The Gas-Phase Ion Chemistry of Substituted Silanes

Thesis by

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In memory of my father

Late Shri N. V. Srineevasa Murthy

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Abstract

Ion-molecule reactions in the chlorosilanes, SiH_nCl_{4-n} (n = 0-3), and in phenylsilane have been studied by the technique of Fourier transform ion cyclotron resonance spectrometry.

In Chapter 1, the motivations for studying the gas-phase ion chemistry of substituted silanes as well as brief descriptions of the gas phase ion chemistry of the chlorosilanes and of phenylsilane are presented.

Chapter 2 deals with the gas-phase ion chemistry of the chlorosilanes, SiH_nCl_{4-n} (n = 0-2). Reactions of the chlorosilyl ions with neutral chlorosilanes and with silane as well as the reactions of the silyl ion with neutral chlorosilanes are presented. The chlorosilyl ions participate in H^-, Cl^- transfer reactions and disproportionation reactions. The mechanisms of these reactions are discussed. The Cl^- affinities of the chlorosilyl ions, $SiH_nCl_{3-n}^+$ (n = 0-2), lie within a range of 1.2 kcal mol^{-1} and decrease in the order $SiH_2Cl^+ > SiHCl_2^+ \approx SiCl_3^+$. The heats of formation of the chlorosilyl ions are determined.

Chapter 3 deals with the gas-phase ion chemistry of monochlorosilane. The difference in the H^- affinities of the ions SiH_2Cl^+ and $SiHCl_2^+$ is determined to be 1.5 ± 0.3 kcal mol^{-1}. The H^- affinities of the chlorosilyl ions, $SiH_nCl_{3-n}^+$ (n = 0-2), lie within a range of 1.8 kcal mol^{-1} and decrease in the order $SiH_2Cl^+ \approx SiCl_3^+ > SiHCl_2^+$. Protonated SiH_3Cl is generated by proton transfer from CH_5^+ and is observed to react with SiH_3Cl to yield $(SiH_3)_2Cl^+$.

Chapter 4 deals with the gas-phase ion chemistry of phenylsilane. In analogy with toluene, two (parent - H)$^+$ cations are

produced by the electron impact ionization of phenylsilane. These cations are identified to be the phenylsilyl and the silacycloheptatrienyl cations.

Chapter 5 explores the gas-phase ion chemistry of phenylsilane in great detail. Reactions of the parent and fragment ions (created by electron impact ionization) with neutral phenylsilane and with C_6D_6 are presented. Two structural isomers are identified for the $C_6H_8Si^+$ cation and three structural isomers are identified for the $C_6H_6Si^+$ cation. The H^- affinity of the phenylsilyl cation is also presented.

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Chapter I

Introduction

Ion-molecule reactions of substituted methanes have been extensively examined during the past few decades. A variety of substituted methanes including the halomethanes, methyl alcohol, toluene and methyl cyanide have been studied by several different mass spectrometric techniques.[1] Early studies in our laboratory focused on the elucidation of the gas phase ion chemistry of halomethanes.[2,3] From these studies much has been learned about the structure, reactivity and heats of formation of ions derived from substituted methanes. In contrast, ion-molecule reactions in substituted silanes have been barely investigated. The gas phase ion chemistry of substituted methanes cannot be directly extended to substituted silanes. *Ab initio* quantum chemical calculations[4,5] indicate that silicon substituted cations have structural isomers whose relative stabilities can be quite different from those of their carbon analogs. Previous studies of the gas phase positive ion-molecule reactions of substituted silanes in our laboratory have been restricted to the methylsilanes[6,7] and to the fluoromethylsilanes.[8] In this thesis, we extend studies of the gas phase positive ion-molecule reactions in substituted silanes to all of the chlorosilanes, SiH_nCl_{4-n} ($n = 0-3$), and to phenylsilane. We obtain information about the structure, reactivity and heats of formation of a number of ions derived by electron impact ionization of chlorosilanes and phenylsilane.

An area where chlorosilanes find extensive application is in the plasma processing of materials.[9] In such environments, the substrate that is being processed is exposed to a cold plasma of a volatile metal or semiconductor compound.[10] Under such conditions a variety of gas phase processes and gas-solid processes take place. The gas phase processes that occur include interactions of electrons, ions, radicals and stable neutrals with each other. These processes are believed to lead to the formation of active species as well as to the production of particulates.[10] The active species are important in the plasma process while the particulates are deleterious substances that impinge upon the substrate being processed and destroys it.

Tetrachlorosilane has been used in the plasma processing of materials. In particular, it has been used to deposit silicon layers in plasma enhanced chemical vapor deposition reactors.[11] Hence, it is of interest to understand the detailed chemical mechanisms that occur within the chlorosilane plasma. The role of chemical reactions in the production of silicon chloride particulates has been examined. One investigation supports the proposition that particulates are produced exclusively at the surface.[12] Other investigators have proposed that particulates are formed through gas phase ion-molecule reactions.[13] The proposed pathway is indicated by process 1. $SiCl_3^+$ may be formed in the silicon chloride plasma by electron impact ionization of $SiCl_4$[14]

$$SiCl_3^+ \xrightarrow[-\,Cl_2]{+\,SiCl_4} Si_2Cl_5^+ \xrightarrow[-\,Cl_2]{+\,SiCl_4} Si_3Cl_7^+ \xrightarrow[-\,Cl_2]{+\,SiCl_4} \xrightarrow[-\,Cl_2]{+\,SiCl_4} Si_xCl_y^+ \qquad (1)$$

or through penning ionization of $SiCl_4$ by rare gas ions such as Ar^+.[15] It can then react sequentially with $SiCl_4$ to give rise to polymeric $Si_xCl_y^+$ species.

Guided Ion-Beam Studies of the Gas Phase Ion Chemistry of $SiCl_4$.

Proposed chemical pathways can only be verified by systematic studies of the ion-molecule reactions of the chlorosilanes through mass spectrometric techniques. Armentrout and co-workers have applied the technique of guided ion beams[15,16] to studies of the ion-molecule reactions of tetrachlorosilane. In one study[16] they looked at the reactions of Si^+ with $SiCl_4$ as indicated by processes 2 to 5. They do not

$$Si^+ + SiCl_4 \rightarrow SiCl^+ + [SiCl_2 + Cl] \qquad (2)$$

$$\rightarrow SiCl_2^+ + SiCl_2 \qquad (3)$$

$$\rightarrow SiCl_2^+ + SiCl + Cl \qquad (4)$$

$$\rightarrow SiCl_3^+ + SiCl \qquad (5)$$

observe the formation of $Si_2Cl_y^+$ species. Under the conditions of their experiments both exothermic and endothermic reactions should be observable. Hence, it is likely to be true that Si^+ does not undergo condensation reactions with $SiCl_4$.

