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Gas-Phase Generation and Characterization of Methyl- and Dimethylsilylene and Their Cations by Collisional Activation and Neutralization–Reionization Mass Spectrometry

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Results of mass spectrometric measurements are reported which characterize the chemical bonding in the radical cations $(CH_3SiH)^{\bullet+}$ and $(CH_3)_2Si^{\bullet+}$ and provide evidence for the existence of the corresponding neutral silylene molecules CH_3SiH and $(CH_3)_2Si$ *in the gas phase*. The experiments were performed with a modified four-sector ZAB mass spectrometer with a BEBE configuration and collision cells mounted in the intermediate field-free regions B(1)/E(1), E(1)/B(2), and B(2)E(2). Observed collisional activation (CA) mass spectra of the ions $[H_4,C,Si]^+$ and $[H_6,C_2,Si]^+$ generated from electron impact of tetramethylsilane and other precursors and CA/CA spectra of the $[C,H_3,Si]^+$ derived from them are most compatible with the connectivities $CH_3SiH^{\bullet+}$ and $(CH_3)_2Si^{\bullet+}$. Neutralization–reionization (NRMS) experiments and CA experiments with the "recovery" signals established identical connectivities for the corresponding neutral species.

Introduction

The growing interest in Si–C double-bonded molecules is exemplified by the continuing attention received by the molecules silaethylene ($H_2Si{=}CH_2$) and 1-methylsilaethylene ($CH_3(H)Si{=}CH_2$) and their silylene isomers methylsilylene ($HSiCH_3$) and dimethylsilylene ($(CH_3)_2Si$) from both experimentalists and theoreticians. Both of these molecules have been invoked as reactive intermediates in the gas phase, particularly in the thermal and photochemical decompositions of organosilicon compounds[1] and in the condensed phase.[2] Evidence for their existence has come from matrix isolation experiments.[3] Dimethylsilylene has been observed in absorption in the gas phase, but methylsilylene has been more elusive.[4]

Very recently, ions with the elemental compositions $[C,H_4,Si]^{\bullet+}$ and $[C_2,H_6,Si]^{\bullet+}$ have become of interest in gas-phase ion chemistry, particularly in the reactions of $Si^{\bullet+}$ with methane and ethane at room temperature and elevated energies.[5-7] The formation of the adduct ion, $Si^{\bullet+}(C_2H_6)$, has been reported in two gas-phase experimental investigations of the reaction of $Si^{\bullet+}$ with ethane.[6,7] Observations of other products and mechanistic arguments favor a structure for this adduct and for the intermediate complex leading to bimolecular products corresponding to ionized dimethylsilylene which may be formed by C–C bond insertion.

Theory has been applied to investigate the absolute and relative stabilities of methyl- and dimethylsilylene, for both the neutrals and their cations. There is agreement between theory and experiment on the relative stability of the neutral isomers. Gas-phase experiments with ion cyclotron double-resonance spectroscopy[8] on the thresholds for deprotonation of the protonated species have established a higher stability for the silaethylene than methylsilylene by 10 ± 3 kcal mol^{-1}, but the difference obtained by the latest theory is somewhat smaller.[9] A third isomer, silylmethylene (H_3SiCH), has been predicted by theory to lie 65.5 kcal mol^{-1} above silaethylene on the singlet surface with a very small barrier (<3 kcal mol^{-1}) to its rearrangement to $H_2Si{=}CH_2$ ($^1A_1$).[10] The barrier to the rearrangement of singlet methylsilylene to singlet silaethylene has been estimated to be about 40 kcal mol^{-1}. One previous report on computed energies of the positive ions of methylsilylene and silaethylene predicts that $HSiCH_3^{\bullet+}$ lies 6.7 kcal mol^{-1} *below* the energy of $H_2SiCH_2^{\bullet+}$ and a barrier of 42.6 kcal mol^{-1} for the interconversion of $HSiCH_3^{\bullet+}$ to $H_2SiCH_2^{\bullet+}$.[6]

