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Experimental Evidence for the Existence of $SiCH_x$ ($x = 1–3$) Molecules in the Gas Phase[†]

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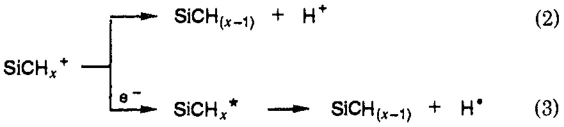
Abstract: The *neutral* silicon carbon hydrides $SiCH_x$ ($x = 1–3$) are viable molecules in the diluted gas phase as evidenced by neutralization–reionization mass spectrometry experiments. Thus, previous suggestions concerning conceivable mechanisms for the generation of these molecules in interstellar space are strongly supported.

The chemistry of organic silicon compounds is one of the fastest growing areas in organic chemistry.[1] Among the several exciting new developments the synthesis of molecules containing multiple bonds to silicon[2] is particularly noteworthy as is the fruitful interplay between experiment and theory, with the latter often preceding and sometimes even guiding experimental work.[3] The chemistry of silicon compounds is also viewed as a fundamental problem in astrophysics and astrochemistry.[4] Here, the understanding of chemical pathways from atomic silicon cation ($Si^+(^2P)$) to *neutral* $SiCH_x$ species is of special interest and importance.[5] Several processes have been suggested for the formation of, for example, $SiCH^\bullet$, $SiCH_2$, and $SiCH_3^\bullet$, respectively. One involves the transfer of a "carbanionic fragment"[6] to $Si^{\bullet+}$, a reaction which is often driven by the formation of stabilized cations (eq 1).

$$Si^{\bullet+} + (CH_3)_3N \rightarrow SiCH_3^\bullet + CH_2NHCH_3^+ \qquad (1)$$

A different route may involve dissociative neutralization of $SiCH_x^+$ species by either proton detachment (eq 2) or electron capture (eq 3).



$$SiCH_x^+ \longrightarrow SiCH_{(x-1)} + H^+ \qquad (2)$$

$$SiCH_x^+ \xrightarrow{e^-} SiCH_x^* \longrightarrow SiCH_{(x-1)} + H^\bullet \qquad (3)$$

However, the evidence for the actual formation of neutral $SiCH_x$ is in most cases at best circumstantial.[7] The failure of directly probing the existence of stable $SiCH_x$ species does, of course, not necessarily imply an intrinsic instability of these molecules. Rather, it may reflect a high propensity to undergo facile *inter*molecular reactions which prevent a successful detection of these electronically unsaturated fragments.

In fact, high-level ab initio MO calculations[8] leave no doubt that, for example, $SiCH^\bullet$ is ca. 60 kcal/mol more stable than its neutral isomer $HSiC^\bullet$.[8b] Similarly, on the theoretically well-studied singlet and triplet potential energy surfaces of $[Si,C,H_2]$ several minima were located.[8a,c] For example, the global minimum is predicted to correspond to 1-silavinylidene, $SiCH_2$; this species is 50 kcal/mol more stable than the trans-bent form of silaacetylene, HCSiH, which at the highest level of theory may not even exist as a minimum. The third isomer H_2SiC is calculated to be even higher in energy (90 kcal/mol relative to $SiCH_2$). Thus under appropriate conditions, e.g. in the diluted gas phase, $SiCH_x$ species are expected to be viable molecules and, as stated by Schaefer,[3a] "experiments probing the theoretical predictions would be particularly welcome". This is precisely what the present paper is aiming at.

