J. Am. Chem. Soc. **1993,** *115,* 10805–10811

Thermochemical Properties and Gas-Phase Ion Chemistry of Phenylsilane Investigated by FT-ICR Spectrometry. Identification of Parent- and Fragment-Ion Structural Isomers by Their Specific Reactivities

Yatsuhisa Nagano,[†] Srihari Murthy, and J. L. Beauchamp[*]

Contribution No. 8647 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

Received November 2, 1992[•]

Abstract: Gas-phase positive ion–molecule chemistry in phenylsilane, in phenylsilane/benzene-d_6 mixtures, and in several binary phenylsilane/hydrocarbon mixtures has been examined by the technique of Fourier transform ion cyclotron resonance spectrometry for the species $C_6H_xSi^+$ (x = 5–8) formed by electron impact ionization of phenylsilane. Reaction pathways and rate constants have been determined for the reactions of the $C_6H_xSi^+$ ions with neutral phenylsilane and with neutral benzene-d_6. Electron impact ionization of phenylsilane yields isomeric $C_6H_xSi^+$ (x = 6–8) ions. The variation of the yields of unreactive $C_6H_6Si^+$ and $C_6H_7Si^+$ ions with electron impact energy enable their identification as Si^+-inserted seven-member rings. Observations of Si^+ transfer from $C_6H_6Si^+$ to C_6D_6 and SiH_2^+ transfer from $C_6H_8Si^+$ to C_6D_6 in phenylsilane/benzene-d_6 mixtures indicate that $C_6H_6Si^+$ and $C_6H_8Si^+$ have structures corresponding to an Si^+–benzene complex and an SiH_2^+–benzene complex, respectively. Comparison of the reactions of $C_6H_6Si^+$ and $C_6H_8Si^+$ in phenylsilane with those of the complex ions $C_6D_6Si^+$ and $C_6D_6H_2Si^+$ in phenylsilane/benzene-d_6 mixtures enable additional reactive $C_6H_6Si^+$ and $C_6H_8Si^+$ isomers to be identified for which a C_6H_5–SiH^+ and a C_6H_5–SiH_2^+ structure, respectively, are suggested. In phenylsilane/hydrocarbon mixtures, hydride-transfer reactions are examined for the two isomers of $C_6H_7Si^+$. ΔH°_{298} of the H^- transfer from phenylsilane to the 2-methylbutyl cation has been determined to be -1.0 ± 0.4 kcal mol^{-1}. Using this value, the H^- affinity of the phenylsilyl cation, $DH^\circ_{298}(PhSiH_2^+–H^-)$, has been determined to be 229.8 ± 0.6 kcal mol^{-1}. The H^- affinity of the silacycloheptatrienyl cation has been determined to be less than that of the cycloheptatrienyl cation. Related thermochemical results provided by the present study include estimates for the Si–H bond energy in $PhSiH_3^+$, $DH^\circ_{298}(PhSiH_2^+–H)$, 38 kcal mol^{-1}, and the ionization potential of the phenylsilyl radical, IP($PhSiH_2$), 6.89 eV.

Introduction

The gas-phase ion chemistry of toluene has been extensively investigated[1] due primarily to the fact that electron impact ionization of toluene yields two (parent – H)$^+$ isomeric ions, namely, the benzyl and the cycloheptatrienyl cations. Interestingly, Fourier transform ion cyclotron resonance (FT-ICR) studies[2] in our laboratory recently indicated that electron impact ionization of phenylsilane, a silicon analog of toluene, also yields two (parent – H)$^+$ isomeric ions, namely, the phenylsilyl and the silacycloheptatrienyl cations. In addition, phenylsilane yields other $C_6H_xSi^+$ (x = 5, 6, 8) ions, the identification of whose isomeric structures is considered in the present study.

Ab initio quantum chemical calculations have suggested that silicon-substituted aromatic ions have structural isomers whose relative stabilities can be quite different from those of their carbon analogues.[3] An organosilicon species of this type that attracted attention recently is the $C_6H_6Si^+$ ion. By observing changes in the reactivity of Si^+ with small molecules upon its capture by benzene, Böhme *et al.*[4] provided evidence for the existence of a stable Si^+–benzene complex (**2a**). Recent theoretical calculations by Schwarz and co-workers[5] suggest that $C_6H_6Si^+$ has three stable isomers (**2a–c**), of which the Si^+–benzene complex is the most stable. Interestingly, their experimental studies[5] indicate that this latter species can be produced by electron impact ionization of phenylsilane.

In this paper, we provide a full account of the gas-phase chemistry of this interesting molecule. We report FT-ICR studies of the ion–molecule reactions of the $C_6H_xSi^+$ (x = 5–8) ions formed by electron impact ionization of phenylsilane. In addition to examining ion–molecule reactions in pure phenylsilane, we have investigated ion–molecule reactions in phenylsilane/benzene-d_6 mixtures in order that SiH_x^+ (x = 0–2) transfer reactions from $C_6H_xSi^+$ (x = 6–8), respectively, to benzene neutrals may aid in the identification of possible ion–molecule complexes.

These studies support one structure (**1**) for $C_6H_5Si^+$, three (**2a–c**) for $C_6H_6Si^+$, two (**3b,c**) for $C_6H_7Si^+$, and two (**4a/4b, 4c**) for $C_6H_8Si^+$. Two ion–molecule complexes, namely, the Si^+–benzene and the SiH_2^+–benzene complex, have been identified. The H^- affinities of the two $C_6H_7Si^+$ ions have been examined. Bond energies and stabilities are discussed in terms of the measured H^- affinities, and comparisons are made with the methylsilanes earlier studied in our laboratory[6] and with the carbon analogues of these compounds.

[†] On leave from the Microcalorimetry Research Center, Faculty of Science, Osaka University, Toyonaka 560, Japan.

[•] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

(1) (a) Howe, I.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 90. (b) McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783. (c) Sen Sharma, D. K.; Kebarle, P. *Can. J. Chem.* **1981**, *59*, 1592. (d) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259.

(2) Murthy, S.; Nagano, Y.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3573. An earlier study of the mass spectra of specifically labeled phenylsilanes failed to provide evidence for or against the formation of a silatropyllium ion: Bohlman, F.; Köppel, C.; Schwarz, H. *Org. Mass Spectrom.* **1974**, *9*, 622.

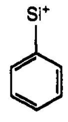
(3) (a) Baldrige, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1987**, *38*, 211. (b) Krog-Jespersen, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 1608.

(4) Böhme, D. K.; Wlodek, S.; Wincel, H. *J. Am. Chem. Soc.* **1991**, *113*, 6396.

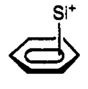
(5) Srinivas, R.; Hrusák, J.; Sülze, D.; Böhme, D. K.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2802.

(6) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900.

