH$_4^+$	1.0	0.005	0.00043
C$_2$H$_6$	SiCH$_3^+$ + CH$_3$	0.80	8.0	0.61
	SiCH$_2^+$ + CH$_4$	0.15		
	SiC$_2$H$_4^+$ + H$_2$	0.03		
	SiC$_2$H$_6^+$	0.02		
C$_2$H$_4$	SiC$_2$H$_4^+$	0.60	5.6	0.43
	SiC$_2$H$_3^+$ + H	0.40		
C$_2$H$_2$	SiC$_2$H$^+$ + H	0.70	3.5	0.30
	SiC$_2$H$_2^+$	0.30		
CH$_2$CCH$_2$	SiC$_3$H$_3^+$ + H	0.70	12	0.86
	SiC$_2$H$^+$ + CH$_3$	0.20		
	SiCH$_2^+$ + C$_2$H$_2$	0.10		
CH$_3$CCH	SiC$_3$H$_3^+$ + H	0.60	12	0.73
	SiC$_2$H$^+$ + CH$_3$	0.25		
	SiCH$_2^+$ + C$_2$H$_2$	0.15		
C$_4$H$_2$	C$_4$H$^+$ + SiH	1.0	16	1.18

[a] Primary product ions which contribute 5% or more. The product distributions have been rounded off to the nearest 5% and are estimated to be accurate to within ±30%. [b] The effective bimolecular rate constant is given at a total helium pressure of 0.35 Torr and a helium density of 1.15 × 10^{16} atoms cm^{-3}. The accuracy of the rate constants is estimated to be better than ±30%. [c] k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition state theory–classical trajectory study of T. Su and W. J. Chesnavich, *J. Chem. Phys.* **1982**, *76*, 5183.

Table II. Rate Constants (10^{-10} cm^3 molecule^{-1} s^{-1}), Product Distributions, and Efficiencies for Secondary Reactions of SiC$_x$H$_y^+$ Ions with Hydrocarbon Molecules at 296 ± 2 K

reaction with product distribution[a]	k_{exp}[b]	k_{exp}/k_c[c]
SiC$_2$H$_4^+$ + C$_2$H$_4$ $\xrightarrow{0.8}$ SiC$_2$H$_3^+$ + C$_2$H$_5$	4.0	0.36
$\xrightarrow{0.2}$ SiC$_4$H$_8^+$		
SiC$_2$H$_4^+$ + C$_2$H$_6$ → products	0.77	0.07
SiC$_2$H$^+$ + C$_2$H$_2$ $\xrightarrow{0.9}$ SiC$_4$H$_3^+$	2.0	0.50
$\xrightarrow{0.1}$ SiC$_4$H$^+$ + H$_2$		
SiC$_2$H$_2^+$ + C$_2$H$_2$ → SiC$_4$H$_4^+$	2.0	0.50
SiCH$_2^+$ + CH$_2$CCH$_2$ $\xrightarrow{0.95}$ SiC$_3$H$_3^+$ + CH$_3$	6.1	0.47
$\xrightarrow{0.05}$ SiC$_4$H$_5^+$ + H		
SiC$_2$H$^+$ + CH$_2$CCH$_2$ → SiC$_5$H$_5^+$	5.6	0.46
SiCH$_2^+$ + CH$_3$CCH $\xrightarrow{0.85}$ SiC$_3$H$_3^+$ + CH$_3$	9.1	0.61
$\xrightarrow{0.15}$ SiC$_4$H$_5^+$ + H		
SiC$_2$H$^+$ + CH$_3$CCH → SiC$_5$H$_5^+$	6.5	0.46

[a] Primary product ions which contribute 5% or more. The product distributions have been rounded off to the nearest 5% and are estimated to be accurate to within ±30%. [b] The effective bimolecular rate constant is given at a total helium pressure of 0.35 Torr and a helium density of 1.15 × 10^{16} atoms cm^{-3}. The accuracy of the rate constants is estimated to be better than ±30%. [c] k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition state theory–classical trajectory study of T. Su and W. J. Chesnavich, *J. Chem. Phys.* **1982**, *76*, 5183.

without Si$^+$ state selection has been reported for the reaction with acetylene which was monitored as a function of collision center-of-mass energy in the range 0.3–2.5 eV at a collision chamber pressure of the order of 10^{-3} Torr.[6] In all three of these studies the ambient pressures were too low to cause collisional stabilization of possible adduct ions. The opportunity for such stabilization is enhanced under the operating conditions of the SIFT experiments which are reported here. There appear not to have been any previous reports of the reactions of Si$^+$(^{2}P) with ethylene, ethane, diacetylene, allene and propyne.

Previous systematic studies of reactions of the same hydrocarbon molecules with C$^+$ under similar operating conditions allow a comparison of the reactivities of the group IV atomic ions Si$^+$(^{2}P) and C$^+$(^{2}P).[7,8] We shall look for differences in the chemical reactivities of these two atomic ions which may result from the substantial difference in their standard enthalpy of formation, 136 kcal mol^{-1} at 298 K. These should be manifested in the nature of the bond-formation channels and their relative efficiency, and also, possibly, in the overall reaction efficiencies.

Experimental Section

All measurements were performed with the selected-ion flow tube (SIFT) apparatus that has been described in detail elsewhere.[9,10] Atomic silicon ions were derived from a 2–3% mixture of tetramethylsilane in deuterium by electron impact at 50–100 eV. The deuterium was added to scavenge the metastable Si$^+$(^{4}P) ions in the source with the following reaction[4]

$$\text{Si}^+(^4\text{P}) + \text{D}_2 \rightarrow \text{DSi}^+ + \text{D} \qquad (1)$$
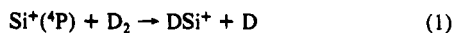
Si$^+$ ions were selected and introduced into helium buffer gas at 0.35 Torr (or 1.15 × 10^{16} He atoms cm^{-3}). The helium carrier gas and the reagent gases methane, ethane, ethylene, and acetylene were of high purity (>99.6 mol %). Allene and propyne were of somewhat lower purity (>96 mol %). To remove traces of water vapor, the helium carrier gas was
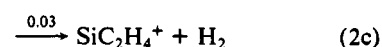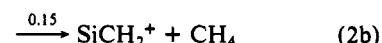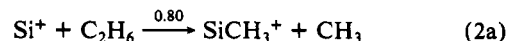
passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperature. The reagent gases were used without further purification. The diacetylene was prepared by the alkaline hydrolysis of 1,4-dichlorobut-2-yne[11] and stored at dry ice temperature to avoid polymerization. Previous experiments with H$_3^+$ as the "chemical ionization" reagent indicated a purity for the gas produced in this manner of greater than 99%. All measurements were made at an ambient temperature of 296 ± 2 K.

Experimental Results

Table I summarizes the rate constants and product distributions observed for the reactions of Si$^+$(^{2}P) with the seven different hydrocarbon molecules investigated in this study. The measured rate constants are compared with computed collision rate constants to provide reaction efficiencies. The reaction efficiency is defined as the ratio of the experimental to the theoretical rate constant. Similar data obtained for the secondary reactions which were observed are summarized in Table II. In this case experimental rate constants were determined with a two-exponential computer-fitting technique.

Methane. No bimolecular product channels were observed with methane. The apparent bimolecular rate constant for the production of the adduct ion SiCH$_4^+$ was small, only 5 × 10^{-13} cm^3 molecule^{-1} s^{-1}. The low magnitude of this reaction rate constant suggests that the adduct is weakly bound.