By using the relatively recent technique of neutralization–reionization mass spectrometry (NRMS)[9] we will demonstrate that $SiCH_x$ ($x = 1–3$) are indeed viable species residing in potential wells deep enough to verify their existence. We were encouraged to conduct these gas-phase experiments by the recent observations that, by using NRMS, several otherwise elusive *organometallic* fragments were generated and characterized as genuine, chemically bound molecules with lifetimes $t > 1$ μs. Typical examples include the following species: $FeCH_x$ ($x = 0–3$),[9] NiL_x complexes ($x = 1, 2$; L = CO, D_2O, ND_3),[11] "end-on" $Cu^{(0)}$ complexes of HCN and HNC,[12] the half-sandwiches MC_5H_5 (M = Fe, Co, Ni),[13] the long sought after metal acetylides MCCH (M = Fe, Co, Ni),[14] and the theoretically predicted organoaluminium fragments $AlCH_2$, $Al(CH_3)_x$ ($x = 1, 2$), and AlC_2H_4, respectively.[15]

These and many other seemingly "unstable" molecules were accessible by first neutralizing a beam of ions in a collision experiment followed by reionization of the fast moving beam through

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[†] Dedicated to Professor Saul Patai, Hebrew University of Jerusalem.

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subjecting it to a second collision experiment. As a primary ion beam we used $SiCH_x^+$ (x = 1–3) (see below). According to both theory[3b,8b,16] and experiments[17] the $SiCH_x^+$ cations are significantly more stable than their isomers $HSiCH_{x-1}^+$. For example, the energy difference between $SiCH^+$ and $HSiC^+$ excedes 70 kcal/mol, and $SiCH_3^+$ is found to be by >57 kcal/mol more stable than $HSiCH_2^+$ (if the latter species corresponds at all to a true minimum). For the $[Si,C,H_2]^+$ system the lowest energy isomer is, according to Armentrout et al.,[17b] almost certainly $SiCH_2^+$.

Experimental Section

The mass spectrometric experiments were performed using our modified ZAB-HF machine which is of BEBE configuration (B stands for magnetic and E for electric sector).[18] $SiCH_x^+$ ions were generated by 100-eV electron impact ionization of H_3SiCH_2Cl employing the following conditions: ion source temperature, 200 °C; trap current, 100 μA; repeller voltage, 20 V; accelerating voltage, 8 kV; mass resolution $m/\Delta m$, 1500. Collision induced dissociations (CIDs),[19] used to characterize the primary ions $SiCH_x^+$, were brought about by mass-selecting a beam of these ions by means of B(1)E(1) and colliding it with helium (80% transmission, T; this transmittance corresponds, on the average, to 1.1–1.2 collisions[20]). Ionic dissociation products were recorded by scanning B(2). In the NRMS experiment, a beam of BE-mass selected $SiCH_x^+$ ions (having 8-keV translational energy) was neutralized in the first cell of a differentially pumped tandem collision cell by colliding it with xenon (75% T). Unreacted ions were deflected away from the beam of neutral species $SiCH_x$ by putting a voltage on a deflector electrode; subsequent reionization of $SiCH_x$ in a second collision cell took place by collision with oxygen (80% T). The mass spectrum of the resulting ions $SiCH_x^+$ was recorded by scanning B(2). The minimal lifetime t (identical with the transit time from collision cell I to cell II) in the present experiment is ca. 0.5–1 μs. The availability of a multisector machine and the fact that collision chambers are present in the field-free regions between B(1)/E(1) and E(1)/B(2) enabled us to perform a further experiment of the following kind: $SiCH_x^+$ ions are mass-selected by B(1), neutralized with Xe (80% T), and reionized with oxygen (80% T) using the tandem collision cell located between B(1) and E(1). The reionized $SiCH_x^+$ are subjected to a kinetic energy analysis by means of E(1), and the interference-free beam of $SiCH_x^+$ species of 8-keV kinetic energy was collisionally activated with helium (80% T) in the collision cell present in the field-free region E(1)/B(2). The CA mass spectra, which basically contain no contribution from reionized neutral fragments, were recorded by scanning B(2); these CA mass spectra of reionized species together with the presence of recovery signals in the NR mass spectra of $SiCH_x^+$ permit a direct identification of neutral $SiCH_x$. Signal-averaging techniques were used to improve the S/N ratio. Between 20 and 50 scans were accumulated by on-line processing the data with the VG 11/250 or the AMD-Intectra systems.