Weber and Armentrout[16] noticed that reaction 2 was the dominant channel at energies in the range from 0.1 to 10 eV. The parenthesis enclosing the neutral products in reaction 2 indicate that the neutral products may be bound together or that they may be separated to $SiCl_2$ and Cl. The cross section of reaction 2 was seen to decrease as a function of increasing electron energy indicating that it is an exothermic process. By performing experiments in which isotopically labeled Si^+ was made to react with $SiCl_4$, Weber and Armentrout succeeded in showing that reaction 2 occurs by three processes: (a) abstraction of a Cl atom by Si^+, (b) rearrangement in a symmetric intermediate followed by fragmentation and (c) dissociation of an intermediate to $SiCl_2^+$ and $SiCl_2$ followed by the dissociation of $SiCl_2^+$ into $SiCl^+$ and Cl. The cross-section for process (a) is greater than that for process (b) by an order of magnitude. Additionally, process (c) is endothermic and is energetically accessible only at energies greater than ~3 eV.

Reactions 3 and 4 are the least favored channels at all electron energies. Reaction 3 is observed to be endothermic by 0.4 ± 0.1 eV. The endothermicity of reaction 3 in conjunction with the heats of formation of $SiCl_2$, $SiCl_4$ and Si^+ enables the heat of formation of $SiCl_2^+$ to be determined to be 188 ± 3 kcal mol^{-1}. Reaction 4 is observed to be endothermic by 5.4 ± 0.2 eV. This value in conjunction with the heats of formation of Si^+, SiCl, $SiCl_4$ and Cl enables the heat of formation of $SiCl_2^+$ to be determined to be 190 ± 6 kcal mol^{-1}. The average value of these two values is 189 ± 5 kcal mol^{-1}.

Three mechanisms are seen to be operable during the formation of $SiCl_2^+$ by reactions 3 and 4. They are as follows: (a) retention of charge by the approaching Si^+ cation, (b) transfer of charge from the approaching Si^+ to the silicon center in $SiCl_4$ and (c) formation of energetically excited $SiCl_3^+$ which fragments to $SiCl_2^+$ and Cl. Processes (a) and (b) are comparable at energies below ~ 5 eV. At energies of ~ 5 eV, process (b) is preferred over process (a) by a factor of 5. Process (c) which is indicated by reaction 4 is preferred at energies greater than ~ 5 eV.

Reaction 5 is endothermic by 0.3 + 0.2 eV. This value in conjunction with the heats of formation of Si^+, $SiCl_3^+$ and $SiCl_4$ enables the heat of formation of SiCl to be determined to be 44 ± 6 kcal mol^{-1}. Isotopic labeling experiments indicate that reaction 5 proceeds by the following mechanisms: (a) Retention of charge by the approaching Si^+ and (b) transfer of charge from the approaching Si^+ to the silicon center in $SiCl_4$. Process (b) is favored over process (a) by 20-40%.

In another study Fisher and Armentrout[15] have looked at the reactions of O_2^+, Ar^+, Ne^+ and He^+ with $SiCl_4$. Reactions of O_2^+ with $SiCl_4$ lead to the production of $SiCl_x^+$ ($x = 1$-4) ions and $OSiCl_x^+$ ($x = 1$-3) ions. Reaction 6 in this system is found to be endothermic by 0.32 ± 0.06

$$O_2^+ + SiCl_4 \rightarrow SiCl_3^+ + Cl + O_2 \qquad (6)$$

eV. This value in conjunction with the ionization potential of O_2 and the heats of formation of $SiCl_4$ and Cl leads to a value of 99.8 ± 1.6 kcal mol^{-1} for the heat of formation of $SiCl_3^+$.

Both Ar^+ and He^+ react with $SiCl_4$ to yield the ions, $SiCl_x^+$ ($x = 0$-4). Reaction 7 is found to be endothermic by 1.58 ± 0.11 eV. This value in

$$Ar^+ + SiCl_4 \rightarrow SiCl_2^+ + Ar + 2Cl \qquad (7)$$

conjunction with the ionization potential of Ar and the heats of formation of $SiCl_4$ and Cl leads to a value of 184.9 ± 2.6 kcal mol^{-1} for the heat of formation of $SiCl_2^+$. Reaction 8 is found to be endothermic by

$$Ar^+ + SiCl_4 \rightarrow SiCl^+ + Ar + 3Cl \qquad (8)$$

1.15 ± 0.11 eV. This value in conjunction with the ionization potential of Ar and the heats of formation of $SiCl_4$ and Cl leads to a value of 203.9 ± 2.5 kcal mol^{-1} for the heat of formation of $SiCl^+$.

Ne^+ reacts with $SiCl_4$ to yield the ions, $SiCl_x^+$ (x = 0-3). The cross-section for the formation of $SiCl^+$ is found to be the greatest in this system. This is interesting because if Ne^+ is used as a diluent in $SiCl_4$ plasmas then $SiCl^+$ would be formed in preference to $SiCl_3^+$. Reaction pathway 1 indicates that $SiCl_3^+$ is the precursor of polymeric silicon chloride ions. If this is correct then addition of Ne^+ would reduce the amount of $SiCl_3^+$ being formed, thereby, reducing the abundance of polymeric silicon chloride ions.

FT-ICR Spectrometric Studies of the Gas Phase Ion Chemistry of the Chlorosilanes.

Despite the work of Armentrout and co-workers on the chlorosilanes, a number of issues remain unresolved. For example, experimental evidence is still lacking for the proposed scheme shown in equation 1 for the growth of silicon chloride particulates. Additionally, the heats of formation of a number of neutral and ionic species in the chlorosilanes have not yet been obtained experimentally. Fourier transform ion cyclotron resonance spectrometry has been utilized previously to study the gas phase ion chemistry of a number of molecules.[17] Exothermic ion-molecule reactions are easily observable in FT-ICR experiments. Hence, if the reactions listed in equation 1 are exothermic then they should be directly observable in low pressure (10^{-6} to 10^{-7} torr) FT-ICR experiments. Additionally, equilibrium and bracketing studies of ion-molecule reactions which can be examined by FT-ICR spectrometric techniques are often useful in providing detailed thermochemical information of neutral and ionic species.[18] Such data are useful inputs to theoretical models of the plasma enhanced chemical vapor deposition process.[19] These considerations motivated Murthy and Beauchamp[14] to examine ion-molecule reactions in the chlorosilanes, SiH_nCl_{4-n} ($n = 0-3$), by FT-ICR spectrometry.

