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Theoretical Enthalpies of Formation of Compounds $SiCH_n$ (n = 0−4), SiC_2H_n (n = 0−4, 6), $SiCH_n^+$ (n = 0−5), and $SiC_2H_n^+$ (n = 0−5, 7)

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High-level *ab initio* molecular orbital calculations are reported for the global minima on the $SiCH_n$ (n = 0−4), $SiCH_n^+$ (n = 0−5), SiC_2H_n (n = 0−4, 6), and $SiC_2H_n^+$ (n = 0−5, 7) potential energy surfaces. The results have been used to calculate standard enthalpies of formation at 298 K for each compound, ionization energies at 0 K, and proton affinities at 298 K for the neutral species. The single-carbon compounds have been investigated at levels of theory up to PMP4SDTQ(full)/6-311++G(2df,p)//MP2(full)/6-311G(d,p) and QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311G(d,p); those with two carbons have been investigated at levels up to PMP4(fc)/6-311++G(2df,p)//MP2(full)/6-31G(d,p) and QCISD(T)(full)/6-311++G(2df,p)// MP2(full)/6-31G(d,p). Harmonic frequency calculations, performed on each optimized geometry, established all the structures to be at minima and also provided zero-point vibrational energies. Calculated thermodynamic values at the PMP4 and QCI levels of theory are in good agreement with each other (except where the removal of spin contamination by spin annihilation is inadequate) and are in good agreement with well-established experimental values where such comparisons are possible. Calculated ionization energies are consistently lower than the experimental values for the carbon analogues; proton affinities of the organosilicon species are higher than those of the carbon analogues for which experimental data are available.

Introduction

During the past decade, there has been considerable interest in the chemistry of organosilicon compounds.[1] This interest has been stimulated by several factors, including the fact that organosilicon radicals are of importance in the chemical deposition of silicon carbide[2] and that the molecules SiC, SiC_2, and SiC_4 exist in interstellar clouds.[3,4] The latter discoveries have led to speculation about the synthesis of molecules by the reaction of silicon carbides with hydrogen in interstellar clouds.[5] Also, fundamental questions concerning similarities and differences in bonding and reactivities between carbon and silicon in such compounds have been addressed by both experiment and high level *ab initio* theory.[6−10,11]

Mass-spectrometric (MS) techniques have been particularly useful in the elucidation of fundamental properties of small silicon-containing species. The first reports of the existence of organosilicon cations in the gas phase originated from experiments in Lampe's group involving tandem MS and high-pressure MS (HPMS). These measurements provided reaction cross sections and thermochemical data for exothermic and endothermic ion−molecule reactions involving the organosilicon cations $SiCH_3^+$, SiC_2H^+, $SiC_2H_2^+$, $SiC_2H_3^+$, $SiC_2H_4^+$, $SiC_2H_5^+$, and $SiC_2H_7^+$.[12]

Considerable thermodynamic data about organosilicon species have been acquired with guided ion beam mass spectrometry. This technique tracks ion−molecule reactions involving silicon as a function of the kinetic energy of the reactant ion and has been used to obtain standard enthalpies of formation for $SiCH_x^+$ (x = 1−3) and of $SiC_2H_x^+$ (x = 3−5).[13,14]

Fourier transform mass spectrometry (FTMS) has been used to distinguish between isomers of silicon-containing ions of the type $SiH_x(CH_3)_{3-x}^+$ (x = 1, 2) and of the formula $SiC_3H_9^+$ on the basis of reactivity measurements.[59] This technique also has been used to derive thermodynamic properties of small organosilicon compounds; Beauchamp and co-workers have reported standard enthalpies of formation for $SiCH_4$ (silaethylene), $SiCH_5^+$, and $SiC_2H_7^+$, as well as the proton affinity of $SiCH_4$.[15,16] This group has also reported a standard enthalpy of formation for $SiC_2H_7^+$ using photoionization mass spectrometry.[17]

In our own laboratory we have studied the kinetics of organosilicon ion−molecule reactions proceeding in helium buffer gas at 0.35 Torr using the selected-ion flow tube (SIFT) technique at room temperature.[5c,d] These experiments have provided insight into the thermodynamics of formation of $SiCH_x^+$ (x = 2−4) and $SiC_2H_x^+$ (x = 1−4).[5b,18]

Considerable theoretical research has been conducted into the structures of the most stable isomers of given organosilicon formulas. Geometry optimizations have been performed on isomers of $SiCH_x$ and $SiCH_x^+$ (x = 1−4); SiC_2H_x (x = 0−4, 6), and $SiC_2H_x^+$ (x = 0−5, 7), and some of the smaller molecules have been investigated up to very high levels of theory.[19] The geometries and electronic states of SiC, for example, have been obtained at levels up to QCISD(T)/MC-311G(d).[19a,20−22] Multireference CI techniques[23] with basis sets of double-ζ plus polarization quality[24] have been used on various isomers and electronic states of SiC^+,[19q] SiCH,[19b] and $SiCH^+$.[19b] The potential energy surface associated with the formula $SiCH_2$[19c] has been studied at levels up to DZ+CI.[25] In addition, G1- and G2-[26a,c] level investigations have been performed on the lowest energy isomers of $SiCH_2^+$ and of $SiCH_3^+$.[19r] The global minimum of the latter formula, as well as that of $SiCH_4^+$, furthermore, have been subjected to geometry optimizations and harmonic frequency calculations at HF/6-31G(d);[27,28,29b,d] also, single-point calculations using these optimized geometries have been performed at MP4(SDTQ)/6-31G(d).[19s,30] Fourth-order Møller−Plesset perturbation theory,[30b] as well as the CISD+Q technique,[31] and coupled cluster methods with single, double, and linearized triple excitations[32] on structures optimized at the CISD/TZ2P level of theory[24a,b,27,33b] have been used on isomers of $SiCH_4$.[8b] In addition, MP4(SDTQ)/6-31G(d,p)[30a,34]//HF/6-31G(d,p)[30b,d] calculations have been performed on neutral and