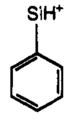
0002-7863/93/1515-10805$04.00/0



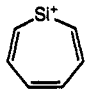
1



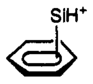
2a



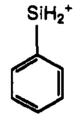
2b



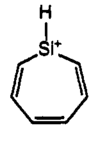
2c



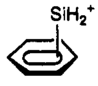
3a



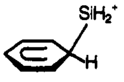
3b



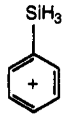
3c



4a



4b



4c

Experimental Section

The experimental aspects of FT-ICR spectrometry[7] have been described elsewhere. Only details relevant to the present studies are outlined here. The FT-ICR spectrometer used for these studies comprises a conventional 1-in. cubic trapping cell with trapping voltages of +1 V located between the poles of a Varian 15-in. electromagnet maintained at 1 T. Data collection is accomplished with an IonSpec Omega/386 FT-ICR data system and associated electronics. Neutral gases are introduced into the cell at desired pressures through separate leak valves. Neutral gas pressures are measured with a Schultz-Phelps ion gauge calibrated against an MKS (Model 390 HA-0001) capacitance manometer.

The $C_6H_xSi^+$ ($x = 5$–8) ions were formed by electron impact ionization of phenylsilane with nominal (uncorrected) electron energies in the range 11–20 eV. 2-Methylbutyl, *p*-xylyl, and phenylsilyl ($PhSiH_2^+$) cations were formed by H^- abstraction from 2-methylbutane, *p*-xylene, and phenylsilane, respectively. Reactant ions were formed by ejecting unwanted ions from the ICR cell using frequency sweep[8] and double-resonance[9] techniques. Sequential reactions were confirmed by continuously ejecting particular ions using double-resonance techniques and observing changes in the reaction processes. Observed temporal variations of reactant and product ion abundances were simulated by pseudo-first-order reaction kinetics schemes in order to determine rate constants. The principal errors in the rate constants arise from uncertainties in pressure measurement. Unless otherwise stated, rate constants reported in this study are within an accuracy of ±20%. The temperature is assumed to be 298 K.

Phenylsilane was obtained from Petrarch Systems Inc. All chemicals were used as supplied but were subjected to several freeze–pump–thaw cycles before use. Purities of samples were examined by mass spectrometry. The mass spectrum of the phenylsilane sample showed six minor peaks with m/z = 54, 78, 93, 114, 138, and 183 at an electron impact energy of 14 eV. These minor peaks may originate from impurities in the phenylsilane sample. However, the intensity of each of these ions was less than 1% of the total ion signal.

Results

A. Reactions of the $C_6H_xSi^+$ ($x = 5$–8) Ions with Phenylsilane. At low pressures (<10^{-7} Torr), ionization of phenylsilane with electron energies below 20 eV yields mainly four cations with m/z = 105, 106, 107, and 108. At the lowest electron energies (~11 eV) only $C_6H_8Si^+$ (m/z = 108) is observed. As the electron energy is increased, m/z = 106 is the first fragment ion to appear, probably being produced by the loss of molecular hydrogen from $C_6H_8Si^+$. The remaining ions, m/z = 105 and 107, appear with a further increase in electron energy. Reactions were examined after the isolation of individual ions in phenylsilane and are described below.

(1) Reactions of $C_6H_5Si^+$ (m/z = 105). The temporal variations of ion abundances following the isolation of $C_6H_5Si^+$ in phenylsilane are shown in Figure 1a. Two competitive ion–molecule reactions of $C_6H_5Si^+$ are observed. The major reaction (1)

$$C_6H_5Si^+ + PhSiH_3 \rightarrow C_{12}H_{13}Si_2^+ \tag{1}$$

$$C_6H_5Si^+ + PhSiH_3 \rightarrow C_{12}H_{11}Si^+ + SiH_2 \tag{2}$$

produces the ion $C_{12}H_{13}Si_2^+$ with m/z = 213 by direct association of $C_6H_5Si^+$ with phenylsilane. The minor reaction (2) produces an ion of m/z = 183, which is tentatively assigned to the diphenylsilyl cation (Ph_2SiH^+). In reaction 2, a neutral silylene radical (SiH_2) is eliminated. The rate constants of reactions 1 and 2 are indicated in sequence I of Figure 2. Reaction 1 is 5 times faster than reaction 2.

(2) Reactions of $C_6H_6Si^+$ (m/z = 106). Electron impact ionization of phenylsilane yields reactive and unreactive populations of the $C_6H_6Si^+$ ion. The abundance of the unreactive isomer does not change over several seconds after ionization. The variation with electron impact energy of the unreactive $C_6H_6Si^+$ isomer yield is shown in Figure 4. The percentage of the unreactive $C_6H_6Si^+$ isomer increases with increasing electron energy until it attains a constant value of 12% at electron energies above 20 eV.

Isolation of $C_6H_6Si^+$ indicates one or more reactive components which yield product ions of m/z = 136 and 183, corresponding to $C_6H_8Si_2^+$ and $C_{12}H_{11}Si^+$ (most probably Ph_2SiH^+), respectively. These reactions are indicated by processes 3 and 4.

$$C_6H_6Si^+ + PhSiH_3 \rightarrow C_6H_8Si_2^+ + C_6H_6 \tag{3}$$

$$C_6H_6Si^+ + PhSiH_3 \rightarrow C_{12}H_{11}Si^+ + SiH_3 \tag{4}$$

Reactions of $C_6H_8Si_2^+$ with phenylsilane were examined by isolating this ion in phenylsilane. Two reaction channels, (5) and (6), were identified. Reactions 3–6 account for the observed

$$C_6H_8Si_2^+ + PhSiH_3 \rightarrow C_{12}H_{11}Si^+ + Si_2H_5 \tag{5}$$

$$C_6H_8Si_2^+ + PhSiH_3 \rightarrow C_{12}H_{13}Si_2^+ + SiH_3 \tag{6}$$

variations in ion abundances shown in Figure 1b. $C_{12}H_{11}Si^+$ and $C_{12}H_{13}Si_2^+$ were not observed to react in the time range shown in Figure 1b. Reactions following the isolation of $C_6H_6Si^+$ in phenylsilane and their rate constants are summarized in sequence II of Figure 2.

(3) Reactions of $C_6H_7Si^+$ (m/z = 107). Figure 1c shows the temporal variations of ion populations following the isolation of $C_6H_7Si^+$ in phenylsilane. Process 7, which leads to the production

$$C_6H_7Si^+ + PhSiH_3 \rightarrow C_{12}H_{11}Si^+ + SiH_4 \tag{7}$$

of $C_{12}H_{11}Si^+$, is observed. The population of the $C_6H_7Si^+$ ion

---

[7] The technique of ion cyclotron resonance spectrometry and its chemical applications are described in the following: (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. FT-ICR spectrometry is reviewed in the following: (b) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (c) Marshall, A. G.; Verdun, F. R. *Fourier Transforms in NMR, Optical and Mass Spectrometry*; Elsevier: Amsterdam, 1990.

[8] Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489.

[9] Anders, L. R.; Beauchamp, J. L.; Dunbar, R. C.; Baldeschwieler, J. D. *J. Chem. Phys.* **1966**, *45*, 1062.