Ethane. Si$^+$(^{2}P) was seen to react with ethane much more efficiently than with methane and a variety of bimolecular products was observed in addition to a minor channel leading to adduct formation.

$$\text{Si}^+ + \text{C}_2\text{H}_6 \xrightarrow{0.80} \text{SiCH}_3^+ + \text{CH}_3 \qquad (2a)$$

$$\xrightarrow{0.15} \text{SiCH}_2^+ + \text{CH}_4 \qquad (2b)$$

$$\xrightarrow{0.03} \text{SiC}_2\text{H}_4^+ + \text{H}_2 \qquad (2c)$$

$$\xrightarrow{0.02} \text{SiC}_2\text{H}_6^+ \qquad (2d)$$

All of the bimolecular channels lead to Si–C bond formation. Formation of SiCH$_3^+$ with methyl elimination (reaction 2a)

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(8) Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* **1983**, *269*, 329.

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(10) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *55*, 69.

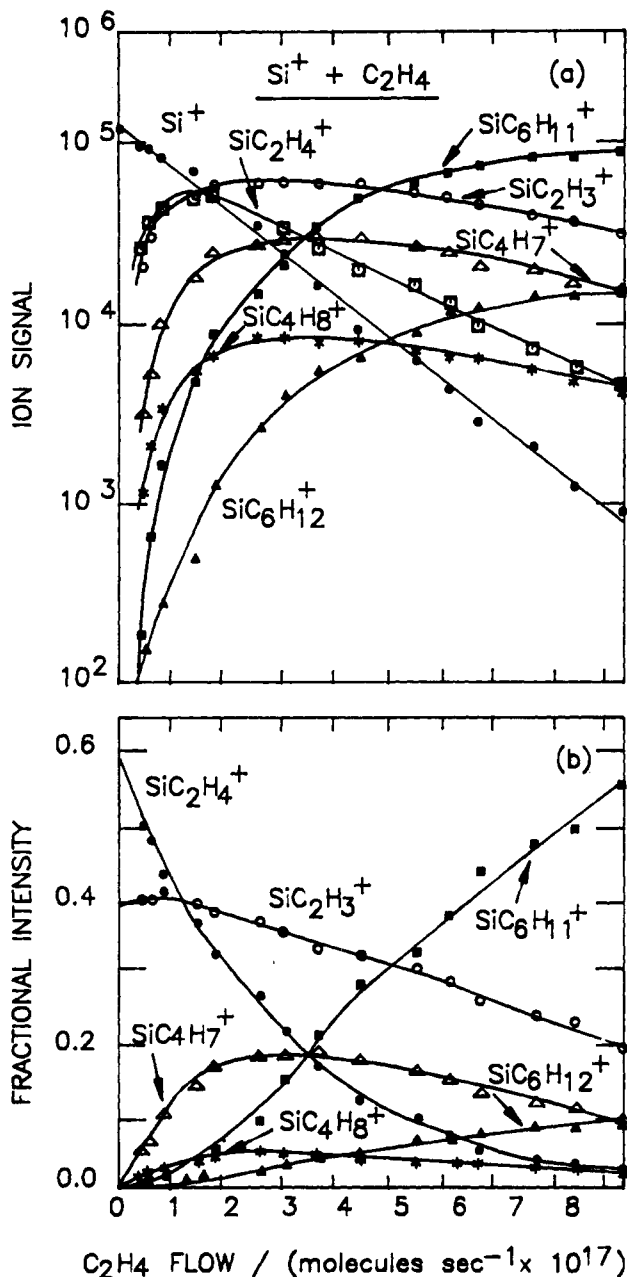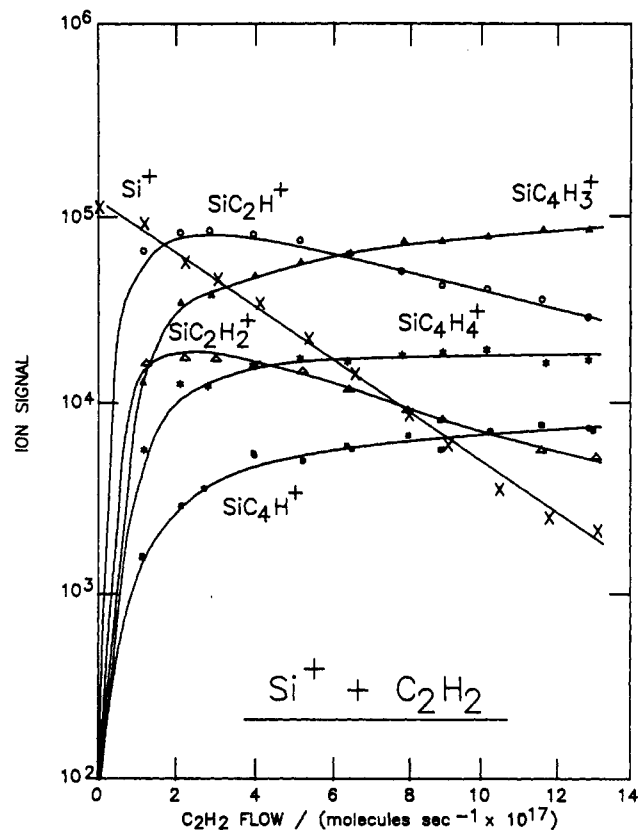(11) Brandsma, L. *Preparative Acetylene Chemistry*; Elsevier Publishing Co.: New York, 1971; pp 122–124.

Figure 1. (a) The observed variations in ion signals recorded for the addition of ethylene into the reaction region of the SIFT apparatus in which Si+(2P) is initially established as the dominant ion in helium buffer gas. $P = 0.345$ Torr, $\bar{v} = 7.0 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 295$ K. The Si+ is derived from tetramethylsilane with added deuterium (3%) at 72 eV. (b) The fractional abundance of the product ions observed in part a. The intercepts at zero flow of cyanogen provide a measure of the initial product distribution, and the ion profiles provide further insight into the evolution of the products.

Figure 2. The observed variations of ion signals recorded for the addition of acetylene into the reaction region of the SIFT apparatus in which Si+(2P) is initially established as the dominant ion in helium buffer gas. $P = 0.351$ Torr, $\bar{v} = 7.0 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 292$ K. The Si+ is derived from tetramethylsilane with added deuterium (3%) at 78 eV.

predominates over the elimination of methane (reaction 2b) and hydrogen (reaction 2c). The formation of the adduct ion, $SiC_2H_6{}^+$, is indicative of the importance of the initial Si+–C_2H_6 interaction. Only the $SiC_2H_4{}^+$ product ion appeared to react further with ethane, $k = 7.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, but low signal intensities prevented an identification of the products of this secondary reaction.