Results and Discussion

The $SiCH^+$ species (m/z 41) is easily accessible by 100-eV electron impact ionization of H_3SiCH_2Cl. Its CA mass spectrum contains signals at m/z 40 ($SiC^{\bullet+}$; 48% total fragment ion current), m/z 29 (SiH^+, 5%), m/z 28 ($Si^{\bullet+}$, 47%), m/z 13 (CH^+, <1%). In view of the above-mentioned high-energy difference between $SiCH^+$ (**1**$^+$) and $HSiC^+$ (**1a**$^+$) we presume that the CA spectrum of m/z 41 is in keeping with a connectivity $SiCH^+$. The relatively small abundance of the m/z 29 ion is perhaps due to a partial collision induced isomerization $SiCH^+ \rightarrow HSiC^+ \rightarrow m/z$ 29. In addition, as the mass resolution $m/\Delta m$ = 1500 (all slits open to provide a good sensitivity for the multi-collision experiments) is not high enough to completely separate the doublet of m/z 41 ($[H,^{28}Si,C]^+$ versus $[^{29}Si,C]^{\bullet+}$), some fraction of m/z 29, in all spectra discussed in this study, may well correspond to $^{29}Si^{\bullet+}$.

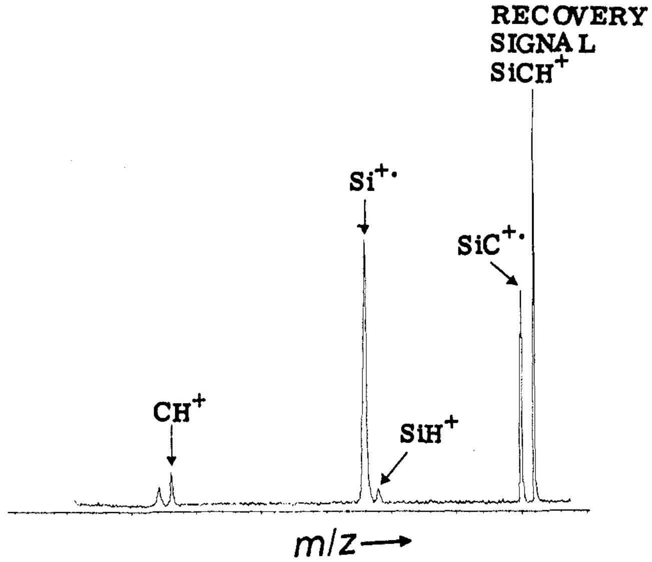

Figure 1. NR mass spectrum of $SiCH^+$, m/z 41 (xenon, 80% T//oxygen 80% T).

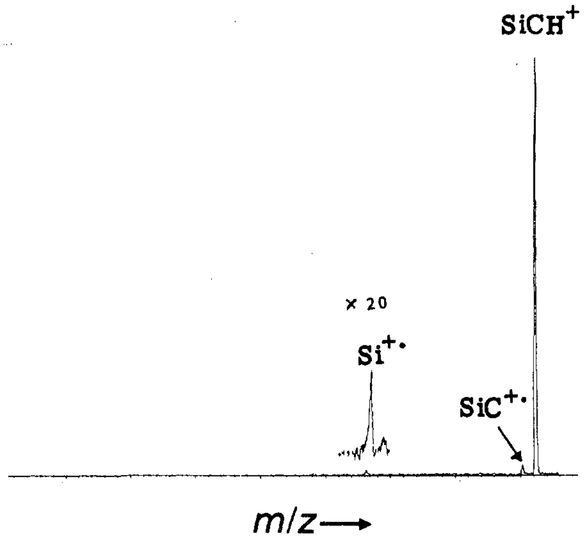

Figure 2. CA mass spectrum of reionized $SiCH^\bullet$ (xenon, 80% T//oxygen 80% T//helium 80% T).