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cationic isomers of the formulas SiC_2H_x (x = 0, 1).[19i,n,t,v] Geometry optimizations of isomers of SiC_2H_x (x = 2, 4) in connection with reactions of neutral Si with acetylene and with ethylene, respectively, have been performed at levels up to spin-projected[35] UMP2/TZ+2P.[19j,l,m,24a,b,36]

An extensive study of the critical points of the potential energy hypersurface associated with the formula $SiC_2H_x^+$ (x = 2)[37] has been made at levels of theory up to MP2(full)[38]/6-311G(d,p);[29e,33a,b] for $SiC_2H_x^+$ ((x = 4),[37] x = (1, 3, 5),[39] and x = 7[40]), thorough studies of the respective surfaces have been made at levels up to MP2(full)/6-311G(d,p)//MP2(full)/6-31G(d,p). On the lowest energy isomer of each of the aforementioned $SiC_2H_x^+$ formulas (x = (1−3)), single-point calculations were performed at QCISD(T)(full)[20]/6-311++G(2df,p)[29e,33c]//MP2(full)/6-311G(d,p) and at MP4(SDTQ)[30](fc)/6-311++G(2df,p)[29e,33c]//MP2(full)/6-311G(d,p); for x = (4, 5), single-point calculations were performed only at the latter level of theory.

In spite of this extensive theoretical and experimental research into gas-phase organosilicon chemistry, however, there is not yet a large thermodynamic data base associated with neutral and ionic organosilicon compounds. Such information is of great utility in assessing the feasibility of formation or existence of these species in the gas phase. It has been shown previously that *ab initio* calculations, if performed at a sufficiently sophisticated level of theory, can be used to calculate accurate enthalpies of formation for small molecules.[26,41,42] All such methods combine calculated electronic energies with experimental enthalpies of formation either for the constituent atoms or, if isodesmic[43] and homodesmic[44] reactions are used, for some set of reference molecules for which enthalpies of formation are firmly established. Most of these methods provide $\Delta H^\circ_{f,298}$ values within ±3 kcal mol^{-1} of the experimental values, and some, using even higher levels of theory, are considerably more accurate.[45,46] Enthalpies of formation of strained cyclic isomers of organosilicon compounds such as $SiC_2H_3^+$ and $SiC_2H_5^+$ [47] have been calculated from isodesmic reactions, and the enthalpy of formation of dimethylsilylene (SiC_2H_6) has been estimated.[48d] Pople's G1 method has been applied to silaethylene ($H_2Si{=}CH_2$) and to methylsilylene (H_3CSiH),[8a] and in the most extensive treatment of organosilicon neutral compounds, Allendorf and Melius have applied empirical bond-additivity corrections[49] to MP4(SDTQ)/6-31G(d,p)-level calculations to obtain enthalpies of formation for molecules of the formulas $SiCH_n$ and SiC_2H_n (n = 1−6).[50]

Computational Methods

Ab initio MO calculations were performed using the GAUSSIAN suite of programs,[51] with gradient techniques.[52] Geometry optimizations were performed using the standard 6-31G(d,p)[29] basis set, as well as the 6-311G(d,p) basis set[29e,30b,33a] for first-row elements, and the MC-311G(d,p)[29e,33b] basis set for silicon, with inclusion of electron correlation to second-order Møller−Plesset (MP2) perturbational theory.[38] Harmonic vibrational frequencies were calculated for the optimized structures at MP2(full)/6-311G(d,p) for $SiCH_n$ and $SiCH_n^+$ species and at MP2(full)/6-31G(d,p) for SiC_2H_n and $SiC_2H_n^+$ compounds. Zero-point vibrational energies (ZPE) for each compound were obtained from these calculations and were multiplied by the appropriate scale factor.[53,54] Single-point calculations, on the previously optimized geometries, at MP4SDTQ/6-311++G-(2df,p)[29,30,33] with the "frozen core" approximation, as well as at the QCISD(T)[20] level, with the inclusion of all electrons, then were performed. These highest level computations were used to calculate standard enthalpies of formation at 298 K ($\Delta H^\circ_{f,298}$) by a variation of the heat of atomization method using isogyric equations.[55] In addition, similar techniques, using the same total electronic energies, have been used to calculate proton affinities at 298 K ($PA^\circ_{a,298}$) and to calculate ionization energies at 0 K ($IE^\circ_{a,0}$). The procedures for the calculations of $\Delta H^\circ_{f,298}$ and of $PA^\circ_{a,298}$ have been described in more detail elsewhere,[42,56] of which a brief review is presented later in this paper. A more detailed discussion of our method of calculating $IE^\circ_{a,0}$ values also is presented in the Results and Discussion section of this paper.

Results and Discussion

In the following sections, we present thermodynamic property values for organosilicon neutral and cationic species. Such values have not been previously investigated for many of the compounds in question, either experimentally or computationally. Our discussion begins with a brief section about the more unusual structural parameters associated with some of the organosilicon species.