Ethylene. Adduct formation and condensation with H-atom elimination were the only two primary product channels observed with ethylene as shown in reaction 3. The overall reaction is fast
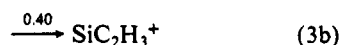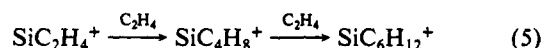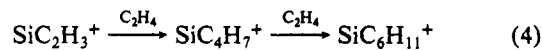
$$Si^+ + C_2H_4 \xrightarrow{0.60} SiC_2H_4{}^+ \tag{3a}$$

$$\xrightarrow{0.40} SiC_2H_3{}^+ \tag{3b}$$

and proceeds at about one-half of the collision rate. Both of the primary ions were seen to react further to form adduct ions by sequential addition reactions:

$$SiC_2H_3{}^+ \xrightarrow{C_2H_4} SiC_4H_7{}^+ \xrightarrow{C_2H_4} SiC_6H_{11}{}^+ \tag{4}$$

$$SiC_2H_4{}^+ \xrightarrow{C_2H_4} SiC_4H_8{}^+ \xrightarrow{C_2H_4} SiC_6H_{12}{}^+ \tag{5}$$

The evolution of the product ions with addition of ethylene is shown in Figure 1a. The product fractional–intensity plot in Figure 1b illustrates that $SiC_2H_3{}^+$ is also produced by the secondary H atom transfer reaction 6a which predominates over adduct formation.

$$SiC_2H_4{}^+ + C_2H_4 \xrightarrow{0.8} SiC_2H_3{}^+ + C_2H_5 \tag{6a}$$

$$\xrightarrow{0.2} SiC_4H_8{}^+ \tag{6b}$$

Acetylene. Acetylene was seen to react with Si+ in a manner analogous to the reaction with ethylene, but in this case H atom elimination predominates over adduct formation as shown in reaction 7 and Figure 2. Figure 2 indicates that both product

$$Si^+ + C_2H_2 \xrightarrow{0.70} SiC_2H^+ + H \tag{7a}$$

$$\xrightarrow{0.30} SiC_2H_2{}^+ \tag{7b}$$
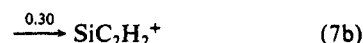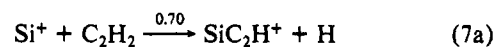
ions of reaction 7 react further by the addition of a second acetylene molecule. We have attributed the formation of SiC_4H^+ to the reaction of SiC_2H^+ rather than $SiC_2H_2{}^+$ because of what is perceived to be a more favorable energetics associated with the elimination of H_2 rather than $H_2 + H$, respectively. Analysis of the data then results in the following reactions and product distributions:
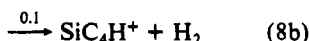
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$$SiC_2H^+ + C_2H_2 \xrightarrow{0.9} SiC_4H_3^+ \quad (8a)$$

$$\xrightarrow{0.1} SiC_4H^+ + H_2 \quad (8b)$$

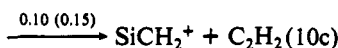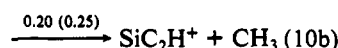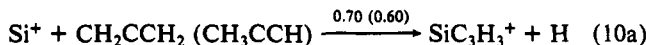$$SiC_2H_2^+ + C_2H_2 \rightarrow SiC_4H_4^+ \quad (9)$$

Figure 2 shows that reactions 8 and 9 proceed with similar rates. Curve fitting of the intermediate SiC_2H^+ and $SiC_2H_2^+$ ion profiles provides an effective bimolecular rate constant of 2.0×10^{-10} cm^3 molecule^{-1} s^{-1} for these two reactions.

Allene and Propyne. These two isomeric molecules were observed to react rapidly with Si^+ at close to the collision rate to give multiple bimolecular products with similar product distributions as summarized in reaction 10. Condensation with H atom
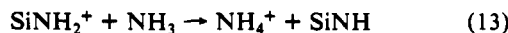
$$Si^+ + CH_2CCH_2 (CH_3CCH) \xrightarrow{0.70 \, (0.60)} SiC_3H_3^+ + H \quad (10a)$$

$$\xrightarrow{0.20 \, (0.25)} SiC_2H^+ + CH_3 \quad (10b)$$

$$\xrightarrow{0.10 \, (0.15)} SiCH_2^+ + C_2H_2 \quad (10c)$$

elimination is the predominant reaction channel, and the ionic product of this channel, $SiC_3H_3^+$, is only moderately reactive toward allene and propyne yielding the adduct ion $SiC_6H_7^+$. The other two primary product ions, SiC_2H^+ and $SiCH_2^+$, which arise from CH_3 and C_2H_2 elimination, respectively, were observed to react rapidly with both allene and propyne (see Table II). Product ion distribution plots showed that, while SiC_2H^+ formed mainly adduct ions with both allene and propyne according to reaction sequence 11, $SiCH_2^+$ reacted only to form bimolecular products, $SiC_3H_3^+ + CH_3$ and $SiC_4H_5^+ + H$ (see Table II for rate constants and product distributions).

$$SiC_2H^+ \xrightarrow{C_3H_4} SiC_5H_5^+ \xrightarrow{C_3H_4} SiC_8H_9^+ \quad (11)$$
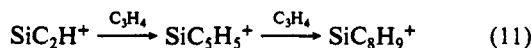
Separate experiments were performed to explore the nature of the $SiC_3H_3^+$ ion produced from allene and propyne. Formation of this ion by C–H bond insertion may lead to different isomeric forms of $SiC_3H_3^+$ which may have different reactivities. As already indicated, no differences were observed in the reactivity toward the respective parent molecules. When ammonia was used as a reactant, two reaction channels were observed, but the measured rate constants and product distributions again showed no significant differences for $SiC_3H_3^+$ produced from allene or propyne. The measured rate constants were equal within experimental error, having values of $(7.2 \pm 1.0) \times 10^{-10}$ and $(6.6 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, where the uncertainties reflect the precision of the measurements. Two product channels which were observed are shown in reaction 12. NH_4^+

$$SiC_3H_3^+ + NH_3 \rightarrow SiNH_2^+ + C_3H_4 \quad (12a)$$

$$\rightarrow SiC_3H_3^+ \cdot NH_3 \quad (12b)$$
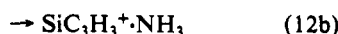
was also observed as a product ion, but the contribution of proton transfer to the loss of $SiC_3H_3^+$ was uncertain due to the presence of impurity ions which proton transfer to ammonia and because of the secondary contribution to NH_4^+ formation from reaction 13 which is known to be rapid.[12] We also report here the interesting secondary reaction 14 of $SiC_3H_3^+ \cdot NH_3$ with ammonia.

$$SiNH_2^+ + NH_3 \rightarrow NH_4^+ + SiNH \quad (13)$$

teresting secondary reaction 14 of $SiC_3H_3^+ \cdot NH_3$ with ammonia. The $SiN_2H_5^+$ product ion can be a doubly N-coordinated silicon species such as $(H_2N)_2SiH^+$ or $H_3NSiNH_2^+$.

$$SiC_3H_3^+ \cdot NH_3 + NH_3 \rightarrow SiN_2H_5^+ + C_3H_4 \quad (14)$$
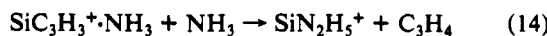
The adduct ions $SiC_2H^+ \cdot C_3H_4$ and $SiC_3H_3^+ \cdot C_3H_4$ were found to be unreactive toward ammonia, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

**Diacetylene.** Hydride abstraction was the only channel observed for the reaction with diacetylene. The reaction is fast and occurs