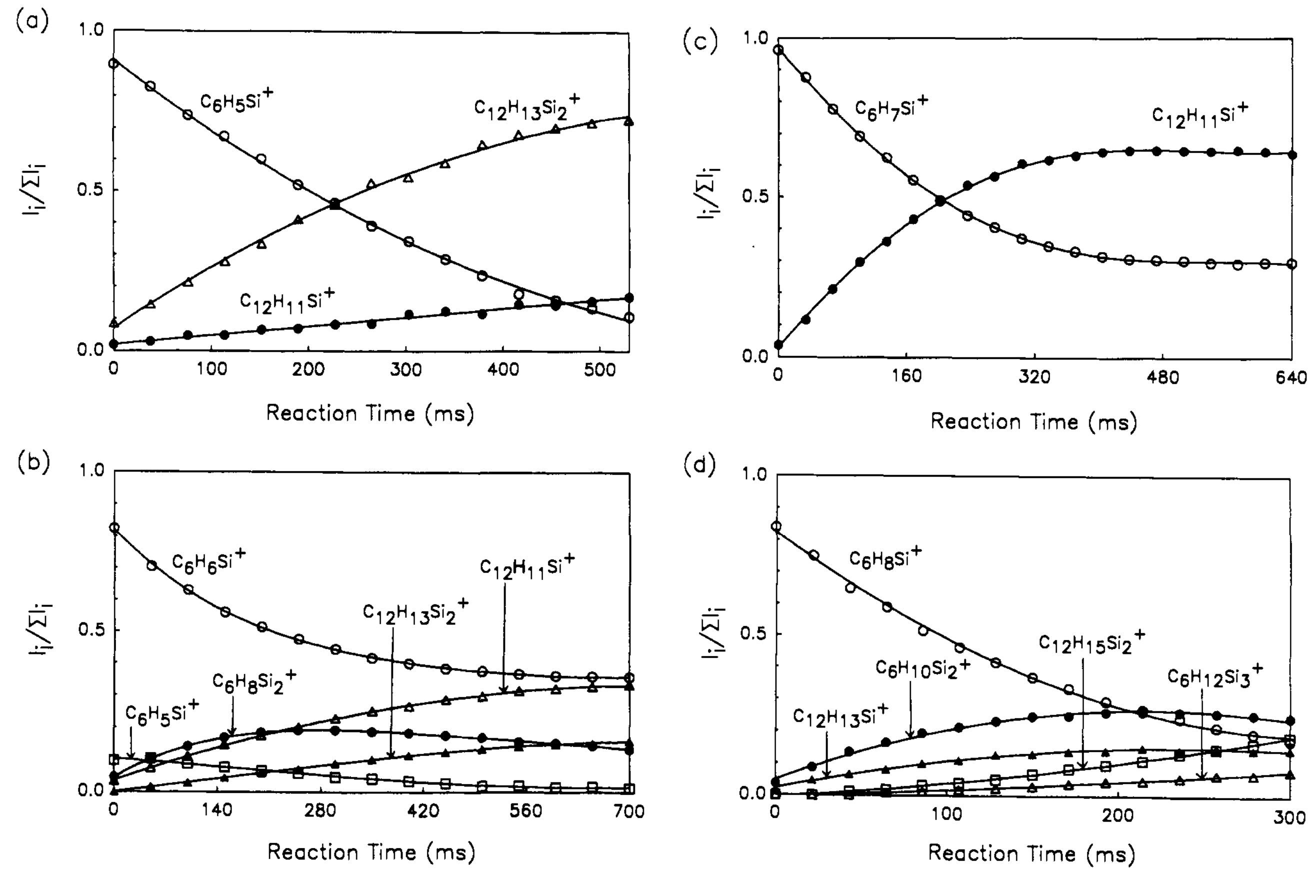


Figure 1. (a) Temporal variations of ion abundances following the isolation of $C_6H_5Si^+$ in phenylsilane at a pressure of 1.8 × 10^{-7} Torr. The energy of ionizing electrons was 19 eV. (b) Temporal variations of ion abundances following the isolation of $C_6H_6Si^+$ in phenylsilane at a pressure of 2.0 × 10^{-7} Torr. The energy of ionizing electrons was 17 eV. Reactions of $C_6H_5Si^+$ with phenylsilane contribute partially to the intensities of $C_{12}H_{11}Si^+$ and $C_{12}H_{13}Si_2^+$. (c) Temporal variations of ion abundances following the isolation of $C_6H_7Si^+$ in phenylsilane at a pressure of 2.6 × 10^{-7} Torr. The energy of ionizing electrons was 20 eV. (d) Temporal variations of ion abundances following the isolation of $C_6H_8Si^+$ in phenylsilane at a pressure of 2.6 × 10^{-7} Torr. The energy of ionizing electrons was 12 eV. For purposes of clarity, minor reaction products $C_6H_9Si^+$ and $C_6H_{11}Si_2^+$ are not shown. These ions are, however, included in the total ion count.

decreases monotonically to a certain limit, revealing the existence of an unreactive component. The rate constant of reaction 7 is indicated in sequence III of Figure 2. In a previous study,[2] the reactive and unreactive isomers of $C_6H_7Si^+$ were assigned to the phenylsilyl and the silacycloheptatrienyl cations, **3b** and **3c**, respectively. As shown in Figure 4, the fraction of the unreactive isomer of $C_6H_7Si^+$, which is the dominant product at energies below 14 eV, decreases sharply until it attains a value of 0.34 at electron energies greater than 20 eV. Interestingly, this behavior is in contrast to that observed in the case of the $C_6H_6Si^+$ ion, wherein the abundance of the unreactive isomer increases with increasing electron energy before attaining a constant value.

(4) Reactions of $C_6H_8Si^+$ (m/z = 108). The $C_6H_8Si^+$ ion was exclusively produced by the ionization of phenylsilane at electron energies below 12 eV. As can be seen from Figure 1d, the ions $C_6H_{10}Si_2^+$ and $C_{12}H_{13}Si^+$ are nascent products of the reactions of $C_6H_8Si^+$ with neutral phenylsilane. These reactions are indicated by processes 8 and 9, respectively. Continuous ejection

$$C_6H_8Si^+ + PhSiH_3 \begin{cases} \rightarrow C_6H_{10}Si_2^+ + C_6H_6 & (8) \\ \rightarrow C_{12}H_{13}Si^+ + SiH_3 & (9) \end{cases}$$

of the $C_6H_{10}Si_2^+$ ion results in the disappearance of the $C_6H_{12}Si_3^+$ ion and a significant decrease in the population of the $C_{12}H_{15}Si_2^+$ ion. Continuous ejection of the $C_{12}H_{13}Si^+$ ion diminishes the production of the $C_{12}H_{15}Si_2^+$ ion. Hence, processes 10–12 correspond to the reactions of $C_6H_{10}Si_2^+$ and $C_{12}H_{13}Si^+$ with phenylsilane. These reactions and their rate constants are summarized in sequence IV of Figure 2. Upon isolation of the m/z = 108 species ($C_6H_8Si^+$), the peak corresponding to m/z =

$$C_6H_{10}Si_2^+ + PhSiH_3 \begin{cases} \rightarrow C_6H_{12}Si_3^+ + C_6H_6 & (10) \\ \rightarrow C_{12}H_{15}Si_2^+ + SiH_3 & (11) \end{cases}$$

$$C_{12}H_{13}Si^+ + PhSiH_3 \rightarrow C_{12}H_{15}Si_2^+ + C_6H_6 \qquad (12)$$