The dimethylsilylene molecule, $(CH_3)_2Si$:, is often invoked as a reactive intermediate and has been studied extensively in the condensed phase.[2] It was first prepared and spectroscopically identified in hydrocarbon glasses and inert gas matrices at low temperatures in 1979.[11] Since then, this molecule has been subjected to IR, UV, and fluorescence studies in inert matrices[11,12] and in solution.[13] The interpretation of the UV spectrum, in particular, has been somewhat controversial.[14] An early theoretical study by Gordon and co-workers addressed the relative stabilities of six isomers of dimethylsilylene.[15]

The relative stability of dimethylsilylene and 1-methylsilaethylene has received much attention, but here again the results are somewhat controversial. Early matrix-isolation experiments, which showed that at 10 K dimethylsilylene rapidly converts upon photochemical excitation to 1-methylsilaethylene but reverts at elevated temperatures (100–120 K), suggested that the silylene is more stable and that the barrier to interconversion is small, <5 kcal mol^{-1}.[12] However, later ICR experiments provided enthalpies of formation of 18 and 46 kcal mol^{-1} for the silaethylene and silylene isomers, respectively, and so indicated an energy difference of 28 kcal mol^{-1} in favor of the silaolefin.[16] Calculations also predicted a sizable barrier, 40.6 kcal mol^{-1}, for the oligomerization.[17] Walsh has derived an enthalpy of formation for the silylene of 26 kcal mol^{-1} on the basis of thermochemical arguments.[18] but this is 20 kcal mol^{-1} lower than the ICR result. The possibility has been raised that this difference is due to the singlet–triplet splitting which has been calculated to be 22.1 kcal mol^{-1}, with the singlet more stable.[19]

In this study the dimethylsilylene cation, $Si(CH_3)_2^{\bullet+}$, is generated directly by electron impact of a molecule which contains its template, e.g., tetramethylsilane. The cation is then interrogated by collisional activation (CA)[20] to deduce its connectivity and by neutralization–reionization (NR)[21] mass spectrometry to generate the corresponding neutral dimethylsilylene molecule $Si(CH_3)_2$ and interrogate its structural features. Similar investigations are performed with $HSiCH_3^{\bullet+}$. CA and NR mass spectrometry together have been shown to provide a powerful method for the interrogation of structural properties of closely related ions and molecules in the gas phase,[22] particularly if they

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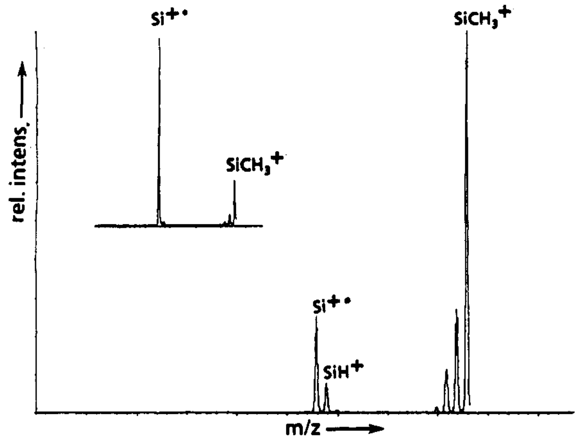

Figure 1. CA mass spectrum (He, 80% T) of *m/z* 44 $[H_4,C,Si]^{\bullet+}$ generated from $Si(CH_3)_4$ by electron impact. The insert shows the MI spectrum of *m/z* 44.

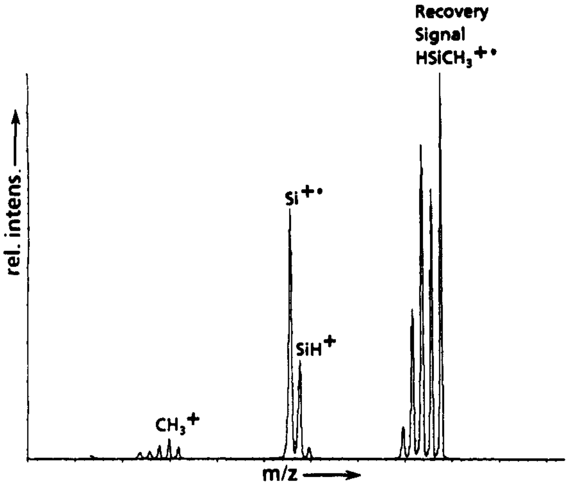

Figure 2. NR mass spectrum (Xe, 70% T; O_2, 70% T) of $[H_4,C,Si]^{\bullet+}$. The total contribution of the isotopic peaks to the recovery signal at *m/z* 44 is 6.4%. The insert shows the NRMS/CA of *m/z* 44 (He II O_2, 70% T).

are inherently reactive so that they cannot easily be isolated and investigated with other techniques.