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Table III. Computed Structural Parameters for the Three Bound Adducts of Si^+ and CH_4 and the First Transition State Shown in Figure 3[a]

| isomer	state (symmetry)	structural parameters
	$^2B_1$ (C_{2v})	Si–C = 2.734, C–H$_1$ = 1.098 C–H$_3$ = 1.0811 $\angle$(SiCH$_1$) = 57.4 $\angle$(SiCH$_3$) = 124.1
	$^2A_1$ (C_s)	Si–C = 2.295, Si–H$_1$ = 1.534 C–H$_1$ = 1.693, C–H$_2$ = 1.077 C–H$_3$ = 1.082 $\angle$(SiCH$_1$) = 41.9 $\angle$(SiCH$_2$) = 124.3 $\angle$(SiCH$_3$) = 92.9 $\angle$(H$_3$CSiH$_1$) = 121.8
	$^2A_1$ (C_s)	Si–C = 1.849, Si–H = 1.471 C–H$_1$ = 1.082, C–H$_2$ = 1.090 $\angle$(HSiC) = 120.0 $\angle$(H$_1$CSi) = 112.9 $\angle$(H$_2$CSi) = 108.3 $\angle$(H$_2$CSiH) = 58.2
	$^2B_1$ (C_{2v})	Si–C = 1.792, Si–H = 1.455 C–H = 1.077 $\angle$(HSiC) = 120.0 $\angle$(HCSi) = 121.9

[a] Bond lengths in Å and angles in deg.

at the collision rate. A fast secondary reaction of C_4H^+ was observed to lead to more carbonaceous ions by addition and condensation with elimination of acetylene, $k = 2.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

$$C_4H^+ + C_4H_2 \xrightarrow{0.8} C_8H_3^+ \quad (15a)$$

$$\xrightarrow{0.2} C_6H^+ + C_2H_2 \quad (15b)$$
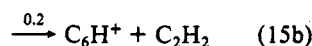
Both of the products of reaction 15 were observed to add a molecule of diacetylene to form $C_{10}H_3^+$ and $C_{12}H_5^+$, respectively. The addition reaction with C_6H^+ was particularly rapid proceeding nearly at the rate of its production from C_4H^+.

A previous ICR measurement[13] yielded a rate constant of 1.6×10^{-9} cm^3 molecule^{-1} s^{-1} for the reaction of C_4H^+ with diacetylene with the following product channel.

$$C_4H^+ + C_4H_2 \rightarrow C_8H_2^+ + H \quad (16)$$
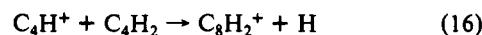
Theoretical Results

Calculations were performed with a GAUSSIAN 82 program to gain insight into the nature of the adduct formed in the association reaction of Si^+ with methane.[14]

The relative stability of three isomers of $SiCH_4^+$ and two transition states for their interconversion were computed at the UMP4(SDTQ)/6-31G**//UHF/6-31G** level. Final energies were corrected for zero-point energies. The results are summarized in Figure 3 and Table III.

Discussion and Conclusions

Methane and Ethane. The low reactivity observed for methane is in sharp contrast to the high reactivity observed for all of the other hydrocarbon reactions of $Si^+(^2P)$ investigated in this study. Cheng et al. have previously pointed out that no exothermic bimolecular channels are available to Si^+ and CH_4 at room tem-

(13) Anicich, V. G.; Blake, G. A.; Kim, J. K.; McEwan, M. J.; Huntress, W. T. *J. Phys. Chem.* **1984**, *88*, 4608.

(14) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release A, Carnegie-Mellon University, Pittsburgh, PA.

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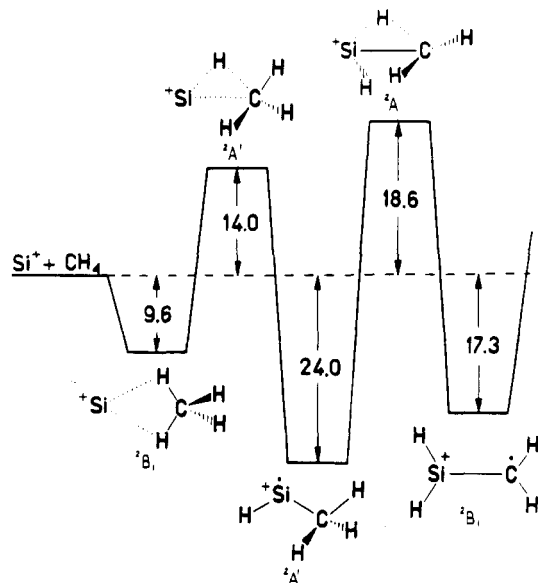*J. Am. Chem. Soc., Vol. 113, No. 12, 1991* 4465

Figure 3. Potential energy profile for the reaction of Si⁺ with methane based on calculations of energies (kcal mol⁻¹) for three isomers of SiCH₄⁺ and two transition states for their interconversion. Computations were performed at the UMP4(SDTQ)6-31-G**//UHF/6-31G** level.

perature so that reactions leading to bimolecular products are not expected to 296 K.[15] Indeed, a previous study by ion cyclotron resonance (ICR) mass spectrometry has shown that silicon ions do not react with methane at low pressures and near-thermal energies.[4] On the other hand, our calculations indicate that the "chemical activation" of methane by C–H bond insertion to form H–Si⁺–CH₃ is exothermic by 24 kcal mol⁻¹ (see Figure 3). This is in accord with the standard enthalpy of formation of 242.6 kcal mol⁻¹ reported recently for this ion[16] which predicts the C–H bond insertion to be exothermic by 35 kcal mol⁻¹. We could therefore expect a substantial rate of association to form a chemically bound adduct ion, were it not for the energy barrier of 14 kcal mol⁻¹ which is indicated by our calculations and which will prevent rapid insertion at room temperature. The experiments indicate that the adduct ion is formed only very slowly and is therefore likely to be only weakly bound. It corresponds almost certainly to the bridged C_{2v} structure (²B₁) shown in Figure 3 which has a dissociation energy of only 9.6 kcal mol⁻¹. The computed barriers of 14.0 and 18.6 kcal mol⁻¹ are too high for isomerization to take place to the more stable HSiCH₃⁺ (²A′) and H₂SiCH₂⁺ (²B₁) cations, respectively. The weakly bound adduct ion has not been observed previously. Our observation of the adduct ion in helium at 0.35 Torr and the failure to observe this ion at the low pressures of the ICR experiments suggest that collisions are required to bring about its stabilization and so to render it observable.