Structural Parameters. The molecular structure at the global minimum for each organosilicon compound was optimized at post-SCF levels of theory. The optimized geometric parameters which involve heavy atoms are included in Table 1. Many of these molecules have been studied previously, computationally or experimentally, and our results, in most cases, are in good agreement with the results of previous computational studies at comparable levels.[19,50]

The geometries of several compounds deserve special comment. In the case of $SiC(^3\Pi)$, there appears to be a significant discrepancy between our computed Si−C bond separation (1.701 Å) and those of high-level computations reported elsewhere.[19a] It should be noted that there is severe spin contamination associated with this molecule at UMP2(full)/6-311G(d,p) ($\langle S^2 \rangle$ = 2.50), a situation which is not improved significantly upon application of spin annihilation. Subsequent single-point calculations on the UMP2(full)/6-311G(d,p) optimized geometry of SiC at UMP4(full)/6-311++G(2df,p) have yielded thermodynamic properties which differ from those obtained at the more sophisticated QCISD(T) level of theory by about 6 kcal mol^{-1}, even with spin projection included. Thus, the MP4 calculations on SiC have not been used in our subsequent calculations of standard enthalpies of formation and of ionization energies. Similar difficulties associated with spin contamination of $SiC^+(^4\Sigma)$ and of $SiC_2^+(^2\Sigma)$ have led us to omit the thermodynamic property values for these compounds as well.

The computed geometry of SiC_2^+ poses unique problems in interpretation. Previous calculations on this ion, at relatively modest levels of theory, have suggested the existence of two isomers, one cyclic and one linear, which lie close in energy.[19n,o] However, these conclusions were reached on the basis of SCF-level optimizations; all of our attempts at locating a cyclic isomer at a local minimum at post-SCF levels of theory have been unsuccessful. In particular, we have investigated the possible existence of each of these two isomers by performing geometry optimizations and subsequent numerical frequency calculations at the QCISD(T)(full)/6-311++G(d,p) level of theory. The results of this investigation have shown the linear isomer to be at a local minimum and the cyclic structure (C_{2v} symmetry) to be a transition state, 0.4 kcal mol^{-1} higher in energy (ZPE not included). However, the zero-point vibrational energy associated with the linear structure is 0.8 kcal mol^{-1} larger than that of the transition structure (at QCISD(T)(full)/6-311++G(d,p); unscaled). This means that the cyclic transition structure is 0.4 kcal mol^{-1} lower in energy than the linear isomer on inclusion of zero-point vibrational energy. Analysis of the motions associated with the imaginary frequency of the transition structure shows an in-plane ring deformation consistent with

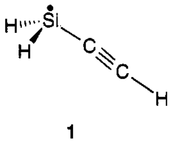
TABLE 1: Total Energies (hartrees) for Global Minima Using MP2/6-311G(d,p) Optimized Structures

structure/symmetry/state	MP2/ 6-311G(d,p)	ZPE[b,c]	PMP4SDTQ/ 6-311 ++ G(2df,p)	QCISD(T)/ 6-311 ++ G(2df,p)	structural parameters involving heavy atoms[d]		
					Si−C	C−C	∠SiCC
$Si{=}C(C_{\infty v})(^{3}\Pi)$	−326.908 38	1.2	−327.002 48[a]	−327.014 19	1.701		
$Si{=}C{-}H(C_{\infty v})(^{2}\Pi)$	−327.586 15	7.4	−327.683 55	−327.685 34	1.621		
$Si{=}CH_2(C_{2v})(^{1}A_1)$	−328.254 02	13.0	−328.346 02	−328.347 36	1.714		
$Si{-}CH_3(C_s)(^{2}A'')$	−328.847 78	20.5	−328.942 33	−328.943 45	1.899		
$H_2Si{=}CH_2(C_{2v})(^{1}A_1)$	−329.469 29	24.0	−329.567 20	−329.568 84	1.709		
$Si{=}C]^{+}(C_{\infty v})(^{4}\Sigma)$	−326.610 56	1.2	−326.683 40[a]	−326.691 25	1.803		
$Si{=}C{-}H]^{+}(C_{\infty v})(^{3}\Sigma)$	−327.284 67	6.5	−327.364 73	−327.366 90	1.780		
$Si{=}CH_2]^{+}(C_{2v})(^{2}B_1)$	−327.942 42	13.5	−328.025 20	−328.027 21	1.809		
$Si{-}CH_3]^{+}(C_{3v})(^{1}A_1)$	−328.600 07	20.2	−328.684 90	−328.686 96	1.818		
$HSi{-}CH_3]^{+}(C_s)(^{2}A')$	−329.172 20	25.2	−329.257 99	−329.259 83	1.833		
$H_2Si{-}CH_3]^{+}(C_1)(^{1}A)$	−329.814 90	30.9	−329.906 63	−329.908 27	1.814		
$c\text{-}SiC_2(C_{2v})(^{1}A_1)$	−365.002 77	3.7	−364.942 20(fc)	−365.115 98	1.836	1.284	
$SiC{\equiv}C{-}H(C_{\infty v})(^{2}\Pi)$	−365.620 21	12.5	−365.570 06(fc)	−365.748 32	1.843	1.198	
$c\text{-}Si(CH)_2(C_{2v})(^{1}A_1)$	−366.276 40	17.7	−366.220 67(fc)	−366.399 52	1.809	1.336	
$H_2Si{-}C{\equiv}C{-}H(C_s)(^{2}A')$	−366.842 04	22.3	−366.793 96(fc)		1.838	1.196	
$H_3Si{-}C{\equiv}C{-}H(C_{3v})(^{1}A_1)$	−367.490 84	25.9	−367.443 76(fc)		1.828	1.225	
$H_3Si(H)C{=}CH_2(C_s)(^{1}A')$	−368.710 61	40.4	−368.671 27(fc)		1.864	1.345	122.3
$Si{-}C{\equiv}C]^{+}(C_{\infty v})(^{2}\Sigma)$	−364.628 81	4.3	−364.578 14(fc)[a]	−364.760 68	1.777	1.202	
$Si{-}C{\equiv}C{-}H]^{+}(C_{\infty v})(^{1}\Sigma)$	−365.375 66	10.7	−365.308 87(fc)	−365.485 90	1.763	1.240	
$c\text{-}Si(CH)_2]^{+}(C_{2v})(^{2}B_2)$	−365.955 56	17.0	−365.894 74(fc)	−366.073 27	1.992	1.269	71.4
$Si(H)C{=}CH_2]^{+}(C_s)(^{1}A')$	−366.601 88	24.3	−366.544 14(fc)		1.794	1.357	87.6
$c\text{-}Si(CH_2)_2]^{+}(C_{2v})(^{2}B_2)$	−367.180 81	31.7	−367.127 73(fc)		2.106	1.403	70.5
$H_2Si(H)C{=}CH_2]^{+}(C_s)(^{1}A')$	−367.814 85	35.3	−367.764 28(fc)		1.786	1.361	118.1
$(H_3C)_2SiH]^{+}(C_{2v})(^{1}A_1)$	−369.061 52	48.6	−369.017 19(fc)		1.819		125.5[e]