Chapters 2 and 3 of this thesis describe the gas-phase ion chemistry of the chlorosilanes in great detail. The main points of these chapters are presented here. Ions in the chlorosilanes were created by electron impact ionization of neutral chlorosilanes. It was found that in SiH_2Cl_2 and $SiHCl_3$, the chlorosilyl ions were the major ions produced. In SiH_3Cl, the ions $SiHCl^+$ and SiH_2Cl^+ were the major ions produced. In $SiCl_4$, the ions $SiCl_3^+$ and $SiCl_4^+$ were the major ions produced. Condensation reactions leading to Si_2^+ type species were not observed in FT-ICR experiments of the ion-molecule reactions of the chlorosilanes. In SiH_2Cl_2 and $SiHCl_3$ it was found that all the ions react to give the chlorosilyl ions. Hence, we decided to concentrate our attention on examining the ion-molecule reactions of the chlorosilyl ions. It was found that the chlorosilyl ions undergo both hydride and chloride transfer reactions with the parent neutral from which they were derived. It was, therefore, of relevance to determine the relative hydride and chloride affinities of the chlorosilyl ions. The X^- affinity of an ion R^+, $DH^o_{298.15}(R^+—X^-)$, is defined as the negative of the enthalpy of reaction 9.

$$R^+ + X^- \rightarrow RX \qquad (9)$$

Determination of the rate constants of hydride and chloride transfer reactions in individual chlorosilanes and in mixtures of chlorosilanes made it possible to determine the relative values of the H^- and Cl^- affinities of the chlorosilyl ions. The H^- and Cl^- affinities of the chlorosilyl ions are indicated by sequences 10 and 11. The H^- and Cl^-

$$\text{Hydride affinities: } SiH_3^+ > SiH_2Cl^+ \approx SiCl_3^+ > SiHCl_2^+ \qquad (10)$$

$$\text{Chloride affinities: } SiH_3^+ > SiH_2Cl^+ > SiCl_3^+ \approx SiHCl_2^+ \qquad (11)$$

affinities of the chloromethyl ions are indicated by sequences 12 and 13.

$$\text{Hydride affinities: } CH_3^+ > CH_2Cl^+ > CHCl_2^+ > CCl_3^+ \qquad (12)$$

$$\text{Chloride affinities: } CH_3^+ > CH_2Cl^+ > CHCl_2^+ > CCl_3^+ \qquad (13)$$

The chlorosilyl ions differ from the chloromethyl ions in the ordering of their relative hydride and chloride affinities. As can be seen from Figures 1 and 2, the H^- and Cl^- affinities of the chlorosilyl ions, $SiH_nCl_{3-n}^+$ ($n = 0\text{-}2$), lie within a range of 1.8 kcal mol^{-1} while the H^- and Cl^- affinities of the chloromethyl ions, $CH_nCl_{3-n}^+$ ($n = 0\text{-}2$), span a range of up to 30 kcal mol^{-1}. Additionally, while the ordering of the relative stabilities of the chloromethyl ions do not seem to depend on the reference base the ordering of the relative stabilities of the chlorosilyl ions depend upon the reference base.

The hydride affinities of substituted silyl cations are listed in Table 1. The hydride affinity of the cation R^+, $DH^o_{298.15}(R^+\text{—}H^-)$,can be related to the homolytic bond dissociation energy of the radical R, $DH^o_{298.15}(R\text{—}H)$, the ionization potential of R, IP(R), and the electron affinity of H, EA(H), through the thermodynamic cycle shown below. Equation 14 relates these quantities to each other. From Table 1 it can be

$$\begin{tikzcd}
R^+ + H^- \arrow[r, "-DH^0_{298.15}(R^+\text{- -}H^-)"] & RH \arrow[d, "DH^o_{298.15}(R\text{--}H)"] \\
R^+ + H \arrow[u, "-EA(H)"] & R + H \arrow[l, "IP(R)"']
\end{tikzcd}$$

$$DH^o_{298.15}(R^+\text{—}H^-) = DH^o_{298.15}(R\text{—}H) + IP(R) - EA(H) \qquad (14)$$

Figure 1. Variation of the hydride affinities of the chloromethyl and chlorosilyl cations as a function of chlorine substitution

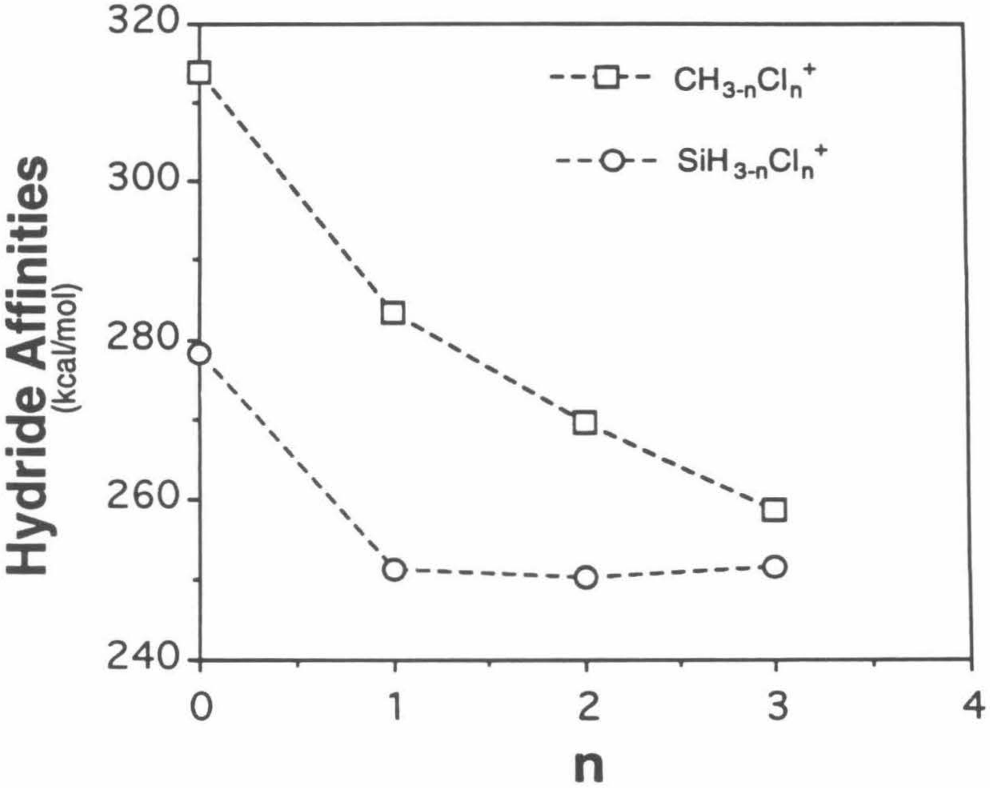

Hydride Affinities (kcal/mol)
320
300
280
260
240
0
1
2
3
4
n
CH$_{3-n}$Cl$_n^+$
SiH$_{3-n}$Cl$_n^+$