Experimental Section

The experiments were performed with a substantially-modified ZAB-HF mass spectrometer (V.G. Analytical Ltd., Wythenshawe, Manchester M23 9LE, U.K.) which has been described in detail previously.[23] The facility is a four-sector mass spectrometer with BEBE configuration. Positive ions $[H_4,C,Si]^+$ were generated by the ionization of tetramethylsilane and methylchlorosilane with 70-eV electrons, while $[H_6,C_2,Si]^+$ were similarly generated from tetramethylsilane, trimethylsilyl chloride, trimethylsilylacetylene, $(CH_3)_3SiC_2H$, and 1,1-dimethylsilacyclobutane, c-$(CH_2)_3Si(CH_3)_2$. The ion source conditions were as follows: ion trap current = 100 μA; ion source temperature = 200 °C; mass resolution $m/\Delta m$ = 1500 (10% valley definition).

Collisional activation[20] used to characterize the ions leaving the source was achieved by mass-selecting the 8-keV ion beam by means of B(1)E(1) and colliding it, in the case of the positive ions, in a collision chamber located in the third field-free region (He, 80% transmittance, T). Ionic products were recorded by scanning B(2). In the NRMS experiments,[21] the 8-keV beam of positive ions was neutralized with xenon (70% T) in the first cell of a differentially-pumped tandem-collision cell located in the field-free region between E(1) and B(2). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1000 V on the deflector electrode. Subsequent reionization occurred in the second collision cell by collision with oxygen (70% T). The resulting mass spectra were recorded by scanning B(2). The minimum lifetime *t* (equal to the transit time from the first to the second cell) is of the order of a microsecond.

In all experiments signal-averaging techniques were used to improve the S/N ratio. The data were accumulated by on-line processes using an AMD-Intectra computer system DP10.

Results and Discussion

Methylsilylene. The CA mass spectrum of the ion at *m/z* 44 with the elemental composition $[H_4,C,Si]^+$ derived from tetramethylsilane by electron impact is shown in Figure 1. By far the most dominant feature in the spectrum is the strong peak at *m/z* 43, $[H_3,C,Si]^+$, corresponding to the loss of $H^\bullet$. The preference of $H^\bullet$ loss is very suggestive of the connectivity H–$SiCH_3$ or H–$CSiH_3$ rather than H_2CSiH_2 and so is consistent with theory which predicts a large barrier (42.6 kcal mol^{-1}) for the interconversion of $HSiCH_3^{\bullet+}$ to $H_2SiCH_2^{\bullet+}$.[6] Peaks corresponding to the loss of up to all four hydrogen atoms are also easily identified, and there is no special intensity associated with the peak corresponding to loss of H_2. The significant signal for SiH^+ corresponds to loss of $CH_3^\bullet$ and so is a signature of the connectivity HSi–CH_3 rather than HC–SiH_3. There is no evidence for a signal at CH^+ to indicate the connectivity HC–SiH_3. The relatively strong $Si^{\bullet+}$ peak corresponds to loss of both $H^\bullet$ and $CH_3^\bullet$ and so is consistent with the connectivity H–Si–CH_3. The observed metastable ion decomposition of *m/z* 44 (see insert, Figure 1) again shows the combined loss of $CH_3^\bullet/H^\bullet$ which in this case predominates over loss of $H^\bullet$. Taken together, the spectral data obtained for the ion $[H_4,C,Si]^+$ derived from tetramethylsilane by electron impact are most compatible with the connectivity H–Si–CH_3, i.e., the existence of the radical cation $HSiCH_3^{\bullet+}$.