[a] Large spin contamination is inadequately treated at PMP4. [b] ZPE for $SiCH_n$ ($n = 0-4$) and for $SiCH_n^+$ ($n = 0-5$) were obtained at MP2(full)/6-311G(d,p) and were scaled by 0.94.[53] [c] ZPE for SiC_2H_n ($n = 0-4, 6$) and for $SiC_2H_n^+$ ($n = 0-5, 7$) were obtained at MP2(full)/6-31G(d,p) and were scaled by 0.93.[54] [d] Bond lengths are in angstroms; bond angles are in degrees. [e] C−Si−C bond angle.

ring opening. However, the potential energy hypersurface associated with SiC_2^+ at this level of theory is almost invariant to changes in the Si−C−C bond angle; thus, the structure of SiC_2^+ can be best described as an Si^+ ion "solvated" by C_2, in which the relative positions of the two fragments make little energetic difference.

The geometry of the most stable isomer of SiC_2H_3 is firmly established; however, its characteristics are anomalous when compared to the global minimum structure of most other organosilicon compounds. Previous studies have shown that, wherever possible, the more stable isomers tend to be those in which the hydrogen atoms are bonded to carbon, rather than to silicon.[37,39,40] The results of preliminary UHF-level computational studies on SiC_2H_3 provide no contradiction to this statement, as the most stable isomer has a geometry reminiscent of ethylene, with a silicon atom replacing one hydrogen atom. However, improvement in the level of theory to UMP2(full)/6-31G(d,p) show that this isomer is 6.3 kcal mol^{-1} higher than the true global minimum, an acetylene-like structure with a pyramidal bonding arrangement about the silicon atom (structure **1**).



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Similarly, the most stable isomers on the SiC_2H_4,[19l,m] $SiC_2H_5^+$,[39] and SiC_2H_6[57] potential energy hypersurfaces contain more than one hydrogen atom bonded to silicon, although on each hypersurface there are low-energy structures with no Si−H bonds.

Standard Enthalpies of Formation. The results of projected MP4SDTQ and QCISD(T) single-point calculations have been used to obtain standard enthalpies of formation by a variation on Pople's method of using heats of atomization,[55] a procedure which has been described previously.[42,56] Calculated quantities for the compounds $SiCH_n$ ($n = 0-4$), $SiCH_n^+$ ($n = 0-5$), SiC_2H_n ($n = 0-4, 6$), and $SiC_2H_n^+$ ($n = 0-5, 7$) are given in Table 2.

The computed $\Delta H°_{f,298}$ values at the QCISD(T) level are consistently slightly higher than those obtained at the PMP4 level but, nevertheless, are in good agreement with each other and with well-defined experimental values (the average difference between PMP4- and QCISD(T)-generated values is 1.9 kcal mol^{-1}). Total electronic energies obtained from QCISD(T)-level calculations are lower than those at the PMP4 level with the same basis set. Furthermore, although spin contamination at the PMP4 level of theory, for the most part, is removed by the application of spin projection for most open-shell molecules, QCI-level calculations are not susceptible to the vagaries of spin contamination and, so, may be regarded as yielding slightly more accurate results. However, it should be recalled that $\Delta H°_{f,298}$ values obtained from PMP4-level calculations on a large number of small molecules are consistently within ±3 kcal mol^{-1} of well-established experimentally determined values.[42,56,58] $\Delta H°_{f,298}$ values from QCISD(T)-level calculations should be at least as reliable and are probably more accurate.