109 gradually increases in intensity to a value larger than that expected from the isotopomer contribution of $C_6H_8Si^+$ to the m/z = 109 ion signal. This ion is assigned as the $C_6H_9Si^+$ ion produced by reaction 13. $C_6H_9Si^+$ is observed to produce

$$C_6H_8Si^+ + PhSiH_3 \rightarrow C_6H_9Si^+ + PhSiH_2 \qquad (13)$$

$C_6H_{11}Si_2^+$ by reaction 14. The $C_6H_{11}Si_2^+$ ion partly contributes

$$C_6H_9Si^+ + PhSiH_3 \rightarrow C_6H_{11}Si_2^+ + C_6H_6 \qquad (14)$$

$$C_6H_{11}Si_2^+ + PhSiH_3 \rightarrow C_{12}H_{13}Si^+ + Si_2H_6 \qquad (15)$$

to the formation of the $C_{12}H_{13}Si^+$ ion by reaction 15. Reactions 13–15 are slower than the main reaction sequences in (8)–(12). Hence, the rate constants of reactions 8–12 were determined from the temporal variations of ion abundances at short reaction times, during which periods the intensity of $C_6H_9Si^+$ was not

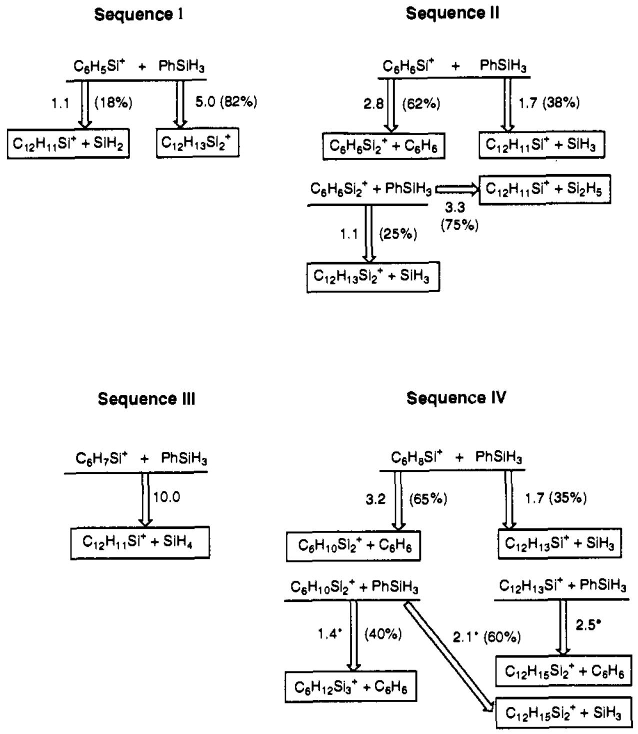


Figure 2. Schematic representation of reaction sequences following the isolation of individual $C_6H_xSi^+$ (x = 5–8) ions in phenylsilane. Rate constants in units of 10^{-10} cm^3 molecule^{-1} s^{-1} are reported for individual reactions. Rate constants are within an accuracy of ±20% unless otherwise indicated. Rate constants with an asterisk have larger uncertainties owing to the complexities of ion–molecule reactions in these systems. Branching ratios are listed within parentheses.

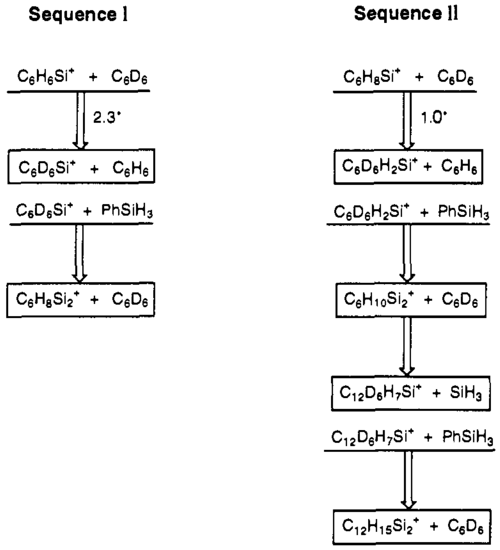


Figure 3. Schematic representation of reaction sequences following the isolation of individual $C_6H_6Si^+$ and $C_6H_8Si^+$ ions in phenylsilane/benzene-d_6 mixtures. Rate constants in units of 10^{-10} cm^3 molecule^{-1} s^{-1} are reported for individual reactions. Rate constants are within an accuracy of ±20% unless otherwise indicated. Rate constants with an asterisk have larger uncertainties owing to the complexities of ion–molecule reactions in these systems.

significant. However, the rate constants of reactions 8–12 would decrease slightly if reactions 13–15 are taken into account.

B. Reactions of the $C_6H_xSi^+$ (x = 5–8) Ions in Phenylsilane/Benzene-d_6 Mixtures. Reactions of $C_6H_xSi^+$ (x = 5–8) ions in phenylsilane/benzene-d_6 mixtures were examined upon the isolation of individual ions. The ions $C_6H_5Si^+$ and $C_6H_7Si^+$ were not observed to react with benzene-d_6. Both $C_6H_6Si^+$ and $C_6H_8Si^+$ were observed to react in phenylsilane/benzene-d_6 mixtures, and their reactions are described below.

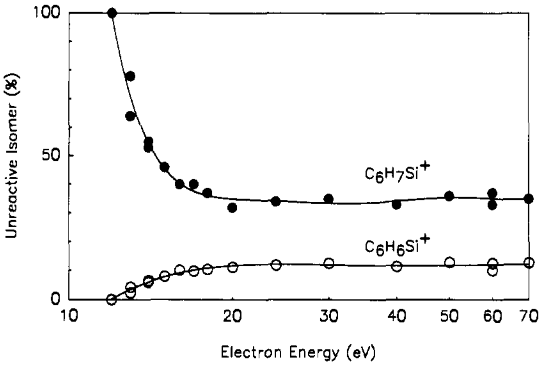


Figure 4. Variations of the percentages of unreactive $C_6H_6Si^+$ (**2c**) and $C_6H_7Si^+$ (**3c**) isomeric ions as a function of electron impact energy of phenylsilane at a pressure of 7.9 × 10^{-8} Torr. The fraction of unreactive isomer is defined as the ratio of the steady-state (measured between 1500–2000 ms) abundance of $C_6H_6Si^+$ and $C_6H_7Si^+$ to the abundance of $C_6H_6Si^+$ and $C_6H_7Si^+$, respectively, measured 5 ms after the electron beam pulse. The width of the electron beam pulse was 20 ms.

(1) Reactions of $C_6H_6Si^+$. Upon isolation of $C_6H_6Si^+$ in phenylsilane/benzene-d_6 mixtures, the formation of an m/z = 112 ion by a direct reaction between $C_6H_6Si^+$ and C_6D_6 was observed in addition to the formation of the ions $C_6H_8Si_2^+$ and $C_{12}H_{11}Si^+$ by reactions 3 and 4, respectively. The ion of m/z = 112 is assigned as the $C_6D_6Si^+$ ion which is produced by the Si^+-transfer reaction (16). The temporal variations of these ions

$$C_6H_6Si^+ + C_6D_6 \rightarrow C_6D_6Si^+ + C_6H_6 \qquad (16)$$

are shown in Figure 5a. From this figure, it can be seen that the population of $C_6D_6Si^+$ is gradually depleted by reactions at long times. Continuous ejection of the $C_6D_6Si^+$ ion diminishes the population of the $C_6H_8Si_2^+$ ion significantly. Isolation of $C_6D_6Si^+$ confirmed that the $C_6H_8Si_2^+$ ion is the main product in the reactions of $C_6D_6Si^+$ with phenylsilane, as indicated by process 17. This reaction is also formally a Si^+-transfer reaction. These reactions are summarized in sequence I of Figure 3.

$$C_6D_6Si^+ + PhSiH_3 \rightarrow C_6H_8Si^+ + C_6D_6 \qquad (17)$$

If there were a competitive process corresponding to reaction 4, involving $C_6D_6Si^+$ as the reactant, it would have produced $C_{12}H_{6-x}D_{5+x}Si^+$ ions (x = 0–1) with m/z = 188 or 189. However, the formation of these ions was not observed. The implications of these observations for the existence of $C_6H_6Si^+$ structural isomers are discussed below.