Figure 2 shows the mass spectrum which is observed when the *m/z* 44 ion is neutralized and reionized in a NRMS-type experiment. The observation of the intense recovery signal implies the occurrence of nearly vertical neutralization and reionization processes and thus a retention of the connectivity and geometry of the initial *m/z* 44 ion, $HSiCH_3^{\bullet+}$. The remainder of the spectrum is generally supportive of this conclusion in that it contains the same diagnostic peaks observed in the CA spectrum of the initial *m/z* 44 ion shown in Figure 1. It also includes a signature of the CH_3 linkage in the form of the $C^{\bullet+}$, CH^+, $CH_2^{\bullet+}$, and CH_3^+ distribution. The trace peak at *m/z* 16 corresponds to $CH_4^{\bullet+}$ and thus the loss of Si by reductive elimination. Apparently, the intermediate $HSiCH_3$ neutral does not isomerize to $H_2Si{=}CH_2$ or H_3SiCH. This is consistent with the barrier of 40 kcal mol^{-1} predicted by theory for the interconversion of singlet methylsilylene to singlet silaethylene and the high energy of silylmethylene, which is predicted by theory to lie 65.5 kcal mol^{-1} above silaethylene.[10]

Dimethylsilylene. The observed metastable ion decompositions of $(CH_3)_4Si^{\bullet+}$ (*m/z* 88) indicate both the direct and sequential loss of two methyl groups to produce *m/z* 58. These results suggest that the connectivity H_3C–Si–CH_3, present in the tetramethylsilane molecule chosen as parent is preserved in the daughter ion at *m/z* 58 produced by electron impact ionization at 70 eV.

The CA mass spectrum of the ion at *m/z* 58 with the elemental composition $[H_6,C_2,Si]^+$ derived from tetramethylsilane by electron impact is shown in Figure 3. By far, the most dominant feature in the spectrum is the strong peak at *m/z* 43 $[H_3,C,Si]^+$, corresponding to the loss of CH_3. Peaks corresponding to the loss of up to six hydrogen atoms are easily identified with the peak corresponding to the loss of two H (H_2) at *m/z* 56 being the most intense. Weak fragment ion signals are observed at *m/z* 42 $[H_2,C,Si]^+$ and 41 $[H,C,Si]^+$. Still weaker signals are evident in the CA spectrum at *m/z* 29 [SiH^+ or $C_2H_5^+$], 28 [$Si^{\bullet+}$

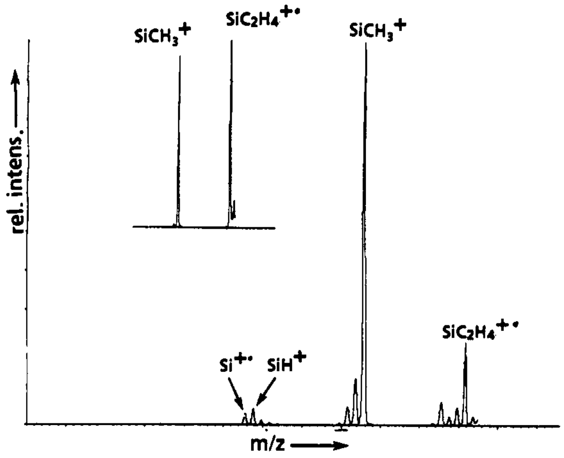

Figure 3. CA mass spectrum (He, 80% T) of *m/z* 58 $[H_6,C_2,Si]^{•+}$ generated from $Si(CH_3)_4$ by electron impact. The insert shows the MI spectrum of *m/z* 58.

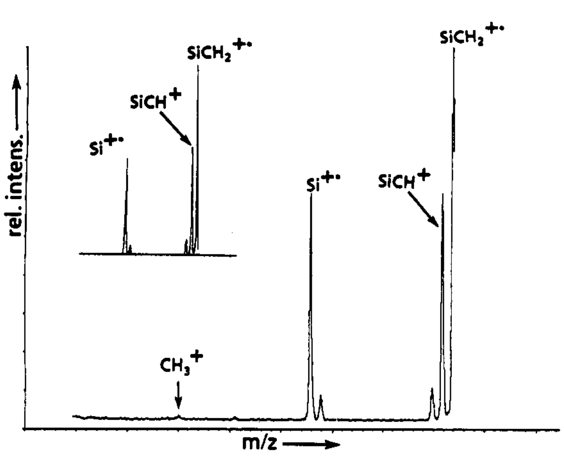

Figure 4. CA/CA mass spectrum of *m/z* 43 generated from *m/z* 58 (He, 80% T; He, 80% T). The insert shows reference CA of *m/z* 43 generated in the source from tetramethylsilane.