The calculated $\Delta H°_{f,298}$ values for $SiCH^+$, SiC_2H_6, and $SiC_2H_7^+$ deviate significantly from experimental results. However, the experimental value (337.5 ± 7 kcal mol^{-1}, ion convention) for $SiCH^+$ is ill-defined, as it represents an average of three widely disparate values as calculated from the measured thresholds of three different reactions of Si^+ with hydrocarbons.[13] Similarly, the experimental value of 1 ± 3 kcal mol^{-1} for SiC_2H_6 has been derived in a questionable manner.[60b] The compound of interest was ignited in a bomb calorimeter, and its $\Delta H°_{f,298}$ value was obtained from its standard enthalpy of combustion. However, Tannenbaum and co-workers, in reporting the results of such experiments, noted evidence of incomplete combustion, not only of SiC_2H_6 but of all organosilicon compounds under study in this manner. The production of a variety of combustion products such as atomic carbon, atomic silicon, and CO frequently rendered reliable analyses of

TABLE 2: Standard Enthalpies of Formation[a] of SiCH$_n$ (n = 0−4) and SiC$_2$H$_n$ (n = 0−4, 6) Molecules and SiCH$_n^+$ (n = 0−5) and SiC$_2$H$_n^+$ (n = 0−5, 7) Ions at 298 K

molecule	$\Delta H^\circ_{f,298}$[PMP4][q]	$\Delta H^\circ_{f,298}$[QCISD(T)(full)]	exptl $\Delta H^\circ_{f,298}$	theoretical
SiC[b]		178.6		
Si=CH	123.1	124.6		124.4 ± 2.9[n]
Si=CH$_2$	74.6	75.7		74.2 ± 2.9[n]
Si−CH$_3$	71.1	73.4	(77.5 ± 7);[k] 71.2;[l] 72.5[c]	(73.0 ± 1.3);[n] 73.4[r]
H$_2$Si=CH$_2$	43.0	45.4	(39 ± 5);[c] (43 ± 3);[d] (37.0 ± 4.8)[p]	40.7 ± 2.4;[n] 46.5[o]
c-SiC$_2$	149.1	152.9	(147 ± 5)[f]	
Si−C≡CH	128.3	129.7		125.8 ± 3.2[n]
c-Si(CH)$_2$	85.3	86.7		
H$_2$SiC≡CH	95.0			91.0 ± 1.8[n]
H$_3$SiC≡CH	51.4			53.0 ± 1.1[n]
H$_3$Si(H)C=CH$_2$	20.2		(1 ± 3)[e]	
SiC^{+}[b]		386.6		
Si=CH]$^+$	327.9	328.9	(348.5 ± 3);[g] (337.5 ± 7)[h]	
Si=CH$_2$]$^+$	280.8	282.3	(280 ± 14)[i]; (283.5 ± 3)[h]	
Si−CH$_3$]$^+$	233.9	235.8	(230 ± 6);[i] (233.5 ± 5);[h] <(240.8)[g]	
HSi−CH$_3$]$^+$	244.0	246.0	242.6;[d] 240.1;[l] (246.5 ± 3)[k]	
H$_2$Si−CH$_3$]$^+$	203.4	205.7	(202.5 ± 1);[d] (213 ± 3);[j] (204.5 ± 2);[m] (208.5 ± 3)[k]	
Si-C≡C]$^{+}$[b]		382.1		
SiC≡CH]$^+$	291.9	294.4	>(255 ± 2);[i] <(305 ± 2)[i]	
c-Si(CH)$_2$]$^+$	294.6	296.2	<(350 ± 2)[i]	
Si(H)C=CH$_2$]$^+$	254.9		(250.5 ± 2);[g] >(223 ± 1);[i] <(255 ± 2)[i]	
c-Si(CH$_2$)$_2$]$^+$	260.3		<(275 ± 1);[i] <275.5[g]	
H$_2$Si(H)C=CH$_2$]$^+$	225.2			
(H$_3$C)$_2$SiH]$^+$	177.7		(173.5);[l] (172 ± 2)[m]	

[a] In kcal mol^{-1}. [b] Large spin contamination is inadequately treated at PMP4. [c] Reference 61. [d] Reference 15. [e] Reference 60. [f] Reference 63. [g] Reference 14. [h] Reference 13. [i] Reference 18. [j] Reference 65. [k] Reference 66. [l] Reference 17. [m] Reference 16. [n] Reference 50. [o] Reference 8a. [p] Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds. Wiley: New York, 1989; pp 371−391. [q] SiCH$_n$ and SiCH$_n^+$ ions at PMP4(full); SiC$_2$H$_n$ and SiC$_2$H$_n^+$ at PMP4(fc). [r] Reference 67.

combustion products difficult, if not impossible. Thus, accurate enthalpies of combustion, and subsequent standard enthalpies of formation, could not be attained.

The experimental $\Delta H^\circ_{f,298}$ values of SiC$_2$H$_7^+$ differ by a smaller amount from our calculated value than do the previous two compounds under discussion; nevertheless, these discrepancies still merit consideration. The $\Delta H^\circ_{f,298}$ value as reported by Beauchamp and co-workers using FT-ICR (172 ± 2 kcal mol^{-1})[16] was obtained from the H$^-$ affinity of Si(CH$_3$)$_2$H$^+$,[16] which has an uncertainty of ±2 kcal mol^{-1}, and from the standard enthalpy of Si(CH$_3$)$_2$H$_2$, which has an uncertainty of ±1 kcal mol^{-1}.[61] The highest $\Delta H^\circ_{f,298}$ value of SiC$_2$H$_7^+$ under these error limits is 175.2 kcal mol^{-1}, 2.5 kcal mol^{-1} below our calculated value. The value derived from photoionization mass spectrometry by the same group (173 kcal mol^{-1})[17] was calculated from appearance potential measurements of the aforementioned ion (with a stated uncertainty of ±0.05 eV or ±1.15 kcal mol^{-1}) as well as from the standard enthalpy of Si(CH$_3$)$_2$H$_2$ (which has an uncertainty of ±1 kcal mol^{-1}).[61] The highest $\Delta H^\circ_{f,298}$ value under these error limits, again, is 175.2 kcal mol^{-1}.