Figure 2. Variation of the chloride affinities of the chloromethyl and chlorosilyl cations as a function of chlorine substitution

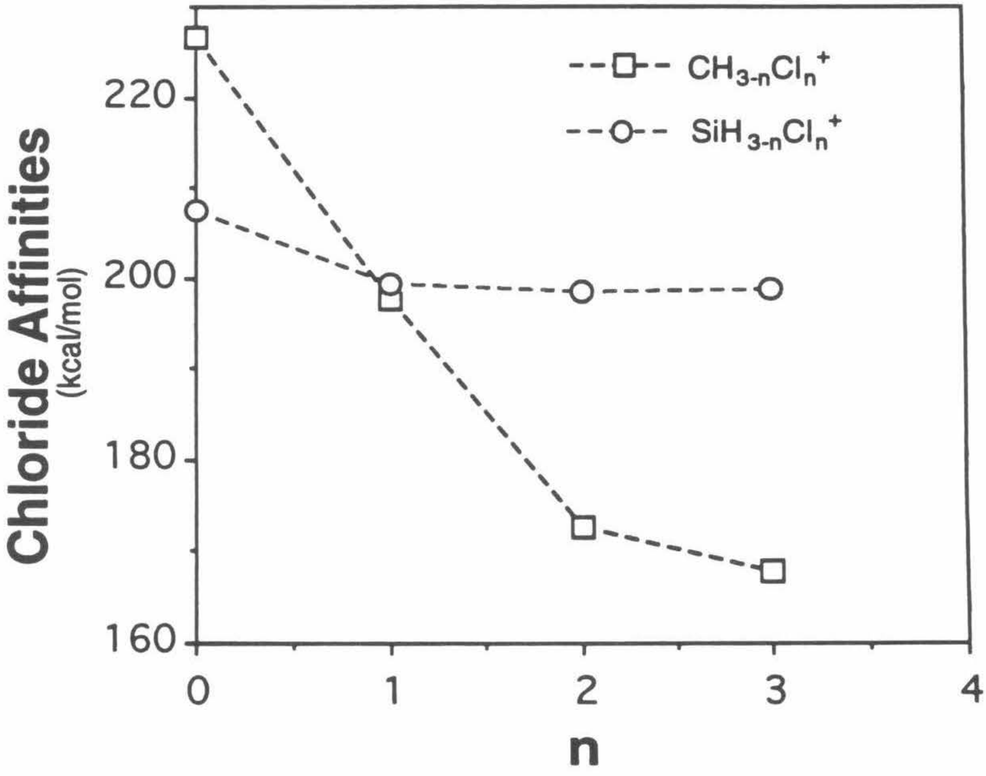

CH$_{3-n}$Cl$_n^+$
SiH$_{3-n}$Cl$_n^+$
Chloride Affinities
(kcal/mol)
220
200
180
160
0
1
2
3
4
n

Table 1. Thermochemical Properties of Substituted Silyl Cations.

R	IP(R)[a] eV	$DH^{o}_{298.15}(R^{+}—H^{-})$ kcal mol^{-1}	$DH^{o}_{298.15}(R—H)$ kcal mol^{-1}
SiH_3	8.17	261.4[b]	90.3[c]
SiH_2Cl	7.68	251.2[d]	92.2[e]
CH_3SiH_2	7.53	245.9[f]	89.6[c]
$PhSiH_2$	6.89	229.8[g]	88.2[c]

[a] $IP(R) = DH^{o}_{298.15}(R^{+}—H^{-}) - DH^{o}_{298.15}(R—H) + EA(H)$. EA(H) = 0.754 eV (from Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985,** 14, 731). [b] Reference 6. [c] Walsh, R. *Acc. Chem. Res.* **1981,** 14, 246. [d] Chapter 3. [e] Ho, P.; Coltrin, M. E.; Blinkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985,** 89, 4647. [f] Reference 45. [g] Chapter 5.

seen that the homolytic bond dissociation energies of the substituted silyl ions lie within a range of 4 kcal mol^{-1} of each other. It is also evident that the lower the ionization potential of the substituted silyl radical the lower is the hydride affinity of the corresponding substituted silyl cation. The effect of substituents on the ionization potential of the radical can be understood by considering the following analysis. Ionization of silyl and substituted silyl radicals corresponds to removal of an unpaired electron from the silicon center. Substituents tend to destabilize this electron in the radical and stabilize the hole at the positively charged silicon center in the cation. Figure 8 of Chapter 2 illustrates the stabilization of the positive center in an SiH_2Cl^+ cation by π donation and forward σ polarization effects. Substituents which tend to participate better in π donation and forward σ polarization effects with the 3p orbital in the positively charged silicon center of the substituted silyl cation are likely to lower the hydride affinity of the corresponding substituted silyl cation. As the phenylsilyl ion has the lowest hydride affinity amongst the substituted silyl cations it is likely that the phenyl substituent participates better in π donation and forward σ polarization effects with the 3p orbital in the positively charged silicon center than either the methyl or the chlorine substituents.

The net effect of the occurrence of reactions 15 and 16 is to

$$SiHCl_2^+ + SiHCl_3 \rightarrow SiCl_3^+ + SiH_2Cl_2 \qquad (15)$$

$$SiCl_3^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiCl_4 \qquad (16)$$

disproportionate two molecules of $SiHCl_3$ into one molecule of SiH_2Cl_2 and one molecule of $SiCl_4$ as indicated by process 17. Processes 15 and

$$2\ SiHCl_3 \rightarrow SiH_2Cl_2 + SiCl_4 \tag{17}$$

16 constitute an ionic chain reaction.[20] Ionic chain reactions have previously been observed in CH_2F_2[3] and H_2/D_2 mixtures.[6] The enthalpy of reactions 15 and 16 were experimentally derived from measurements of the values of the equilibrium constants of these reactions. This enabled the enthalpy of reaction 17 to be experimentally determined. The enthalpy of reaction 17 was also calculated from available literature data sets of the heats of formation of neutral chlorosilanes. It was found that the theoretical data set of Ho and Melius[21] was in best agreement with the experimentally determined value of the enthalpy of reaction 16.

The H^- or Cl^- affinities of the chlorosilyl ions were used in conjunction with the heats of formation of neutral chlorosilanes and equation 18 to obtain the relative heats of formation of the chlorosilyl

$$\begin{aligned}\Delta H_f(R_1^+) - \Delta H_f(R_2^+) = {} & [D(R_1^+{-}X^-) - D(R_2^+{-}X^-)] \\ & + [\Delta H_f(R_1X) - \Delta H_f(R_2X)] \end{aligned} \tag{18}$$

ions. Values of the heats of formation of neutral chlorosilanes were taken from the data set of Ho and Melius.[21] Absolute values of the heats of formation of the chlorosilyl ions were obtained by using the experimentally measured heat of formation of $\mathrm{SiCl_3^+}$ determined by Fisher and Armentrout[15] as a standard.