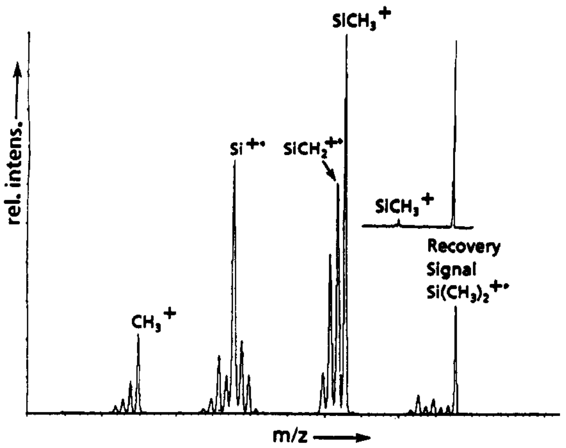

Figure 5. NR mass spectrum (Xe, 70% T; O_2, 70% T) of $[H_6,C_2,Si]^{•+}$. The insert shows the NRMS/CA of *m/z* 58 (He, 70% T).

or $C_2H_4^{•+}$], and 30 [$SiH_2^{•+}$ or $C_2H_3^+$]. The metastable ion mass spectrum (insert in Figure 3) of *m/z* 58 indicates that the energetically most favored channels are due to dehydrogenation (to form $SiC_2H_4^{•+}$) and loss of a methyl radical (to form $SiCH_3^+$).

In analyzing the CA mass spectrum shown in Figure 3, we may note first that the strong peak at *m/z* 43 requires the connectivity SiC and arises from the loss of [C,H_3], most likely bound as a methyl group. (Loss of more than one fragment, e.g., $H^•$ + CH_2 where $H^•$ might be bound initially on the Si, should be less likely to lead to such a predominant signal at *m/z* 43.) There is little direct evidence for a C–C connectivity because ions at $C_2H_x^+$ (x = 0–6) at *m/z* = 24–30 are essentially absent in the spectrum. The small peaks at *m/z* 28 and 29 also may be due to $Si^{•+}$ and SiH^+. As a consequence, the backbone CSiC rather than CCSi is indicated for the *m/z* 58 ion. Support for methyl group bonding of the hydrogen atoms comes from the CA/CA mass spectrum shown in Figure 4, which shows a strong peak at $Si^{•+}$ which can arise from the direct loss of a methyl group and no corresponding $C^{•+}$ peak which might arise from the loss of a $SiH_3^•$ group. There is also some evidence for the production of CH_3^+. The CA/CA mass spectrum is identical to the CA mass spectrum of $[H_3,C,Si]^+$ derived by electron impact of tetramethylsilane (see insert in Figure 2). The bonding of three $H^•$ atoms on C rules out a cyclic structure having a CSiC backbone.

Figure 5 shows the mass spectrum which is observed when the *m/z* 58 ion is neutralized and reionized in a NRMS-type experiment. The observation of the recovery signal again implies the occurrence of nearly vertical neutralization and ionization processes and thus, in this case, a retention of the connectivity of the initial *m/z* 58 ion. The remainder of the spectrum is generally supportive of this conclusion in that it contains the diagnostic peaks observed in the CA mass spectrum of the initial *m/z* 58 ion shown in Figure 3. It also includes a signature of the CH_3 linkage in the form of the $C^{•+}$, CH^+, $CH_2^{•+}$, and CH_3^+ distribution. Further support for our assignment is provided by the interference-free CA mass spectrum of reionized [H_6,C_2,Si], the insert in Figure 5, which clearly establishes a signal due to loss of $CH_3^•$ (to form $SiCH_3^+$).

Conclusions

1. Collisional activation experiments have provided evidence for the radical cations $HSiCH_3^{•+}$ and $(CH_3)_2Si^{•+}$ arising from various silane derivatives by electron impact at 70 eV.

2. Neutralization-reionization experiments have provided evidence for the existence of the neutral species $HSiCH_3$ and $(CH_3)_2Si$ derived from their corresponding radical cations by neutralization at high collision energies of 8 keV.

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