The Si–C bonds formed in the reaction of Si⁺ with ethane may arise either by C–C bond insertion or by C–H bond insertion followed by β-methyl transfer according to the mechanism postulated in Figure 4. The nature of the adduct ion, SiC₂H₆⁺, is not known, but its observation as a product ion is consistent with the mechanism shown in Figure 4 in which the chemically bound intermediates I and II may be collisionally stabilized in competition with their decomposition or rearrangement. The C–C and C–H bond insertion shown in Figure 4 is easily rationalized in terms of interactions of molecular orbitals. The 3p(Si⁺) electron can be donated to the 3a₂ᵤ antibonding (σ*) molecular orbital of C₂H₆ leading to C–C bond breaking with concomitant Si–C bond formation since one of the MO's of the interacting complex has to be bonding and populated with one electron. On the other hand, an appropriate collision orientation can lead to the delocalization
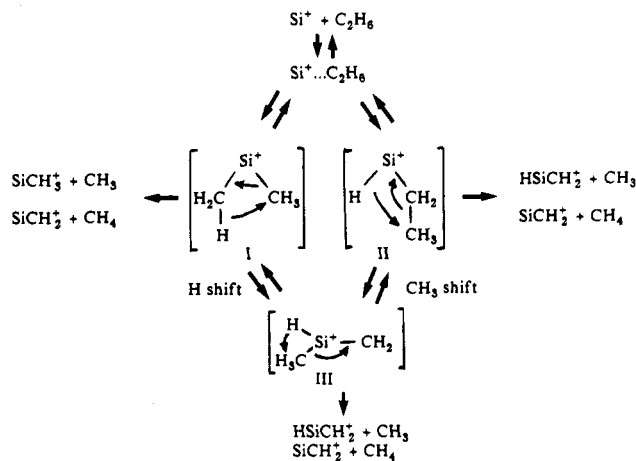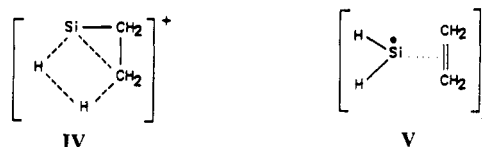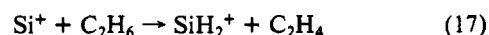
of an 1eₘ electron of C₂H₆ onto the half-filled 3p(Si⁺) orbital and the destabilization of the C–C and one of the C–H bonds. Formation of SiCH₂⁺ from I requires a four-center transition state or a rearrangement to III with a subsequent passage over a three-center transition state, while SiCH₃⁺ results from a simple Si–C bond scission. This could account for the large value of 5.3 observed for the product ratio of [SiCH₃⁺] to [SiCH₂⁺]. Formation of SiCH₃⁺ should be preferred over formation of the isomer HSiCH₂⁺ according to ab initio calculations at the double-ζ level[17a] with configuration interaction[17b] which predict that, for singlet states, HSiCH₂⁺ is 50.3 kcal mol⁻¹ less stable than SiCH₃⁺. In fact, these results imply that formation of HSiCH₂⁺ is 43 kcal mol⁻¹ endothermic while formation of SiCH₃⁺ is 7 kcal mol⁻¹ exothermic. H₂ elimination is likely to occur from the insertion intermediate II which can pass over the four-center transition state IV. Alternately, II may rearrange to V and subsequently eliminate H₂. Intermediate V cannot eliminate ethylene since reaction 17

Figure 4. Possible mechanism for the reaction of Si⁺ with ethane initiated by C–C or C–H bond insertion.

IV · · · · · · V

is endothermic by 12 kcal mol⁻¹. Finally, the dehydrogenation

$$Si^+ + C_2H_6 \rightarrow SiH_2^+ + C_2H_4 \qquad (17)$$

of I has to be considered. If we assume that the SiC₂H₄⁺ product ion is a C_{2v} symmetry species in its ground ²B₂ state as shown in VI (see next section), its direct formation in a concerted H₂ elimination from I is unlikely because it is symmetry forbidden.


VI
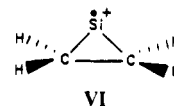
Ethylene and Acetylene. The adduct ions SiC₂H₄⁺ and SiC₂H₂⁺ are important primary products for the reactions of ethylene and acetylene with Si⁺ at the temperature and helium pressure of the SIFT experiments reported here. The dominant short-range interaction when Si⁺ approaches these two molecules can be expected to involve overlap of the half-filled 3p(Si⁺) orbital with antibonding π* or bonding π orbitals. Such overlap could result in the formation of symmetric cyclic species of type VI for SiC₂H₄⁺ and type VII for SiC₂H₂⁺. Our preliminary calculations performed at the UMP2/6-31G**//UHF/6-31G** level suggest that both of these structures are quite stable with $D_e(Si^+–C_2H_4) = 43.1$ kcal

(15) Chen, T. M. H.; Yu, T. Y.; Lampe, F. W. *J. Phys. Chem.* **1973**, *77*, 2587.

(16) Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 24.

(17) (a) Hopkinson, A. C.; Lien, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 107. (b) A. C. Hopkinson, private communication. (c) Sirois, S.; Wlodek, S.; Hopkinson, A. C.; Bohme, D. K. Unpublished results from this laboratory.

VII

XII   XIII
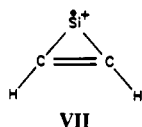
mol^{-1} and $D_e(Si^+–C_2H_2) = 43.7$ kcal mol^{-1} ($^2A_1$ ground state for VII), respectively.[17c] The ground state of SiC$_2$H$_4^+$ represented by structure VI is a $^2B_2$ state which implies that the bonding between Si$^+$ and C$_2$H$_4$ involves 3p(Si$^+$) → π^*(C$_2$H$_4$) electron backdonation with the main interaction being π(C$_2$H$_4$) → p(Si$^+$) electron donation. This vibrationally excited state could probably rearrange to the open structure VIII or IX which have energies of only 5.6 and 4.7 kcal mol^{-1}, respectively, above the $^2B_2$ structure VI. VIII in turn can dissociate to H and SiC$_2$H$_3^+$. The latter

VIII   IX
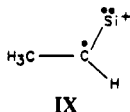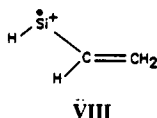
ion is likely to be the protonated linear SiCCH$_2$ molecule, although the formation of the cyclic structure X cannot be excluded without knowledge of the full potential energy surface of the Si$^+$–C$_2$H$_4$ system. It should be noted that the rearrangement of VI to VIII could occur driven by entropy unless it is energetically forbidden.

X
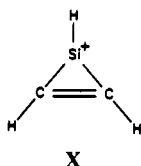
The structure of the quenched SiC$_2$H$_4^+$ which is observed in our experiments does not necessarily correspond to VI. It could also have structures VIII or IX, or even structure XI. XI cannot

XI
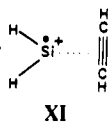
dissociate at room temperature since the overall reaction (18) is endothermic by about 21 kcal mol^{-1}. However, the occurrence of the secondary reaction (6) is more consistent with the formation

$$Si^+ + C_2H_4 \rightarrow SiH_2^+ + C_2H_2 \qquad (18)$$
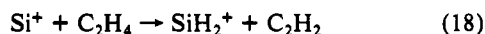
of structure VIII as a transient intermediate since it can readily lose a Si-bonded hydrogen atom to an incoming ethylene molecule.

The ground state of the cyclic SiC$_2$H$_2^+$ cation is $^2A_1$ in which the bonding between Si$^+$ and C$_2$H$_2$ results from π(C$_2$H$_2$) → 3p(Si$^+$) donation. Our preliminary calculations indicate this state is only 0.5 and 8.5 kcal mol^{-1} more stable than the isomers SiCCH$_2^+$ ($^2B_2$) and HSiC$_2$H$^+$ ($^2A_1$), respectively.[17] The rearrangement from structure VII to SiCCH$_2^+$ is therefore energetically allowed. Again, however, the question whether the SiC$_2$H$_2^+$ can explore more than one minimum before it dissociates cannot be answered until information about the full potential energy surface becomes available. An H atom can be eliminated directly from structure VII. The closed-shell product ion, SiC$_2$H$^+$, is a protonated silicon carbide SiC$_2$. The ground state of SiC$_2$ has been shown to be a cyclic T-shaped molecule[2] but the structure of the protonated form is not known (see Note Added in Proof).