In addition to hydride and chloride transfer reactions the chlorosilyl ions undergo disproportionation reactions. Examples of disproportionation reactions are given by processes 19 and 20. These

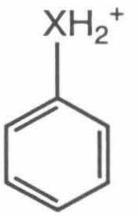
$$\mathrm{SiH_3^+ + SiCl_4 \rightarrow SiHCl_2^+ + SiH_2Cl_2} \tag{19}$$

$$\phantom{\mathrm{SiH_3^+ + SiCl_4}} \mathrm{\rightarrow SiH_2Cl^+ + SiHCl_3} \tag{20}$$

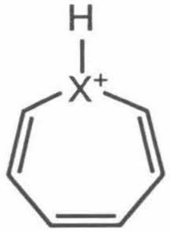
reactions are termed as disproportionation reactions because they are suggestive of the partitioning of atoms amongst the reactants rather than the transfer of a $\mathrm{H^-}$ or $\mathrm{Cl^-}$ moiety from the neutral chlorosilane to the chlorosilyl/silyl ion. The mechanisms of these reactions are discussed in Chapters 2.

FT-ICR Spectrometric Studies of the Gas Phase Ion Chemistry of Phenylsilane.

Phenylsilane is the silicon analog of toluene. The gas phase ion chemistry of toluene has been extensively studied due to the fact that electron impact ionization of toluene yields two $\mathrm{C_7H_7^+}$ structural isomers as indicated by **Ia** and **Ib**.[22] An earlier study[23] of the electron impact ionization of phenylsilane failed to provide positive proof for the formation of the silacycloheptatrienyl cation (**IIb**). However, recent studies in our laboratory indicate that the electron impact ionization of phenylsilane yields two isomeric ions one of which is reactive while the other is unreactive. The yield of the unreactive $C_6SiH_7^+$ isomer as a function of the electron impact ionization energy is similar to the yield of the unreactive $C_7H_7^+$ isomer. This leads us to believe that the unreactive $C_6SiH_7^+$ isomer is the silacycloheptatrienyl cation (**IIb**). The reactive $C_6SiH_7^+$ isomer can be generated by hydride abstraction from phenylsilane and is most likely the phenylsilyl cation (**IIa**). Chapter 4 discusses the assignment of structures to the two $C_6SiH_7^+$ isomers in great detail.



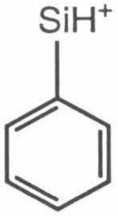
Ia: C
IIa: Si



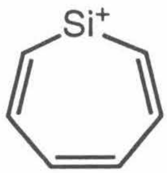
Ib: C
IIb: Si

Unlike toluene which yields only $C_7H_7^+$ structural isomers upon ionization, phenylsilane yields structural isomers of the $C_6SiH_8^+$ and the $C_6SiH_6^+$ cations as well. The structural isomers of $C_6SiH_6^+$ are indicated by **IIIa, IIIb** and **IIIc**. **IIIa** is an Si^+-benzene ion-molecule complex. Theoretical calculations indicate that it is the most stable of the three isomeric forms of the $C_6SiH_6^+$ cations. Evidence for its existence comes from the fact that upon isolation of $C_6SiH_6^+$ in a mixture of phenylsilane and deuterated benzene, $C_6SiH_6^+$ transfers an Si^+ moiety to C_6D_6. $C_6SiH_6^+$ also consists of an unreactive population of ions which is proposed to have the structure indicated by **IIIc**. It is proposed that the other reactive $C_6SiH_6^+$ cation has the structure indicated by **IIIb**.

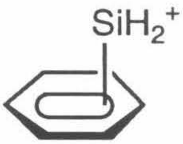
IIIa



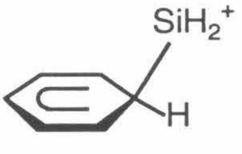
IIIb



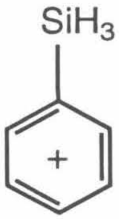
IIIc



IVa



IVb



IVc

$C_6SiH_8^+$ has two structural isomers. One of the structural isomers transfers an SiH_2^+ moiety to C_6D_6 indicating that it has the structural form represented by either **IVa** or **IVb**. The other structural isomer is proposed to have the structure indicated by **IVc**. Chapter 5 discusses the structural assignments of the $C_6SiH_8^+$ and $C_6SiH_6^+$ cations and their gas phase chemistry in great detail.

Summary of Previous Studies of the Gas Phase Ion Chemistry of Substituted Silanes and Related Systems.

The gas phase ion chemistry of silane has been extensively investigated. Lampe pioneered these investigations. He and his research group have looked at the reactions of ions derived by electron impact ionization of silane with silane[24-26] and have examined the radiation chemistry implications of these reactions.[27] Lampe and co-workers were also the first to generate protonated silane by proton transfer from acidic species such as CH_5^+[28] and $C_3H_8^+$.[29] They measured the proton affinity of silane to be 153 ± 3 kcal mol^{-1}. More recently Mandich and co-workers have looked at sequential ion-molecule condensation reactions in silane.[30] Their goal was to identify reaction pathways that lead to the formation of particulates. In their studies they found that the sequential reactions usually lead to bottlenecks that prevented further growth of the ionic species. They, however, discovered that reactions of ions derived from silane with water lead to the formation of large ions.[31] Ion-molecule reactions in water-silane mixtures were previously examined by Lampe and co-workers.[32] Mandich and co-workers also examined the reactions of silicon clusters with silane and deuterated silane.[33] Such studies are useful in providing information at the molecular level about the deposition of silicon.