(2) Reactions of $C_6H_8Si^+$. Isolation of $C_6H_8Si^+$ in phenylsilane/benzene-d_6 mixtures results in the production of ions with m/z = 114 and 191. These ions are not produced by reactions of $C_6H_8Si^+$ with phenylsilane. They are produced by reactions of $C_6H_8Si^+$ with benzene-d_6 and correspond to $C_6D_6H_2Si^+$ and $C_{12}D_6H_7Si^+$, respectively. Although the phenylsilane sample has a minor impurity which gives rise to an ion of m/z = 114, this ion was ejected in the isolation procedure. Temporal variations of the $C_6H_8Si^+$ ion and other reaction product ions are shown in Figure 5b. The formation of $C_6D_6H_2Si^+$ by process 18 involves

$$C_6H_8Si^+ + C_6D_6 \rightarrow C_6D_6H_2Si^+ + C_6H_6 \qquad (18)$$

the transfer of a silylene cation (SiH_2^+) from $C_6H_8Si^+$ to C_6D_6. Continuous ejection of the $C_6D_6H_2Si^+$ ion considerably diminishes the populations of ions with m/z = 138, 139, 185, 191, and 215. Isolation of $C_6D_6H_2Si^+$ shows that the ion of m/z = 138 is a direct reaction product, while the ion of m/z = 191 is not. The ion with m/z = 138 is the precursor of the ions with m/z = 191

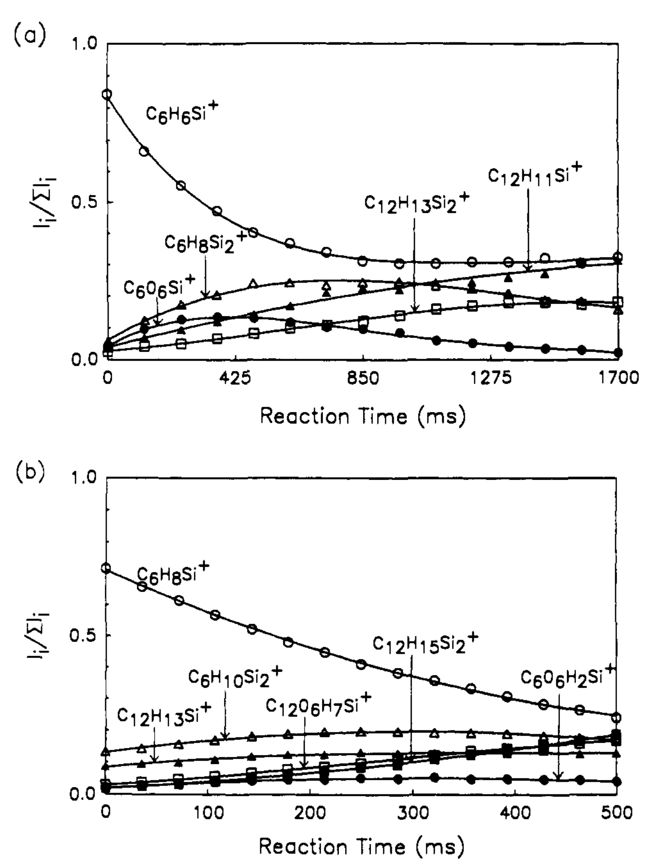


Figure 5. (a) Temporal variations of ion abundances following the isolation of $C_6H_6Si^+$ in a 1:1.4 phenylsilane/benzene-d_6 mixture maintained at a total pressure of 1.9 × 10^{-7} Torr. The energy of ionizing electrons was 18 eV. (b) Temporal variations of ion abundances following the isolation of $C_6H_8Si^+$ in a 1:1.2 phenylsilane/benzene-d_6 mixture maintained at a total pressure of 1.7 × 10^{-7} Torr. The energy of ionizing electrons was 12 eV. For purposes of clarity, minor reaction products $C_6H_{12}Si_3^+$, $C_6H_9Si^+$, and $C_6H_{11}Si_2^+$ are not shown. $C_6H_{12}Si_3^+$ is included in the total ion count.

and 215. The ion with m/z = 191 reacts to produce the ion with m/z = 215. The ions of m/z = 138 and 215 are assumed to be identical to the $C_6H_8Si_2^+$ and $C_{12}H_{15}Si_2^+$ ions, respectively, observed upon the isolation of $C_6H_8Si^+$ in pure phenylsilane. The reactions that take place upon the isolation of $C_6D_6H_2Si^+$ in phenylsilane/benzene-d_6 mixtures are given by processes 19–21. Reaction 19 is formally an SiH_2^+-transfer reaction. These reactions are summarized in sequence II of Figure 3.

$$C_6D_6H_2Si^+ + PhSiH_3 \rightarrow C_6H_{10}Si_2^+ + C_6D_6 \quad (19)$$

$$C_6H_{10}Si_2^+ + C_6D_6 \rightarrow C_{12}D_6H_7Si^+ + SiH_3 \quad (20)$$

$$C_{12}D_6H_7Si^+ + PhSiH_3 \rightarrow C_{12}H_{15}Si_2^+ + C_6D_6 \quad (21)$$

The $C_{12}D_6H_7Si^+$ ion behaves like the deuterated analog of the $C_{12}H_{13}Si^+$ ion formed by reaction 9. However, the $C_{12}D_6H_7Si^+$ ion is formed not by an analogous reaction between $C_6D_6H_2Si^+$ and $PhSiH_3$ but by process 20, which is a reaction between $C_6H_{10}Si_2^+$ and C_6D_6. Reaction 21 may correspond to reaction 12. Interestingly, the alternate reaction (22), in which neutral

$$C_{12}D_6H_7Si^+ + PhSiH_3 - X \rightarrow C_{12}D_6H_9Si_2^+ + C_6H_6 \quad (22)$$

C_6H_6 is released, is not observed since an ion of m/z = 221 is not formed. The loss of C_6D_6 in reaction 21 implies that the C_6D_6 group is a chemically distinct structural entity incorporating a C_6 ring in the $C_{12}D_6H_7Si^+$ ion. The formation of an ion of m/z = 139 is observed following the isolation of the $C_6D_6H_2Si^+$ ion. If we suppose that $C_6D_6H_2Si^+$ has the structure C_6D_5–$SiDH_2^+$, then a $SiDH^+$-transfer reaction would probably yield a singly deuterated $C_6DH_9Si_2^+$ ion of m/z = 139 with a probability twice that of reaction 19. However, the population of the ion of m/z = 139 is less than that of the ion of m/z = 138. Hence, the ion of m/z = 139 is $C_6H_{11}Si_2^+$, which is observed in pure phenylsilane as a product of reaction 14, rather than $C_6DH_9Si_2^+$. This result suggests that the $C_6D_6H_2Si^+$ ion does not have a C_6D_5–$SiDH_2^+$ structure.