Allene and Propyne. Our experiments have shown that Si$^+$ eliminates an H atom from allene and propyne to form molecular ions, SiC$_3$H$_3^+$, which present the same reactivity toward ammonia. Therefore it is reasonable to assume that the same isomer of SiC$_3$H$_3^+$ is formed in these two reactions. It is likely that Si$^+$ initially interacts with the π electrons of C$_3$H$_4$ leading to cyclic transient complexes of type XII and XIII and that their interconversion (or conversion to a common transient) is responsible for the nearly identical product distribution which was observed. Structure XIII can easily lose an H atom or CH$_3$ radical giving
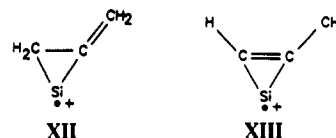
rise to SiCCCH$_3^+$ and SiCCH$^+$ respectively, while C-C and Si-C bond rupture is required for structure XII to form SiCH$_2^+$.

While the structure of SiC$_3$H$_3^+$ is unknown, some insight is provided by the observed reactivity pattern with NH$_3$. The efficient SiNH$_2^+$ and adduct formation is consistent with a silylene, R–Si:$^+$, character for this ion since silylene can insert in N–H bonds. The R$^\bullet$ group is likely to be CH$_3$–C≡C$^\bullet$ since SiCCCH$_3^+$ can be formed directly from structure XIII.

Comparison with C$^+$(^{2}P) Reactions. Due to its much larger enthalpy of formation ($\Delta H°_{f,298}(C^+) = 431.0$ kcal mol^{-1}, $\Delta H°_{f,298}(Si^+) = 295$ kcal mol^{-1}),[18] C$^+$ is much more reactive toward most of the neutral reactants employed in this study. The difference in reactivity is most dramatic with methane for which no exothermic bimolecular channels exist with Si$^+$. Our calculations show that C-H bond insertion is prevented by an energy barrier when the semifilled 3p atomic orbital of Si$^+$ interacts with σ electrons of CH$_4$. No barrier appears to be present in the stronger 2p(C$^+$)–σ(CH) interaction leading to (HCCH$_3^+$)* and subsequently to (H$_2$CCH$_2^+$)* and decay by H and H$_2$ elimination as shown in reaction 19 which has a rate constant (k) of 1.3 × 10^{-9} cm^3 molecule^{-1} s^{-1}.[19] Charge transfer was not observed with

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H \qquad (19a)$$

$$\rightarrow C_2H_2^+ + H_2 \qquad (19b)$$
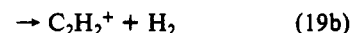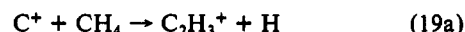
Si$^+$ but has been reported for C$^+$ reacting with all of the unsaturated molecules studied here, C$_2$H$_4$, CH$_2$CCH$_2$, CH$_3$C$_2$H, and C$_4$H$_2$, except C$_2$H$_2$.[7,8,20] This is consistent with the exothermicity for these reactions. Adduct ions of the type observed in the reactions of Si$^+$ with C$_2$H$_2$ and C$_2$H$_4$ have not been reported for the corresponding reactions of C$^+$ occurring under similar SIFT conditions.[7,8] However, H atom elimination is an important competitive channel in the reactions of these two molecules, being more predominant for the reactions of C$^+$. These differences in adduct formation and H atom elimination can be accounted for if the intermediates (C$_3$H$_2^+$)* and (C$_3$H$_4^+$)* have a shorter lifetime. We may also note that the product channels in the reaction of C$^+$ with C$_2$H$_4$ leading to the formation of C$_3$H$_2^+$ and C$_2$H$_3^+$ do not have their analogues in the reaction of Si$^+$ with C$_2$H$_4$. In the latter reaction the formation of SiC$_2$H$_2^+$, SiCH$_3^+$, or C$_2$H$_3^+$ is endothermic.

Allene, propyne, and diacetylene all react rapidly with C$^+$ and Si$^+$, but there are large differences in the observed product distributions. The reactions of C$^+$ with allene and propyne favor elimination of H$_2$ and hydride transfer[7] while the reactions with Si$^+$ favor H atom and CH$_3$ elimination. Only elimination of C$_2$H$_2$ is common to both sets of reactions. The reaction of diacetylene with C$^+$ favors H atom elimination and charge transfer[20] while with Si$^+$ hydride transfer is the only channel.

Except for the reactions with allene and propyne, the reactions of Si$^+$ are uniformly slower and less efficient than the reactions with C$^+$, all of which proceed with rate constants of 1.3 × 10^{-9} cm^3 molecule^{-1} s^{-1} or higher.[7,8,19]

Thermochemistry. The observation and failure to observe reactions at thermal energies at 296 ± 2 K can provide useful limits to the standard enthalpies of formation of the silicon-containing hydrocarbon ions, most of which are still not well established. The enthalpies of formation derived from this study are summarized in Table V. The temperature is assumed to be 298 K. The required standard enthalpies of formation are taken from Table IV.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement No. 1.
(19) Curtis, R. A.; Farrar, J. M. *J. Chem. Phys.* **1985**, *83*, 2224.
(20) Dheandhanoo, S.; Forte, L.; Fox, A.; Bohme, D. K. *Can. J. Chem.* **1966**, *64*, 641.

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Table IV. Standard Enthalpies of Formation (kcal mol⁻¹) Used in the Text[a]

ion/molecule	$\Delta H°_{f,298}$	ref	ion/molecule	$\Delta H°_{f,298}$	ref
Si	108 (2)	b	H	52.10	b
Si⁺	295 (1)	b	H⁺	365.7	b
SiH	90.0 (2.0)	b	C⁺	431.0	b
SiH⁺	272.3 (1.2)	c	CH₃	34.8 (0.3)	b
SiH₂⁺	274.1	d	CH₄	−17.8 (0.1)	b
SiCH₂⁺	283.5 (3)	e	C₂H₂	54.5 (0.25)	b
SiCH₃⁺	233.5 (5)	e	C₂H₄	12.5 (0.2)	b
HSiCH₃⁺	242.6	d	C₂H₅	28	b
H₂SiCH₂⁺	247 (4)	d	C₂H₆	−20.1 (0.05)	b
SiNH₂⁺	212.7	f	CH₂CCH₂	45.6 (0.2)	b
HSiNH⁺	266.3	f	CH₃CCH	44.6 (0.5)	b
NH₃	−11.0	b	C₄H₂	105	h
CN	104.0 (2)	b			
HC₃N	87	g			

[a] The stationary electron convention has been adopted for the enthalpies of formation of ions so that these are 1.48 kcal mol⁻¹ lower than values that include the enthalpy of the electron. Uncertainties are in parentheses when they are available. [b] Reference 18. [c] Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549. [d] Reference 16. [e] Reference 5. [f] Reference 12. [g] Reference 23. [h] Reference 22.

Table V. Standard Enthalpies of Formation (kcal mol⁻¹) for Silicon-Containing Hydrocarbon Ions Deduced in This Study[a]

ion	$\Delta H°_{f,298}$ this work	other values	ref
SiCH₂⁺	280 (14)	283.5 (3)	5
SiCH₃⁺	230 (6)	233.5 (5)	5
SiC₂H⁺	<288 (3), >255 (2)	<278	21
SiC₂H₂⁺	<350 (2)		
SiC₂H₃⁺	<255 (3), >233 (1)		
SiC₂H₄⁺	<275 (1)		
SiC₂H₆⁺	<275 (1)		
SiC₃H₃⁺	280 (17)		
SiC₄H⁺	<343 (3), >348		
SiC₄H₅⁺	<276 (4)		

[a] The stationary electron convention has been adopted for the enthalpies of formation of ions so that these are 1.48 kcal mol⁻¹ lower than values that include the enthalpy of the electron. Uncertainties are in parentheses when they are available.