Previous calculations in our research group[42,56,58] have yielded standard enthalpies of formation which consistently are within ±3 kcal mol^{-1} of well-defined experimental values; thus, we are able to present, with confidence, the $\Delta H^\circ_{f,298}$ value of SiC$_2$H$_7^+$ as shown in Table 2.

TABLE 3: Ionization Energies[a] of SiCH$_n$ (n = 0−4) and SiC$_2$H$_n$ (n = 0−4, 6) Molecules at 0 K

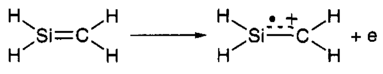
molecule	[(PMP4-(full)]	[QCISD(T)-(full)]	exptl	exptl of C analogue[d]
SiC[b]		8.94		12.11 ± 0.05
Si=CH	8.81	8.78		11.7 ± 0.5
Si=CH$_2$	8.92	8.89		8.9 ± 0.5
Si−CH$_3$	6.99	6.96		
H$_2$Si=CH$_2$	8.95[e]	8.88	8.85[c]	10.507 ± 0.004
c-SiC$_2$[b]		9.86	10.2 ± 0.5[d]	12.1 ± 0.3
SiC≡CH	7.03(fc)	7.06		
c-Si(CH)$_2$	9.01(fc)	9.00		
H$_2$SiC≡CH	7.38(fc)[f]			8.68 ± 0.05
H$_3$SiC≡CH	10.1(fc)[g]			10.36 ± 0.01

[a] In eV. [b] Large spin contamination is inadequately treated at PMP4. [c] Reference 68. [d] Reference 63. [e] Total energy for H$_2$SiCH$_2^{\bullet+}$ in eq 2 is −329.246 54 hartrees (PMP4), −329.248 45 (QCI); scaled ZPE is 24.1 kcal mol^{-1}. [f] Total energy for H$_2{}^+$Si−C≡C−H is −366.793 96 hartrees; scaled ZPE is 22.3 kcal mol^{-1}. [g] Total energy for H$_2$SiCH=CH$^{\bullet+}$ is −367.080 48 hartrees; scaled ZPE is 27.4 kcal mol^{-1}.

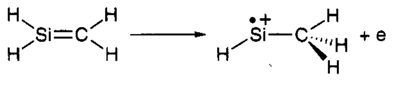
Ionization Energies. The adiabatic ionization energy of molecule A at 0 K is defined as ΔH° for the removal of an electron from ground-state A to form ground-state ion A$^+$,

$$A \rightarrow A^+ + e \qquad (1)$$

For the majority of compounds under present consideration, the global minimum isomers of species A and A$^+$ are structurally similar; that is, no bond breaking occurs in the ionization process. However, such is not the case for SiCH$_4$, SiC$_2$H$_3$, and SiC$_2$H$_4$. When the lowest energy isomer of each of these compounds is ionized, structural rearrangements are required in order to form the global minimum of A$^+$. Such processes usually require investment of additional energy. For this reason, the IE values for these three anomalous molecules listed in Table 3 represent the energy required for the direct removal of an electron to form a stable ion, which is structurally similar to the neutral molecule, but which does not reside at the global minimum on its potential energy hypersurface. For example, in the case of SiCH$_4$, the IE listed in Table 3 corresponds to the direct removal of a π-electron,

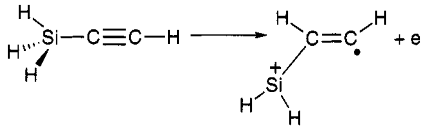

(2)

rather than to the process


(3)

which requires, first, the formation of the product ion shown in eq 2, followed by a 1,2-H shift to form the methylsilyl cation. This latter process has a substantial isomerization barrier (37.5 kcal mol^{-1} at UMP2(full)/6-31G(d,p)).

Ionization of SiC_2H_4 is unusual because it involves structural rearrangement. The structure formally obtained by removal of a π-electron from the global minimum, silylacetylene, is assumed to undergo a 1,2-H shift *without* a barrier (the calculated barrier at UHF/6-31G(d,p) is 14.7 kcal mol^{-1}, but at PMP2(full)/6-311G(d,p) it disappears). The ionization energy quoted in Table 3 then is for the following reaction:



(4)

We have calculated ionization energies by using a variation on Pople's method using isogyric equations.[55] Our procedure is illustrated for SiCH at PMP4/6-311++G(2df,p). In separating this molecule into the cation and an electron there are three unpaired spins on the right-hand side of eq 5,

$$SiCH \rightarrow SiCH^+ + e \tag{5}$$

but only one on the left-hand side. The reaction is made isogyric by adding two hydrogen atoms to the left-hand side and is balanced chemically by adding a hydrogen molecule to the right (eq 6).

$$2H + SiCH \rightarrow SiCH^+ + e + H_2 \tag{6}$$

Total electronic energies for each species at the PMP4 level are used to calculate ΔE for this reaction, as follows.

$$\Delta E_{rxn} = \sum E_{tot,products} - \sum E_{tot,reactants} \tag{7}$$

In reaction 6, $\Delta E = (-328.53249) - (-328.68319) = 0.15070$ hartrees. To calculate ΔE_{elec} for the process of interest, however, it is necessary to add the energy of the reaction $H_2 \rightarrow 2H$ (=0.17447 hartrees);[62] thus, ΔE_{elec} for the ionization reaction in eq 5 is 0.32517 hartrees. To obtain the IE, it is necessary to add the difference in zero-point vibrational energies for this reaction. For reaction 5, $\Delta ZPE = (0.0103987 - 0.0117612) = -0.0013625$ hartrees, and IE(SiCH) = 0.32381 hartrees = 8.81 eV.