Endothermic reactions have been examined in silane by Gasper and co-workers[34] and by Boo and Armentrout.[35] By examining the reactions of Si^+ with silane, Boo and Armentrout[35] were able to obtain the heats of formation of SiH_n, SiH_n^+ (n= 1-3) and $Si_2H_n^+$ (n= 0-3) species. A value of 3.23 ± 0.04 eV for the Si^+—H bond dissociation energy in SiH^+ has been obtained by Elkind and Armentrout[36] from measurements of the threshold for the reaction of Si^+ with H_2. The electron impact appearance potentials of the SiH_n^+ (n= 0-3) from SiH_4 have been measured by Potzinger and Lampe.[37] From this work the upper limits of the heats of formation of the SiH_n^+ (n= 0-3) were derived as well as the value of the heat of formation of SiH_3. More recently Lampe and co-workers[38] have employed the technique of molecular beam photoionization mass spectrometry to obtain the heats of formation of SiH_n^+ (n= 2-3) and the ionization potentials of SiH_n (n= 2-3). The electron affinity of SiH_3 and other organosilyl radicals such as $C_6H_5SiH_2$, $C_6H_5(CH_3)SiH$, CH_3SiH_2 and $(CH_3)_3Si$ have been determined by Brauman and co-workers.[39]

Ion-molecule reactions in disilane have been studied by Lampe and co-workers.[40] Mandich and Reents[31] have studied ion-molecule reactions in water-disilane mixtures. The electron impact appearance potentials of parent and fragment ions from disilane have been studied by Potzinger and Lampe.[37] Ruscic and Berkowitz have studied disilane using photoionization mass spectrometry.[41] From these studies they have obtained the ionization potential of Si_2H_6 and the heats of formation of a variety of fragment ions. In addition, Ruscic and

Berkowitz[42] have prepared transient species Si_2H_5, Si_2H_4, Si_2H_3 and Si_2H_2 for the first time by reacting F atoms with Si_2H_6 and have measured the adiabatic ionization potentials of these species. They have obtained heats of formation of the radicals Si_2H_5, Si_2H_4, Si_2H_3 and Si_2H_2. They also obtain values of the proton affinities of Si_2H_2 and Si_2H_4.

Ion-molecule reaction in methylsilane was also originally studied by Lampe and co-workers.[43,44] Shin and Beauchamp[45] have obtained the hydride affinities of $(CH_3)SiH_2^+$, $(CH_3)_2SiH^+$ and $(CH_3)_3Si^+$. Lim and Lampe[46] as well as Armentrout and co-workers[47] have examined the reactions of Si^+ with methylsilane. From their studies, Armentrout and co-workers have been able to extract thermodynamic information for a number of disilicon ions and monosilicon ions and radicals. The reactions of transition metal ions with methylsilane has been studied by Beauchamp and co-workers.[48] Mandich *et al.*[49] have looked at the reactions of silicon clusters with methylsilane. Jacobson and co-workers[50] have looked at the reactions of $SiH_x(CH_3)_{3-x}^+$ ($x = 1$-3) with propene and 2-methyl propene. Beauchamp and co-workers[51] have studied the methyl silanes $Si(CH_3)_nH_{4-n}$ ($n = 0$-3) by using photoionization mass spectrometry.

Murphy and Beauchamp[8] have studied the gas phase ion chemistry of the fluoromethylsilanes in great detail using photoionization mass spectrometry and ion cyclotron resonance spectrometry. Reactions of Si^+ with SiF_4 have been studied by Armentrout and co-workers.[52] Bohme and co-workers have studied the reactions of Si^+ with a number of small organic and inorganic molecules. A number of these studies are summarized in a review article by Bohme.[53] A recent and interesting observation by Bohme and co-workers is the capture of Si^+ by benzene leading to the formation of the Si^+— benzene ion-molecule complex (**IIIa**).[54] The formation of this ion by electron impact ionization of phenylsilane and its structural assignment is discussed in Chapter 5 of this thesis.

The photoelectron spectrum of SiH_4 has been measured by Pullen *et al*.[55] SiH_3 has been generated by reactions of F atoms with SiH_4 and its photoelectron spectrum has been measured by Dyke and co-workers.[56] The photoelectron spectra of the halosilanes have been studied in great detail.[57] McLean[58] has measured the photoelectron spectrum of phenylsilane. Beauchamp and co-workers[59] have produced $SiCl_2$ by pyrolysis of $SiHCl_3$ and SiH_2Cl_2 and have measured its photoelectron spectrum. Recently Irikura *et al*.[60] have measured the REMPI mass spectrum of $SiCl_3$ by generating this molecule through the reactions of $SiHCl_3$ with F atoms. From this study they have obtained the heat of formation of $SiCl_3$.

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Chapter II

Examination of Ion-Molecule Reactions in Chlorosilanes by FT-ICR Spectrometry and Determination of the Relative Stabilities of Chlorosilyl Ions

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Abstract

Gas-phase positive ion-molecule chemistry in pure chlorosilanes, in silane-chlorosilane mixtures, and in a binary mixture of chlorosilanes has been investigated by the technique of Fourier Transform Ion Cyclotron Resonance Spectrometry for the species SiH_nCl_{4-n} (n = 0-2). Reaction pathways and rate constants have been determined for the reactions of chlorosilyl ions with neutral chlorosilanes and with silane, and for the reactions of the silyl ion with chlorosilanes. In pure chlorosilanes, chlorosilyl ions react with neutral chlorosilanes by Cl^- and H^- transfer processes. In silane-chlorosilane mixtures, additional disproportionation reactions are observed. The mechanisms of these reactions are discussed. Where possible, the relative Cl^- and H^- affinities of the chlorosilyl ions have been quantitatively determined. The H^- and Cl^- affinities of SiH_3^+ are both greater than those of the chlorosilyl ions. The values of the Cl^- affinity of the chlorosilyl ions are within 1.2 kcal mol^{-1} of each other and decrease in the order $SiH_2Cl^+ > SiHCl_2^+ \approx SiCl_3^+$, while the values of their H^- affinity decrease in the order $SiCl_3^+ > SiHCl_2^+, SiH_2Cl^+$. The relative heats of formation of chlorosilyl ions have been determined to an accuracy limited by the available literature values of the heats of formation of neutral chlorosilanes, and are critically examined using electronic structure considerations.