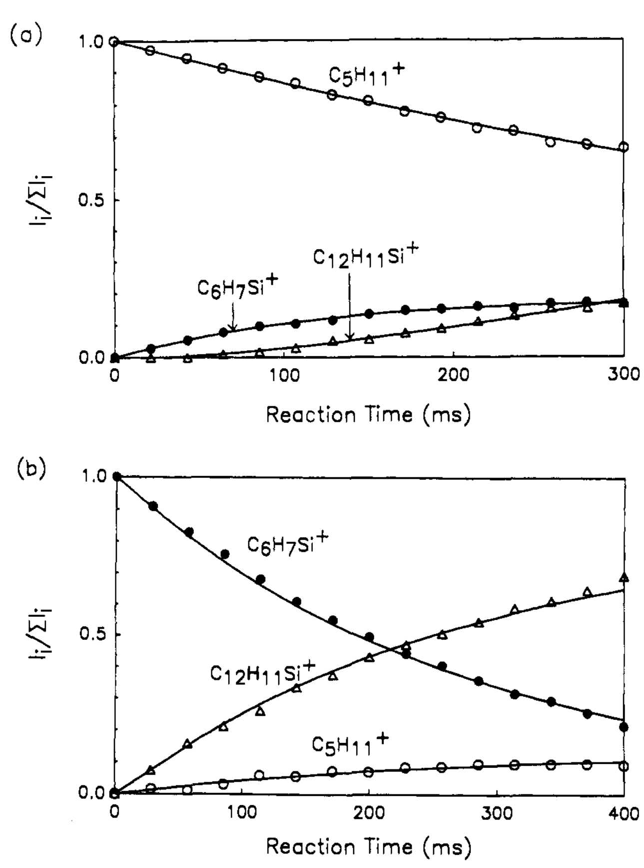


Figure 6. (a) Temporal variations of ion abundances following the isolation of $C_5H_{11}^+$, which was formed by H^- abstraction from 2-methylbutane in a 1.1:1 phenylsilane/2-methylbutane mixture maintained at a total pressure of 2.4 × 10^{-7} Torr. (b) Temporal variations of ion abundances following the isolation of the phenylsilyl cation, $PhSiH_2^+$, which was formed by H^- abstraction from phenylsilane in a 1:1.6 phenylsilane/2-methylbutane mixture maintained at a total pressure of 2.7 × 10^{-7} Torr. In both (a) and (b), points are from experiment; solid lines are from numerical simulation of the reaction kinetics.

C. Hydride-Transfer Reactions and Hydride Affinities of the $C_6H_7Si^+$ Ions. In both 2-methylbutane/phenylsilane and p-xylene/phenylsilane gas mixtures, hydride-transfer reactions of the phenylsilyl cation (**3b**) with 2-methylbutyl and p-xylyl cations, respectively, were observed. For the determination of quantitative thermochemical data, only results from hydride-transfer equilibria studies in 2-methylbutane/phenylsilane mixtures were used because the signal of protonated p-xylene at m/z = 107 overlaps with that of the phenylsilyl cation. Parts a and b of Figure 6 show the temporal variations of ion abundances following the isolation of $C_5H_{11}^+$ and $PhSiH_2^+$ ions, respectively, in 2-methylbutane/phenylsilane mixtures. Reaction 23 represents the

$$C_5H_{11}^+ + PhSiH_3 \rightleftharpoons PhSiH_2^+ + C_5H_{12} \quad (23)$$

hydride-transfer equilibrium between $C_5H_{11}^+$ and $PhSiH_2^+$. The rate constants of the forward and reverse reactions of process 23 are determined to be (3.6 ± 0.5) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} and (1.0 ± 0.4) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively. The equilibrium constant for reaction 23 is determined to be 3.6 (+3.2, −1.4) from the ratio of the rate constants. Assuming a reaction temperature of 298 K, the free energy change of reaction 23 is calculated to be −0.8 ± 0.4 kcal mol^{-1}. The entropy change of reaction 23 is estimated to be 2.2 eu resulting from changes in symmetry numbers[10] (3/2 for phenylsilane/phenylsilyl cation and 2/1 for 2-methylbutyl cation/2-methylbutane). Assuming the same magnitude of internal rotation of the SiH_3 group in phenylsilane as that of the CH_3 group in toluene, the contribution of the loss of rotation is estimated to be −3 eu.[11] Finally, the enthalpy change of the hydride transfer from phenylsilane to the 2-methylbutyl cation is determined to be −1.0 ± 0.4 kcal mol^{-1}. For obtaining a common reference in order to compare the hydride affinity of the phenylsilyl cation with that of the methylsilyl cation from earlier studies in our laboratory,[6] we use 230.8 ± 0.2 kcal mol^{-1} for the hydride affinity of the 2-methylbutyl cation, which is derived from that of the *tert*-butyl cation, 233.6 kcal mol^{-1},[6] and $\Delta H = -2.80 \pm 0.20$ kcal mol^{-1} for reaction 24.[12] The hydride

$$(CH_3)_3C^+ + (CH_3)_2(CH_3CH_2)CH \rightleftharpoons (CH_3)_2(CH_3CH_2)C^+ + (CH_3)_3CH \quad (24)$$

affinity of the phenylsilyl cation, which is defined by eq 25, is

$$DH^\circ_{298}(PhSiH_2{}^+\text{–}H^-) = \Delta_f H^\circ_{298}(PhSiH_2{}^+) + \Delta_f H^\circ_{298}(H^-) - \Delta_f H^\circ_{298}(PhSiH_3) \quad (25)$$

determined to be 229.8 ± 0.6 kcal mol^{-1}. Hydride-transfer reactions of the unreactive isomer of $C_6H_7Si^+$, namely, the silacycloheptatrienyl cation (**3c**), were not observed even in cycloheptatriene/phenylsilane mixtures. The cycloheptatrienyl cation has a hydride affinity of 194 kcal mol^{-1},[13] which is one of the lowest hydride affinities known for common organic ions. Hence, it is remarkable that the hydride affinity of the silacycloheptatrienyl cation is less than 194 kcal mol^{-1}.

Discussion

A. Structures of the $C_6H_xSi^+$ (x = 5–8) Ions. (1) Unreactive Isomers of $C_6H_6Si^+$ and $C_6H_7Si^+$. As mentioned above, the unreactive isomer of the $C_6H_7Si^+$ ion is more stable than the cycloheptatrienyl cation when H^- is the reference base. The formation of the cycloheptatrienyl cation by electron impact ionization of toluene, which is the carbon analog of phenylsilane, has been well documented.[1] As previously pointed out,[2] the electron energy dependence of the unreactive $C_6H_7Si^+$ isomer yield shown in Figure 4 is quite similar to that of the unreactive $C_7H_7^+$ isomer from toluene. Additionally, the hydride affinity of the unreactive isomer of $C_6H_7Si^+$ relative to that of the reactive isomer of $C_6H_7Si^+$ is quite similar to the hydride affinity of the cycloheptatrienyl cation relative to that of the benzyl cation. These studies further support the proposition that the unreactive $C_6H_7Si^+$ is the silacycloheptatrienyl cation (**3c**). Hydride abstraction from phenylsilane yields only the reactive isomer which is most likely the phenylsilyl cation (**3b**) for reasons mentioned previously.[2] Since $C_6H_7Si^+$ does not react with C_6D_6, it is unlikely that $C_6H_7Si^+$ supports a structure indicated by **3a**.