Table 3 lists the ionization energies at 0 K for the neutral organosilicon compounds at the PMP4 and QCISD(T) levels of theory. While experimental ionization energies for most of these compounds are not known, the excellent agreement between our calculated values at the two levels of theory instills confidence that the calculated values are accurate. (Due to difficulties caused by spin contamination, the ionization energies of SiC and of SiC_2 at PMP4 are not reported here.)

The IE values of these organosilicon compounds are between 0.7 and 3.3 eV lower than those of the analogous C_2H_n and C_3H_n species, with the exception of SiC_2H_2, for which the IE is slightly higher than that calculated for C_3H_2 (8.8 eV).[64] These results can be understood on the grounds that silicon, being less electronegative than carbon, holds electrons less tightly than carbon. Indeed, the IE of atomic silicon (8.15172 ± 0.00003 eV) is considerably lower than that of atomic carbon (11.260 eV).[63] Ionization of the most stable isomer of each of the molecular formulas listed in Table 3 involves the removal of an electron which either is in a σ-orbital formally on silicon or is in a π-bond between a silicon atom and a carbon atom. In either situation, the charge on the resulting cation resides primarily on the silicon atom. It is not surprising, therefore, that organosilicon compounds have lower ionization energies than their carbon analogues.

TABLE 4: Proton Affinities[a] of $SiCH_n$ (n = 0−4) and SiC_2H_n (n = 0−4, 6) Molecules at 298 K

molecule	[(PMP4-(full)]	[QCISD(T)-(full)]	exptl	other theoretical	exptl of C analogue
SiC[b]	216.5				
Si=CH	210.2	210.4			
$Si{=}CH_2$	207.5	207.7			
$Si{-}CH_3$	195.0	195.5			
$H_2Si{=}CH_2$	207.7	207.7	205 ± 3[c]		162.6[e]
c-SiC_2	225.0(fc)	227.0		230.5[d]	≈185[e]
$SiC{\equiv}CH$	201.3(fc)	201.5			
c-$Si(CH)_2$	198.2(fc)				
$H_2SiC{\equiv}CH$	176.6(fc)[f]				
$H_3SiC{\equiv}CH$	193.9(fc)				
$H_3SiC(H)CH_2$	192.3(fc)[g]				179.5[e]

[a] In kcal mol^{-1}. [b] Large spin contamination is inadequately treated at PMP4. [c] Reference 16. [d] Reference 19t. [e] Reference 63. [f] Using structure $H_2Si^+CH{=}CH$ (eq 10), total energy = −367.080 48 hartrees, scaled ZPE = 27.4 kcal mol^{-1}. [g] Using structure $H_2Si^+CH_2CH_3$ (eq 11), total energy = −368.988 30 hartrees, scaled ZPE = 49.3 kcal mol^{-1}.

The anomalous result associated with the relative ionization energies of C_3H_2 and of SiC_2H_2 can be attributed to the different ground electronic states of the cations. Although both cations are three-membered rings, the most stable isomer of $C_3H_2^+$ has a $^2A_1$ electronic state;[64] that of $SiC_2H_2^+$ has a $^2B_2$ state.[39]

Proton Affinities. The proton affinity (PA) of a molecule B is defined as $\Delta H°_{298}$ for removal of a proton from BH^+ at 298 K. Our procedure for calculating proton affinities is illustrated using results for $SiCH_2$ at PMP4/6-311++G(2df,p). The proton affinity of this molecule is the enthalpy change associated with the reaction

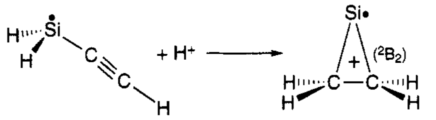
$$SiCH_3^+(g) \rightarrow SiCH_2(g) + H^+(g) \tag{8}$$

Total electronic energies for each species at PMP4 are used to calculate ΔE_{elec} from eq 8. For this reaction, $\Delta E_{elec} = (-328.34602) - (-328.68490) = 0.33888$ hartrees. The difference in ZPE for the two sides of the equation, obtained at MP2/6-311G(d,p) and scaled by 0.94,[38] must be added; here, it is $0.0321274 - 0.0206731 = 0.0114543$ hartrees. Therefore $\Delta E°_0 = \Delta H°_0 = 0.32743$ hartrees = 205.5 kcal mol^{-1}, the proton affinity of $SiCH_2$ at 0 K. To obtain $PA°_{298}$, the difference in thermal energies for the two sides of the equation must be included. The thermal energies of $SiCH_3^+$ and $SiCH_2$ were obtained by adding the vibrational energies at 298 K (from harmonic frequency calculations) to the rotational and translational energies (both $^3/_2RT$). For the proton the only thermal energy comes from translational motion ($^3/_2RT$). The total thermal energy correction to bring reaction 8 to 298 K is 0.9 kcal mol^{-1}. In addition to this energy, since there is a difference in the number of reactant and product molecules ($\Delta n = 1$), it is necessary to add a work term of RT. The proton affinity of $SiCH_2$ then corrected to 298 K is 205.5 + 0.9 + 0.6 = 207.0 kcal mol^{-1}.