Introduction

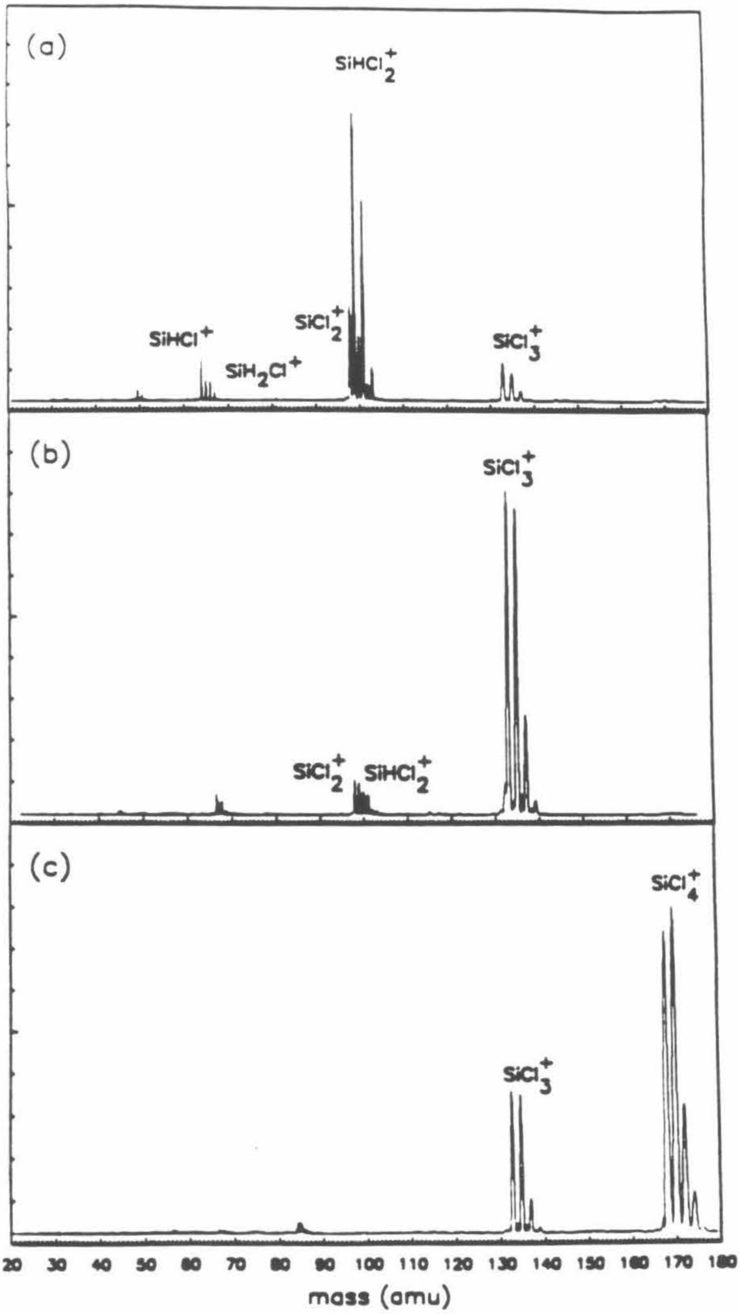
Halosilanes are extensively used in energetic chemical processes such as plasma enhanced chemical vapor deposition[1]. Under such conditions, ion-molecule processes will be operative and are likely to play an important role.[2] In spite of this, the systematic delineation of the pathways and energetics of ion-molecule reactions in halosilanes[3,4] is still in its infancy. In contrast, the ion-molecule chemistry of halomethanes has been explored in great detail.[5-9] Although they are congeners, halosilanes and halomethanes differ significantly in their properties and reactivity[10] including their ionic fragmentation behavior. For example, unlike the parent ions of some of the chloromethanes, the parent ions of analogous chlorosilanes are insignificant products even at low electron energies (Figures 1a and 1b). Hence, the ion-molecule chemistry in chlorosilanes will be dominated by fragment ions, principal amongst which are the chlorosilyl ions.

It is of interest to compare the reactions of halosilyl ions (with halosilanes) to the reactions of halomethyl ions (with halomethanes). The halomethyl ions are known to undergo hydride and halide transfer reactions with neutral halomethanes as shown in reaction 1. The enthalpy of this reaction measures the relative

$$R_1^+ + R_2X \rightarrow R_2^+ + R_1X \tag{1}$$

stabilities of the ions, R_1^+ and R_2^+, with respect to the reference base

Figure 1. FT-ICR mass spectra of (a) SiH_2Cl_2 at a pressure of 1.5×10^{-6} torr ($SiCl_3^+$ observed in the spectrum is from the approximately 7% $SiHCl_3$ impurity in the sample), (b) $SiHCl_3$ at a pressure of 1.0×10^{-6} torr, (c) $SiCl_4$ at a pressure of 0.7×10^{-6} torr. All three mass spectra were recorded after a 15 msec, 14 eV electron beam pulse. The set of peaks at half the mass of the most intense set of peaks in each of the three spectra is due to the first harmonic of the cyclotron frequency of these ions.


(a)
SiHCl$_2^+$
SiHCl$^+$
SiH$_2$Cl$^+$
SiCl$_2^+$
SiCl$_3^+$
(b)
SiCl$_3^+$
SiCl$_2^+$
SiHCl$_2^+$
(c)
SiCl$_4^+$
SiCl$_3^+$
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
mass (amu)

X^- commonly taken to be F^-, Cl^-, or H^-. Such stabilities are usually described by the X^- affinity, $D(R^+\cdots X^-)$, which is defined as the negative of the enthalpy of reaction 2. Lower values of $D(R^+\cdots X^-)$

$$R^+ + X^- \rightarrow RX \qquad (2)$$

indicate greater stability of the ion with respect to the reference base X^-.

Halogen substituted methyl cations show interesting trends in their stabilities with respect to different bases. Trends in the chloride and hydride affinities of the chloromethyl ions,[11] sequences 3 and 4 respectively, indicate that chlorine substitution stabilizes the positive carbon center in a similar manner for both reference bases. In

Chloride Affinities: $CH_3^+ > CH_2Cl^+ > CHCl_2^+ > CCl_3^+$ (3)

Hydride Affinities: $CH_3^+ > CH_2Cl^+ > CHCl_2^+ > CCl_3^+$ (4)

contrast, trends in the fluoride and hydride affinities of the fluoromethyl ions,[7,11] sequences 5 and 6 respectively, show non-monotonic behavior. This is suggestive of a complex role played

Fluoride Affinities: $CH_3^+ > CF_3^+ > CHF_2^+ > CH_2F^+$ (5)

Hydride Affinities: $CH_3^+ > CF_3^+ > CH_2F^+ > CHF_2^+$ (6)

by fluorine substitution. Of related importance is the role played by halogen substitution on the stability of silicenium ions. The relative stabilities of two different silicenium ions, R_1^+ and R_2^+, with respect to the base X^- can be quantitatively determined by carrying out X^- transfer equilibria measurements[12] between the two ions. When experimental conditions do not permit the determination of the value of the equilibrium constant, the relative stabilities of the two ions may be compared by observing the direction of the X^- transfer reaction (reaction 1).