The $C_6H_6Si^+$ ion also has an unreactive component. The electron energy dependence of the $C_6H_6Si^+$ ion shown in Figure 4 indicates that the abundance of the unreactive $C_6H_6Si^+$ ion increases concomitantly with a decrease in the abundance of the unreactive $C_6H_7Si^+$ ion. Above 20 eV, the fractions of both the unreactive $C_6H_6Si^+$ and the unreactive $C_6H_7Si^+$ ions are constant. This suggests that both the unreactive $C_6H_7Si^+$ and the unreactive $C_6H_6Si^+$ ions may have a related origin, with the simplest process leading to the formation of the unreactive $C_6H_6Si^+$ ion coming about by loss of an H atom from the silacycloheptatrienyl cation. Hence, we suggest that the unreactive $C_6H_6Si^+$ ion has a seven-member-ring structure (**2c**).

(2) The C_6H_6–Si^+ Complex. Upon isolation of $C_6H_6Si^+$ in phenylsilane/benzene-d_6 mixtures, $C_6D_6Si^+$ was observed to be formed by reaction 16. This reaction can be described as one in which an Si^+ ion transfers from the $C_6H_6Si^+$ ion to neutral C_6D_6. The only reactive channel of the $C_6D_6Si^+$ ion thus produced is represented by process 17, in which $C_6D_6Si^+$ transfers an Si^+ ion to $PhSiH_3$ to yield the $C_6H_8Si_2{}^+$ ion. On the other hand, $C_6H_6Si^+$ is observed to undergo both reactions 3 and 4. Reaction 3 is formally similar to reaction 17. Reaction 4 is a reaction which produces the $C_{12}H_{11}Si^+$ (most probably Ph_2SiH^+) ion. A reaction of $C_6D_6Si^+$ corresponding to reaction 4 is not observed. Hence, we propose that electron impact ionization of phenylsilane yields two reactive $C_6H_6Si^+$ structural isomers, one of which is similar in structure to the $C_6D_6Si^+$ ion.

Recent theoretical calculations by Schwarz and co-workers[5] indicate that the $C_6H_6Si^+$ ion has three possible structural isomers (**2a–c**). In the same report, they provide evidence for the existence of the Si^+–C_6H_6 complex ion (**2a**) from neutralization–reionization studies of the $C_6H_6Si^+$ ion. In the present study, we observe the production of two reactive isomers and one unreactive isomer of the $C_6H_6Si^+$ ion by electron impact ionization of phenylsilane. As discussed above, the unreactive isomer may have the seven-member-ring structure (**2c**). The Si^+-transfer reaction which is observed in phenylsilane/benzene-d_6 mixtures can be readily explained by invoking the ion–molecule complex structure **2a**. Hence, the isomer which contributes to reaction 3 has the Si^+–C_6H_6 complex ion structure while the isomer contributing to reaction 4 has the C_6H_6–Si^+ structure **2b**. We suggest that reaction 4 produces a Ph_2SiH^+ ion by supposing a phenylsilylyl C_6H_6–Si^+ structure for the reactant ion.

(3) The C_6H_6–$SiH_2{}^+$ Complex. Upon isolation of $C_6H_8Si^+$ in phenylsilane/benzene-d_6 mixtures, an $SiH_2{}^+$ transfer from $C_6H_8Si^+$ to benzene-d_6 is observed to take place, as indicated by process 18. The product ion, $C_6D_6H_2Si^+$, reacts with phenylsilane to yield $C_6H_{10}Si_2{}^+$, as indicated by process 19. This reaction is also suggestive of an $SiH_2{}^+$-transfer reaction. $C_6H_8Si^+$ is observed to undergo reactions 8 and 9 with neutral phenylsilane. Reaction 8 is an $SiH_2{}^+$-transfer reaction and is similar to reaction 19. A reaction of $C_6D_6H_2Si^+$ corresponding to reaction 9 is not observed. It was suggested in the case of the reactive $C_6H_6Si^+$ isomeric ions that the ion which participates in the Si^+-transfer reaction is the Si^+–C_6H_6 complex ion (**2a**). Similarly in the case of the reactive $C_6H_8Si^+$ isomeric ions, it is proposed that the ion which is observed to undergo the $SiH_2{}^+$-transfer reaction is the $SiH_2{}^+$–C_6H_6 complex ion (**4a** or **4b**).

The photoelectron spectrum of phenylsilane is very similar to that of toluene except for the energy of the band which corresponds to ionization of the SiH_3 group, which is lower than the analogous one in toluene.[14] In both cases, the lowest energy band corresponds to ionization from a ring π orbital and molecular ions with little excess energy can be formed. Hence, it is likely that the unrearranged structure of the molecular ion (**4c**) should be formed upon ionization of phenylsilane. We, therefore, assign the structure **4c** to the $C_6H_8Si^+$ isomer that is observed to undergo reaction 9.

The structural characteristics of the Si^+–C_6H_6 (**2a**) and the

---

[10] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[11] Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612.

[12] Goren, A.; Munson, B. *J. Phys. Chem.* **1976**, *80*, 2848.

[13] Determined using the following: (a) Mallard, W. G. *NIST Standard Reference Database 19A, NIST Positive Ion Energetics Database*, version 1.1; NIST: Washington, DC, 1989. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17* (1).

[14] McLean, R. A. N. *Can. J. Chem.* **1973**, *51*, 2089.

[15] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[16] Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835.

SiH_2^+–C_6H_6 (**4a** or **b**) complexes are of interest. For the Si^+–C_6H_6 complex, theoretical calculations[5] suggest a structure in which the Si^+ ion locates not on the C_{6v} axis of benzene but near one of the carbon atoms of the ring. The C–H bond of that carbon atom is bent slightly out of plane, away from the Si^+ ion. This structure for the Si^+–C_6H_6 complex is suggestive of a π complex with a slight admixture of a σ complex. The SiH_2^+–C_6H_6 complex may also have a structure intermediate between that of a π (**4a**) and a σ (**4b**) complex.

$C_6H_5Si^+$ does not react with C_6D_6. Reactions 1 and 2 of the $C_6H_5Si^+$ ion with $PhSiH_3$ may both be explained by assuming the σ-bonded C_6H_5–Si^+ structure (**1**) for $C_6H_5Si^+$. All the other ions $C_6H_xSi^+$ (x = 6–8) do support C_6H_5–SiH_x^+ (x = 1–3) structures, respectively. Hence, it is not unreasonable for $C_6H_5Si^+$ to support such a structure.

In summary, these studies support a single structure (**1**) for $C_6H_5Si^+$, three structures (**2a–c**) for $C_6H_6Si^+$, two structures (**3b**,**c**) for $C_6H_7Si^+$, and two structures (**4a**/**4b**, **4c**) for $C_6H_8Si^+$.