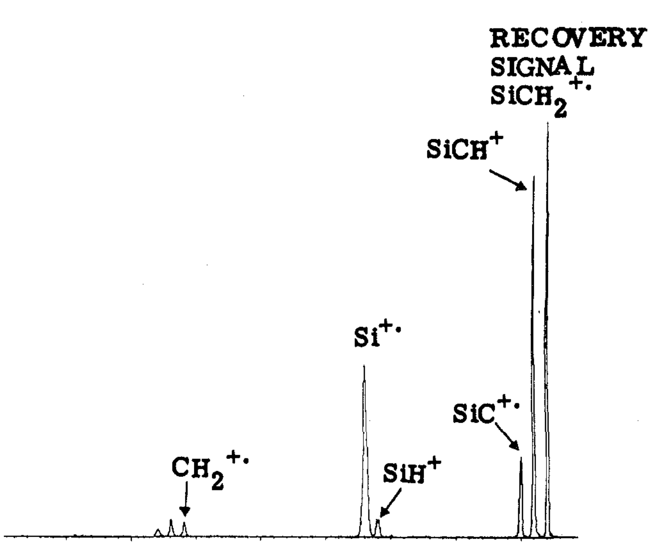

Figure 3. NR mass spectrum of $SiCH_2^{\bullet+}$, m/z 42 (xenon, 80% T//oxygen 80% T).

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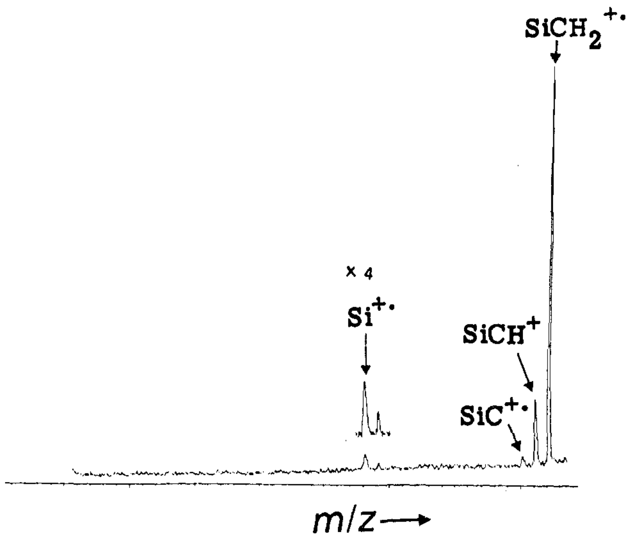

Figure 4. CA mass spectrum of reionized $SiCH_2$ (xenon, 80% T//oxygen 80% T//helium 80% T).

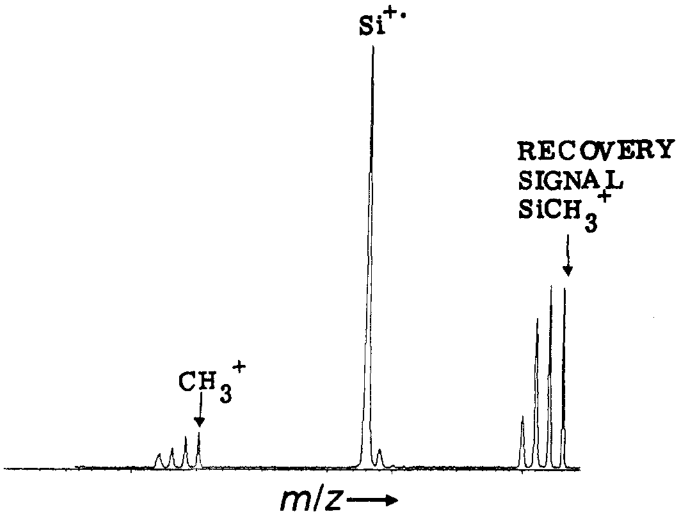

Figure 5. NR mass spectrum of $SiCH_3^+$, *m/z* 43 (xenon, 80% T// oxygen 80% T).

Reduction of $SiCH^+$ in NRMS experiments yields an intense recovery signal at *m/z* 41 (100%). This may reflect the stability of the neutral $SiCH^{\bullet}$ and may point to relatively favorable Franck–Condon factors in the vertical electron transfer processes $SiCH^+ \rightarrow SiCH^{\bullet} \rightarrow SiCH^+$. The fragmentation pattern is, again, compatible with a connectivity $SiCH^{\bullet}$ (**1**). Further evidence for this assignment is provided by the multistep collision experiment $SiCH^+ (+Xe) \rightarrow SiCH^{\bullet} (+O_2) \rightarrow SiCH^+ (+He) \rightarrow$ fragment ions. The CA spectrum of reionized $SiCH^+$ (Figure 1) thus obtained contains all features characteristic for a connectivity $SiCH^{\bullet}$.