SiCH₂⁺, SiCH₃⁺. The observation of the product of these two ions in the reaction of Si⁺ with ethane and their failure to be produced from the reaction of Si⁺ with methane sets $\Delta H°_f$(SiCH₂⁺) = 280 ± 14 kcal mol⁻¹ and $\Delta H°_f$(SiCH₃⁺) = 230 ± 6 kcal mol⁻¹ which are consistent with the values of 283.5 ± 3 and 233.5 ± 5 kcal mol⁻¹, respectively, determined recently in an ion beam study of the reaction of Si⁺ with methane by Boo and co-workers.[5]

SiC₂H⁺. This ion has been observed as a product in the reactions of Si⁺ with C₂H₂, CH₂CCH₂, and CH₃CCH. The latter reaction provides the lowest upper limit of 288 ± 3 kcal mol⁻¹ to $\Delta H°_f$(SiC₂H⁺). An even lower upper limit of 278 kcal mol⁻¹ is provided by the observation of SiC₂H⁺ as a product of the reaction of Si⁺ with cyanoacetylene which we have reported previously.[21] A lower limit of 255 ± 2 kcal mol⁻¹ can be deduced from the failure of the reaction of Si⁺ with C₂H₄ to produce SiC₂H⁺ if this failure is due to endothermicity.

SiC₂H₃⁺. The observation of this ion as a major product in the reaction of Si⁺ with ethylene places an upper limit of 255 ± 2 kcal mol⁻¹ to $\Delta H°_f$(SiC₂H₃⁺). A lower limit of 233 ± 1 kcal mol⁻¹ is appropriate if we accept that the non-observation of SiC₂H₃⁺ in the reaction of Si⁺ with ethane is due to endothermicity.

SiC₂H₂⁺, SiC₂H₄⁺, SiC₂H₆⁺. The observation of the formation of these adduct ions sets upper limits of 350 ± 2, 308 ± 2, and 275 ± 1 kcal mol⁻¹ respectively to their standard enthalpies of formation. The observation of SiC₂H₄⁺ in the reaction of Si⁺ with ethane, if it has the same structure as the adduct ion, reduces the upper limit of $\Delta H°_f$(SiC₂H₄⁺) to 275 ± 1 kcal mol⁻¹.

(21) Wlodek, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 61.

SiC₃H₃⁺, SiC₄H₅⁺. The product of these two ions from the reaction of Si⁺ with CH₃CCH sets the upper limits $\Delta H°_f$(SiC₃H₃⁺) < 293 ± 4 kcal mol⁻¹ and $\Delta H°_f$(SiC₄H₅⁺) < 276 ± 4 kcal mol⁻¹. A lower limit for $\Delta H°_f$(SiC₃H₃⁺) = 267 kcal mol⁻¹ may be derived from the production of SiNH₂⁺ and propyne from the reaction of SiC₃H₃⁺ with NH₃. Production of the higher energy isomer HSiNH⁺ is probably endothermic since it would lead to a lower limit for $\Delta H°_f$(SiC₃H₃⁺) which is 28 kcal mol⁻¹ higher than the upper limit deduced from the reaction of Si⁺ with propyne. These observation lead to a recommended value for $\Delta H°_f$(SiC₃H₃⁺) 280 ± 17 kcal mol⁻¹.

SiC₄H⁺. It is interesting to note that SiC₄H⁺ is not produced from C₄H₂ while SiC₂H⁺ is readily formed from C₂H₂. The former observation implies a lower limit of 348 kcal mol⁻¹ to $\Delta H°_f$(SiC₄H⁺) assuming no barrier to reaction. Here we have adopted a value of 105 kcal mol⁻¹ for $\Delta H°_f$(C₄H₂) which has been estimated from "group additivity".[22] With the unknown uncertainty of this limit, this result is barely consistent with the upper limit of 343 ± 3 kcal mol⁻¹ which can be deduced from the observation of SiC₄H⁺ as a product of the reaction of SiC₂H⁺ with C₂H₂ when 288 ± 3 kcal mol⁻¹ is adopted as the upper limit to the standard enthalpy of formation of SiC₂H⁺ derived from the propyne reaction. The value of $\Delta H°_f$(SiC₂H⁺) = 278 kcal mol⁻¹ derived from the cyanoacetylene reaction leads to an upper limit of 333 kcal mol⁻¹ which is somewhat out of line with the lower limit of 348 kcal mol⁻¹, presumably because of errors in the standard enthalpies of formation of both cyanoacetylene, which is a calculated value and has an unknown uncertainty,[23] and diacetylene determined from group additivity.[22]

Circumstellar Chemistry and Molecule Formation. There is a need to understand the contribution of ion chemistry to the formation of the silicon–carbide molecules which have been identified in partially ionized carbon-rich circumstellar envelopes. The laboratory identification of new ion–molecule reactions which trigger the formation of chemical bonds between silicon and carbon and chemical pathways which lead to further ionic and molecular growth is therefore valuable, not only in accounting for the known silicon–carbide molecules but also for the prediction of new circumstellar silicon-bearing molecules and for the assessment of the early stages of the gas-phase transition from atomic silicon to silicon carbide particles in such envelopes. Neutral molecules can be generated by ion chemistry in these environments either directly as products of ion–molecule reactions or through neutralization reactions such as proton transfer, charge transfer, or recombination with electrons.[24] For example, neutralization of SiC₄H⁺ may produce the SiC₄ molecule by proton transfer or recombination with electrons as shown in reaction 20. A wide

$$SiC_4H^+ + M, e \rightarrow SiC_4 + MH^+, H \qquad (20)$$
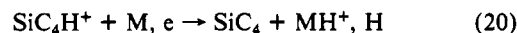
variety of silicon–hydrocarbon ions is generated by the ion chemistry identified in this study, viz. SiCH₂⁺, SiCH₃⁺, SiC₂H⁺, SiC₂H₂⁺, SiC₂H₃⁺, SiC₂H₄⁺, SiC₃H₃⁺, SiC₄H⁺, SiC₄H₃⁺, SiC₄H₄⁺, and SiC₅H₅⁺. The neutralization of these ions provides possible sources for the neutral molecules SiCH, SiCH₂, SiC₂, SiC₂H, SiC₂H₂, SiC₂H₃, SiC₃H₂, SiC₄, SiC₄H₂, SiC₄H₃, and SiC₅H₄, respectively. Many of these ions and molecules are novel and little is known about their structures and energetics. They need to be investigated theoretically and with other experimental techniques. Also, in quantitative treatments of this chemistry, as in the modelling of complex kinetic environments, it must be recognized that both temperature and pressure may influence reaction rates and product distributions. For example, as the pressure drops collisional stabilization will compete less effectively and adduct formation must proceed by radiative stabilization. We may also note that adduct ions of the type observed in the case of methane, viz. Si⁺·CH₄, in which there is a barrier to the formation of a covalent Si–C bond, neutralization by electron/ion