B. Thermochemical Properties of $PhSiH_2^+$. The H^- affinity of $PhSiH_2^+$, $DH°_{298}(PhSiH_2^+–H^-)$, has been determined in the present study to be 229.8 ± 0.6 kcal mol^{-1}. The electron affinity of the hydrogen atom, EA(H), has been previously measured to be 0.754 eV.[17] From a photoelectron spectroscopic study of $PhSiH_3$, its adiabatic ionization potential, IP($PhSiH_3$), is taken to be 9.09 eV.[14] From eq 26,

$$DH°_{298}(PhSiH_2^+–H) = DH°_{298}(PhSiH_2^+–H^-) + EA(H) - IP(PhSiH_3) \quad (26)$$

therefore, the Si–H bond dissociation energy in $PhSiH_3^+$, $DH°_{298}(PhSiH_2^+–H)$, is calculated to be 38 kcal mol^{-1}. This stronger Si–H bond in $PhSiH_3^+$ is due to the localization of the positive charge on the phenyl ring. The following analysis supports this contention. Recently, Shin *et al.*[18] reported the observation of SiH_4^+ ions produced by the photoionization of SiH_4, although methylsilane cations, $(CH_3)_nH_{4-n}Si^+$ (n = 1–3), were not observed. From a value of 11.0 eV[18] for the appearance potential of SiH_4^+ formed from SiH_4 and a value of 261.4 kcal mol^{-1} [19] for the hydride affinity of SiH_3^+, the Si–H bond dissociation energy in SiH_4^+ is calculated to be 25 kcal mol^{-1}. The photoelectron spectrum of phenylsilane[14] indicates that the band of the highest bonding orbital centered on Si has a vertical ionization potential of 11.0 eV. If the bandwidth of this peak is assumed to be similar to that which is observed in the first photoelectron band of SiH_4,[20] then the onset of this band would be at ~9.8 eV. The Si–H bond dissociation energy of this electronically excited phenylsilane cation would then be ~26 kcal mol^{-1}, a value that is approximately equal to the Si–H bond dissociation energy of SiH_4^+.

Table I. Thermodynamic Quantities of Silyl, Methylsilyl, and Phenylsilyl Radicals and Their Carbon Analogues[a]

R	IP(R)[b] eV	$DH°_{298}(R^+–H^-)$, kcal mol^{-1} [c]	$DH°_{298}(R–H)$, kcal mol^{-1}
SiH_3	8.17	261.4[d]	90.3[e]
CH_3SiH_2	7.53	245.9[f]	89.6^{4}e
$PhSiH_2$	6.89	229.8[g]	88.2[e]
CH_3	9.84	314.4[f]	104.8[f]
C_2H_5	8.12	270.5[f]	100.6[f]
$PhCH_2$	7.20[h]	236.9[f]	88.3[e]

[a] The values of all physical quantites are at 298 K. [b] IP(R) = $DH°_{298}(R^+–H^-) - DH°_{298}(R–H)$ + EA(H). EA(H) = 0.754 eV (ref 17). [c] 1 kcal mol^{-1} = 4.1840 kJ mol^{-1} = 0.043 360 eV. [d] Reference 19. [e] Reference 15. [f] Reference 6. [g] This work. [h] Reference 21.

The ionization potentials of silyl, methylsilyl, and phenylsilyl radicals are shown in Table I along with the ionization potentials of their carbon analogues. Values of the homolytic and heterolytic bond dissociation energies of these species with hydrogen are also listed. The electronic structures of both the MH_3^+ (where M is C[22,23] or Si[24,25]) cations have been investigated previously. Both these cations are planar with the M^+ center containing an empty p orbital located perpendicular to the plane of the ion. The MH_3^+ cations are known to be stabilized by substituents that have the ability of forming a π bond with the empty orbital.[26–28] The formation of this π bond enables the σ bond between M^+ and the substituent to be concomitantly polarized toward the substituent, an effect which is stabilizing in nature. Ionization of silicenium or carbenium radicals corresponds to the removal of an unpaired electron from an orbital located at the Si or C center, respectively.[22,24] Values of $DH°_{298}(R–H)$ for the silicenium radicals listed in Table I are approximately equal. This may be a reflection of the fact that the highest energy orbitals in these radicals are energetically equivalent. If this is the case, then differences in ionization potentials would be indicative of the extent to which the corresponding silicenium ions have been stabilized by the respective substituents. From the ionization potentials of the radicals listed in Table I, it appears, therefore, that the methyl and the phenyl groups stabilize the positive silicon center of the methylsilyl and the phenylsilyl cations by ~0.6 and ~1.3 eV, respectively. In the case of the carbenium radicals listed in Table I, the ionization potentials of both the ethyl and the benzyl radicals are lower than that of the methyl radical. While this trend seems to be similar to the one observed in the case of the silicenium ions listed in Table I, it is not readily apparent that a decrease in ionization potential of the ethyl or benzyl radicals relative to that of the methyl radical directly quantifies the amount by which the respective cation is stabilized relative to the methyl cation. Nonetheless, the fact that the ionization potential of the benzyl radical is less than that of the methyl radical by 2.64 eV is a likely indication that the phenyl substituent stabilizes the carbenium ion to a greater extent than it does the corresponding silicenium ion. This is because the Ph–C^+ bond distance in the benzyl cation is likely to be shorter than the Ph–Si^+ bond distance in the phenylsilyl cation. Additionally, there is likely to be better overlap between the π system of the phenyl group and the 2p C^+ orbital in a Ph–C^+ π bond when compared to overlap between the π system of the phenyl group and a 3p Si^+ orbital in a Ph–Si^+ π bond.

From Table I, it can be seen that within the given series of carbenium and silicenium radicals, a decrease in IP(R) is matched by a decrease in $DH°_{298}(R^+–H^-)$. Additionally, in the case of the silicenium ions, within experimental uncertainty, $DH°_{298}(R^+–H^-)$ correlates linearly with IP(R). This is because $DH°_{298}(R–H)$ is approximately the same in each of these radicals.

Acknowledgment. This work was supported by Grant CHE-91-08318 from the National Science Foundation. Y.N. gratefully acknowledges financial support from the Yamada Science Foundation of Japan for a visiting associateship at the California Institute of Technology.

---

(17) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

(18) Shin, S. K.; Corderman, R. R.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 257.

(19) Corderman, R. R.; Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.*, to be submitted for publication.

(20) Potts, A. W.; Price, W. C. *Proc. R. Soc. London, A* **1972**, *326*, 165.

(21) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

(22) Dyke, J. M.; Jonathan, N.; Lee, E. P. F.; Morris, A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1385.

(23) Botschwina, P. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; pp 59–108.

(24) Dyke, J. M.; Jonathan, N.; Morris, A.; Ridha, A.; Winter, M. J. *Chem. Phys.* **1983**, *81*, 3297.

(25) Wirsam, B. *Chem. Phys. Lett.* **1973**, *18*, 578.

(26) Apeloig, Y.; Schleyer, P. v. R. *Tetrahedron Lett.* **1977**, *17*, 4647.

(27) Apeloig, Y.; Godlanski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *22*, 3297.

(28) Kispert, L. D.; Pittman, C. U., Jr.; Lee Allison, D.; Patterson, T. B., Jr.; Gilbert, C. W., Jr.; Hains, C. F.; Prather, J. *J. Am. Chem. Soc.* **1972**, *94*, 5979.