The next species studied corresponds to $SiCH_2^{\bullet+}$ (*m/z* 42), which is also accessible by dissociative ionization of H_3SiCH_2Cl. Its CA mass spectrum is quite simple and it contains fragment ions which are, again, in favor of a connectivity $SiCH_2^{\bullet+}$ ($\mathbf{2}^{\bullet+}$).

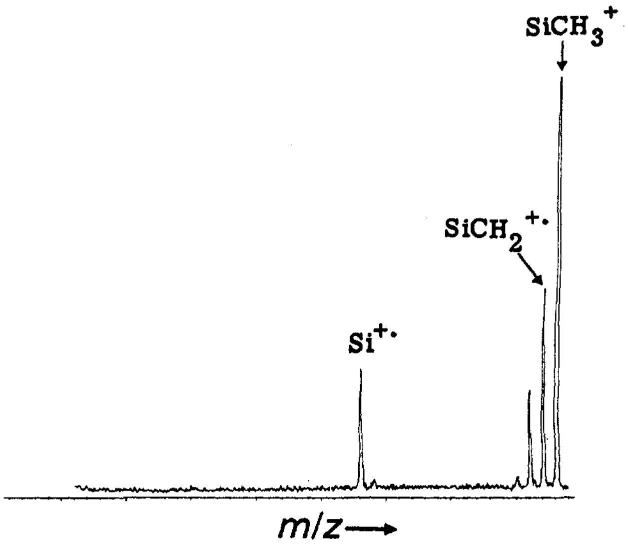

Figure 6. CA mass spectrum of reionized $SiCH_3^{\bullet}$ (xenon, 80% T// oxygen 80% T//helium 80% T).

The base peak is due to loss of $H^{\bullet}$ (*m/z* 41, 79%); other fragment ions are *m/z* 40 (6%), *m/z* 29 (2%), *m/z* 28 (13%), *m/z* 14 (<1%).

Neutralization–reionization of $SiCH_2^{\bullet+}$ ($\mathbf{2}^{\bullet+}$) gives rise to the spectrum shown in Figure 3: The recovery signal at *m/z* 42 signifies that neutral $SiCH_2$ (**2**) is indeed a viable molecule, and the fragmentation pattern is compatible with this assignment. This conclusion is, again, supported by the CA mass spectrum of reionized $SiCH_2$ (Figure 4).

For the generation of $SiCH_3^+$ (*m/z* 43) H_3SiCH_2Cl turned out to be the most suitable precursor among many other silane derivatives tried. In the CA spectrum of mass-selected *m/z* 43 we observe the already familiar fragmentation products, i.e. consecutive losses of hydrogen (*m/z* 42, 36%; *m/z* 41, 20%; *m/z* 40, 4%) and formation of *m/z* 29 (2%), *m/z* 28 (38%), and of *m/z* 15 (<1%). In view of the thermochemical preference of $SiCH_3^+$ ($\mathbf{3}^+$) versus the remaining isomers (see above), we conclude that it is indeed **3** we are probing experimentally.

Neutralization of $\mathbf{3}^+$ followed by reionization provides us with a spectrum (Figure 5) which together with the CA spectrum of reionized $SiCH_3^{\bullet}$ (Figure 6) permits the conclusion to be drawn that the long sought after $SiCH_3^{\bullet}$ is indeed a stable gas-phase molecule.

In conclusion, the present study provides for the first time direct experimental evidence that the neutral molecules $SiCH^{\bullet}$, $SiCH_2$, and $SiCH_3^{\bullet}$ are viable molecules in the gas phase, thus putting previous conjectures concerning some astrophysical pathways for the genesis of $SiCH_x$ fragments on solid experimental ground.

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