Table 4 lists computed proton affinities for the organosilicon compounds. Our computed values for $SiCH_4$, both at PMP4 and at QCISD(T), are in good agreement with the experimental value.[16] No other experimental proton affinity values for the compounds under study have been reported to date, so further comparisons are not possible. It can be seen, however, that our calculated values at PMP4 and at QCISD(T) are in good agreement with each other, as is the case for ionization energies.

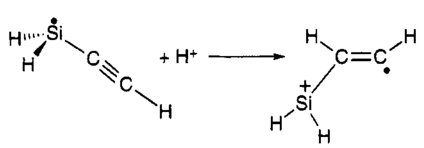
In the $SiCH_n$ series of molecules, when n = 0−2, all hydrogen atoms are attached to the carbon atom and protonation also occurs at this atom. Protonation of Si−CH_3 and CH_3SiH occurs at the only possible site, silicon. For these molecules the neutral bases and their conjugate acids have similar structures.

In the SiC_2H_n series, protonation again occurs at carbon, but this is frequently accompanied by large structural changes. SiC_2 has a cyclic structure and protonation yields the linear ion H−C≡C−Si^+; conversely protonation of linear neutral Si−C≡C−H results in a cyclic ion, *c*-$Si(CH)_2^+$, while protonation of cyclic neutral *c*-$Si(CH)_2$ gives the open ion $Si(H)C{=}CH_2^+$. The case of the protonation of SiC_2H_3, however, is more unusual. The process of starting from the most stable isomer of SiC_2H_3 and ending with the most stable isomer of $SiC_2H_4^+$ can be depicted formally as follows:



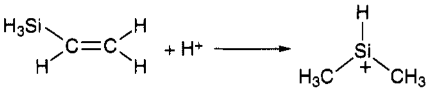
(9)

Clearly, such a process cannot occur directly in the gas phase without considerable isomerization. The PA of SiC_2H_3 listed in Table 4 thus refers to the process



(10)

In a similar manner, the proton affinity of SiC_2H_6 listed in Table 4 refers to the following process:



(11)

The second step in this sequence occurs with a very small barrier (5.2 kcal mol^{-1} at MP2(full)/6-31G(d,p)[40]). For practical purposes, in most proton transfer reactions the intermediate $H_3SiC(H)CH_3^+$ ion is likely to be a transient intermediate, and we have used the $H_2SiCH_2CH_3^+$ ion in calculating the proton affinity of 192.3 kcal mol^{-1} for $H_3SiC(H){=}CH_2$ in Table 4. If the reaction in which $H_3SiC(H){=}CH_2$ is protonated does not provide sufficient energy to overcome the barrier to rearrangement, then the proton affinity will be lower by ~27 kcal mol^{-1}.[40]

Protonation of $H_3SiC{\equiv}CH$ has been assumed to form the ion $H_2SiC(H){=}CH_2^+$, which is the global minimum on the $SiC_2H_5^+$ surface. There is a barrier to the formation of this ion (8.9 kcal mol^{-1} at MP2(full)/6-31G(d,p)) from the initial product of protonation, the bridged vinyl cation. If this latter ion is taken to be the conjugate acid, then the proton affinity of $H_3SiC{\equiv}CH$ is lowered to ~164 kcal mol^{-1}.[39]

The computed proton affinity values for the organosilicon compounds listed in Table 4 are considerably higher than those of the analogous hydrocarbon compounds. This fact is attributable to the greater polarizability and electropositive character of silicon. The presence of the Si atom in an organosilicon compound serves to increase the electron density around the remaining carbon atoms, thereby increasing their basicities relative to those in the analogous hydrocarbon. Silicon also stabilizes the cation by accommodating much of the positive charge.

Conclusions

Standard enthalpies of formation, ionization energies, and proton affinities have been computed for organosilicon neutral and cationic species using projected MP4SDTQ and QCISD(T) levels of theory. The latter method has yielded $\Delta H^\circ_{f,298}$ values which are in excellent agreement with but, consistently, are very slightly higher than those obtained from PMP4 calculations; however, good agreement is observed between our computed results and well-defined experimental values. In addition, the lack of complications arising from spin contamination at QCISD(T) leads us to suggest that values obtained at this level of theory are slightly more reliable than those obtained from PMP4-level calculations. Discrepancies between our calculated values and experimental results exist for a few compounds; however, previous theoretical studies at PMP4 have yielded the calculation of $\Delta H^\circ_{f,298}$ values which, consistently, are within ±3 kcal mol^{-1} of well-defined experimental results.[42,56,58] This level of theory then entitles us to question the reliability of experimental values which differ significantly from the computed results.

Calculated proton affinities and ionization energies at the two levels of theory are in good agreement with each other and with the very few experimental values which are available. Our computed results also show that ionization energies of the organosilicon neutral compounds under study are consistently lower than those of the analogous hydrocarbon species and that the organosilicon neutrals are considerably more basic than the hydrocarbon analogues for which comparisons can be made.

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References and Notes

(1) For an excellent compilation of this work see: Patai, S.; Rappoport, Z. *The Chemistry of Functional Groups*; Wiley Interscience: New York, 1989; Parts 1 and 2.

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