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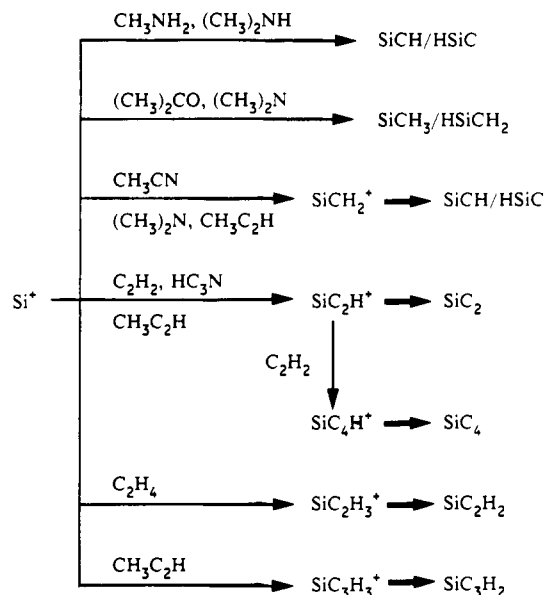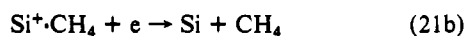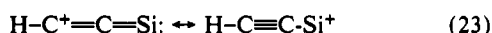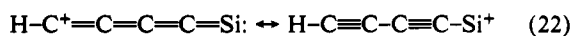
Figure 5. Limited reaction scheme for the synthesis of silicon–carbide molecules initiated by atomic silicon ions. The heavy arrows indicate neutralization reactions such as recombination with electrons and proton transfer.

recombination is likely to re˜stablish the methane molecule together with a silicon atom as in reaction 21. A catalytic role in the recombination of atomic silicon ions with electrons can therefore be postulated for methane at low pressures and electron densities when the adduct ion forms by radiative association. The complete sequence is given by the following reactions

$$Si^+ + CH_4 \rightarrow Si^+ \cdot CH_4 \tag{21a}$$

$$\underline{Si^+ \cdot CH_4 + e \rightarrow Si + CH_4} \tag{21b}$$

$$Si^+ + e \rightarrow Si \tag{21c}$$

In the absence of methane the recombination of atomic silicon ions with electrons would need to occur radiatively and likely would have a specific rate much smaller than that for radiative association in the presence of methane.

We have previously drawn attention to the possible role of silicon ion/molecule reactions as sources of silicon–carbide molecules in interstellar and circumstellar environments.[25,26] A qualitative summary of some of the chemistry is given in Figure 5. The scheme for the production of SiC$_4$ which we first proposed in 1988[25] is of particular interest as the SiC$_4$ molecule has just recently been identified in the envelope of the evolved carbon star IRC+10216.[3] Laboratory microwave spectroscopy of a discharge of silane and acetylene together with quantum chemical calculations have established that this circumstellar molecule is in its linear $^2\sigma^+$ ground electronic state. We note here that the ionic mechanism which we have proposed may be more favorable at low pressures at which the collisional association channels 7b and 8a are no longer competitive and all of reactions 7 and 8 may lead to bimolecular products. The mechanism of formation of the linear SiC$_4$H$^+$ ion (22), a possible source of the linear SiC$_4$ molecule, from the acetylene reaction of SiC$_2$H$^+$, probably also linear as shown in (23) (see Note Added in Proof), is intriguing. To produce

$$H-C^+{=}C{=}C{=}C{=}Si: \leftrightarrow H-C{\equiv}C-C{\equiv}C-Si^+ \tag{22}$$

$$H-C^+{=}C{=}Si: \leftrightarrow H-C{\equiv}C-Si^+ \tag{23}$$

structure (22) in which the silicon atom is at one end, acetylene will need to interact with HC$^+$=C=Si: at C$^+$ to form H–C$^+$=CH–CH=C=Si: and eliminate H$_2$, or, alternatively, interact with H–C≡C–Si$^+$ at Si$^+$ to form H–C$^+$=CH–Si–C≡C–H followed by internal electrophilic attack of C$^+$ with the triple bond to form a five-membered ring and ring opening by breaking the C–Si bond to form H–C$^+$=CH–CH=C=Si:.

We also note again the possible formation of a doubly N-coordinated silicon ion, (H$_2$N)$_2$SiH$^+$ or H$_3$NSiNH$_2^+$, in reaction 14. Neutralization of this ion by proton transfer or recombination with electrons is likely to lead to the diaminosilene molecule (NH$_2$)$_2$Si:. We note also that the SiN$_2$H$_5^+$ ion is not directly accessible in pure ammonia. Sequential reactions of Si$^+$ with ammonia terminate exclusively and directly in the formation of the neutral molecule :SiNH as indicated in the following steps.[12] In the presence of allene or propyne the SiN$_2$H$_5^+$ ion is also

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \tag{24}$$

$$\underline{SiNH_2^+ + NH_3 \rightarrow NH_4^+ + SiNH} \tag{13}$$

$$Si^+ + 2NH_3 \rightarrow NH_4^+ + H + SiNH \tag{25}$$

established as summarized below. In fact,

$$Si^+ + C_3H_4 \rightarrow SiC_3H_3^+ \tag{10a}$$

$$SiC_3H_3^+ + NH_3 \rightarrow SiC_3H_3^+ \cdot NH_3 \tag{12b}$$

$$\underline{SiC_3H_3^+ \cdot NH_3 + NH_3 \rightarrow SiN_2H_5^+ + C_3H_4} \tag{14}$$

$$Si^+ + 2 NH_3 \rightarrow SiN_2H_5^+ + H \tag{26}$$

the C$_3$H$_4$ molecule acts as a catalyst. A similar role for C$_3$H$_4$ is seen in the reaction sequence of eqs 10a and 12a which leads to the formation of SiNH$_2^+$, the precursor of hydrogen silaisonitrile, :SiNH.

Of course the interest in synthetic aspects of ion/molecule reactions initiated by Si$^+$ and silicon-containing derivative ions with hydrocarbon molecules is not restricted to extraterrestrial environments. For example, silane glow discharges with and without added compounds recently have attracted considerable attention as a means of producing hydrogenated amorphous silicon (a-Si:H) films in the semiconductor industry.[27] In this connection there is also an interest in the chemistry which may occur at a silicon surface exposed to hydrocarbon gases. Recent FTMS experiments have shown the production of the silicon–hydrocarbon ions SiC$_2$H$_x^+$ with $x = 1, 2$, and 3 when silicon surfaces are exposed to acetylene and ethylene and vaporized with a laser, but the nature of the reactions, whether surface or gas phase, is uncertain.[28] Interestingly, no such ions were observed in the FTMS experiments when methane was deposited, as might be expected from our results if gas-phase ion/molecule reactions predominate.

Note Added in Proof. A recent report on the gas-phase generation and structural characterization of SiC$_2$H and SiC$_2$H$^+$ by neutralization–reionization mass spectrometry provides evidence for the existence of silicon acetylide, HC≡CSi$^\bullet$, and its cation, HC≡CSi$^+$.[29] The experiments provide support for ab initio studies at the MP/6-31G**//6-31G** level which predict that HC≡C—Si$^+$ ($C_{\infty v}$) is 94 kcal mol^{-1} more stable than $^+$C≡C—SiH ($C_{\infty v}$) and that the cyclic C_{2v} structure of (SiC$_2$H)$^+$ apparently does not have a minimum.[30]
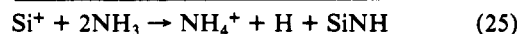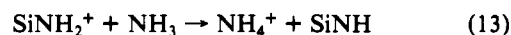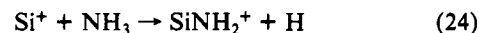
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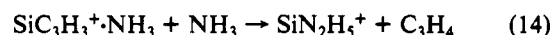
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