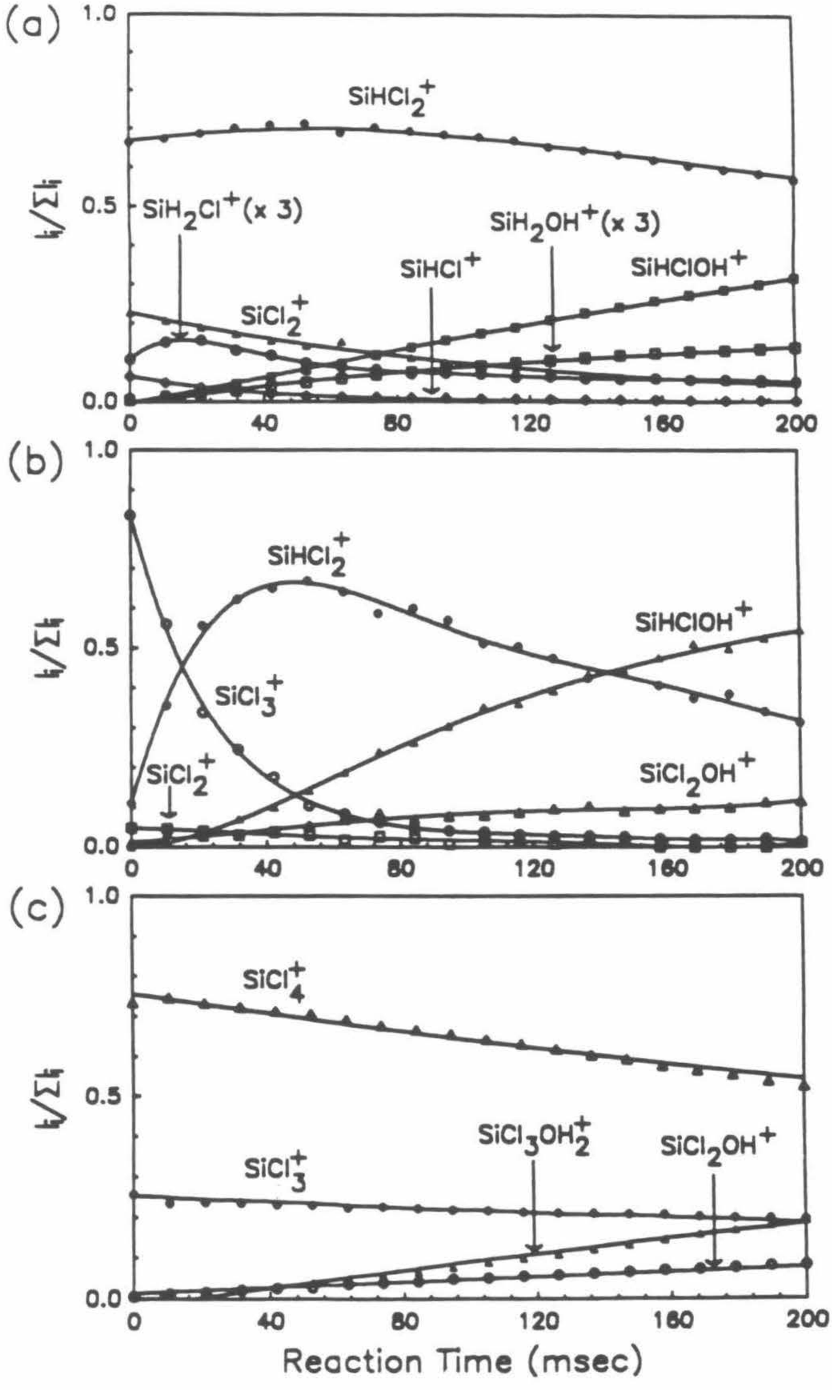
In this paper, we report a systematic study of the kinetics and pathways of bimolecular ion-molecule reactions for the chlorosilanes SiH_nCl_{4-n} (n = 0-2) using the technique of Fourier Transform Ion Cyclotron Resonance (FT-ICR) Spectrometry.[13a,b] We determine the relative stabilities of the chlorosilyl ions, and use this to examine the effect of successive chlorine substitution in neutral chlorosilanes. From the experimental results and the available heats of formation of neutral chlorosilanes, we calculate the relative heats of formation of the chlorosilyl ions and critically examine these values using electronic structure considerations.

Experimental Section

The experimental aspects of FT-ICR spectrometry have been discussed in the literature.[13b] Only details relevant to these experiments are outlined in this section. The FT-ICR spectrometer used to conduct these experiments comprises a conventional 1 inch cubic trapping cell located between the poles of a Varian 15 inch electromagnet maintained at 1 T. Data collection is accomplished with an Ion-Spec Omega/386 FT-ICR data system and associated electronics. Neutral gases are introduced into the cell at desired pressures by separate leak valves. Neutral gas pressures are measured with a Schultz-Phelps ion gauge calibrated against an MKS (type 390 HA-00001SP05) capacitance manometer.

Ions were formed by electron impact ionization of neutral molecules with electron energies in the range 14-16 eV. The temporal variation of ion abundances in neutral backgrounds of SiH_2Cl_2, $SiHCl_3$, and $SiCl_4$, as shown in Figure 2, was indicative of ongoing ion-molecule reaction processes in these systems. Reactant ions, formed either by electron impact ionization of neutral molecules or by ion-molecule reactions, were selectively isolated in the cell by ejecting unwanted ions using the technique of double resonance[14] and/or frequency sweep excitation.[15] Non-resonant translational excitation of reactant ions was minimized by using the lowest possible levels of radio frequency fields during ion ejection. The shortest possible frequency sweep excitation pulses were used during ion detection. Interrelations of reactants and products in a complicated reaction scheme involving consecutive and/or parallel reactions was possible by continuously ejecting all the isotopomers of a particular ion and observing changes in the reaction processes. The identified reaction scheme was used to perform a psuedo-first order

Figure 2. Temporal variation of ion abundances following (a) ionization by a 13 msec, 14 eV electron beam pulse in SiH_2Cl_2 at a pressure of 2.0×10^{-6} torr, (b) ionization by a 3 msec, 14 eV electron beam pulse in $SiHCl_3$ at a pressure of 3.6×10^{-6} torr, and (c) ionization by a 15 msec, 14 eV electron beam pulse in $SiCl_4$ at a pressure of 0.6×10^{-6} torr. In all the three figures, intensities of all hydroxyl ions resulting from the occurrence of reaction 8 and subsequent reactions have been summed together and represented as the intensity of the product ion of reaction 8.


(a)
SiHCl$_2^+$
SiH$_2$Cl$^+$(x 3)
SiH$_2$OH$^+$(x 3)
SiHCl$^+$
SiHClOH$^+$
SiCl$_2^+$
(b)
SiHCl$_2^+$
SiHClOH$^+$
SiCl$_3^+$
SiCl$_2^+$
SiCl$_2$OH$^+$
(c)
SiCl$_4^+$
SiCl$_3$OH$_2^+$
SiCl$_2$OH$^+$
SiCl$_3^+$
1.0
0.5
0.0
0
40
80
120
160
200
$I_i/\Sigma I_i$
Reaction Time (msec)

reaction kinetics[16] simulation of the experimentally observed temporal variation of reactant and product ion abundances. Rate constants of individual reaction steps were obtained from the simulation of the reaction kinetics when the reactant ion for that particular step was initially isolated. The reported rate constants are averages of several different sets of experimental data taken at different pressures of neutral gases. In reactions where ions have multiple isotopomers, the isotopomer abundances of each ion were summed to give single ion abundances. The temperature was assumed to be 298.15 K.

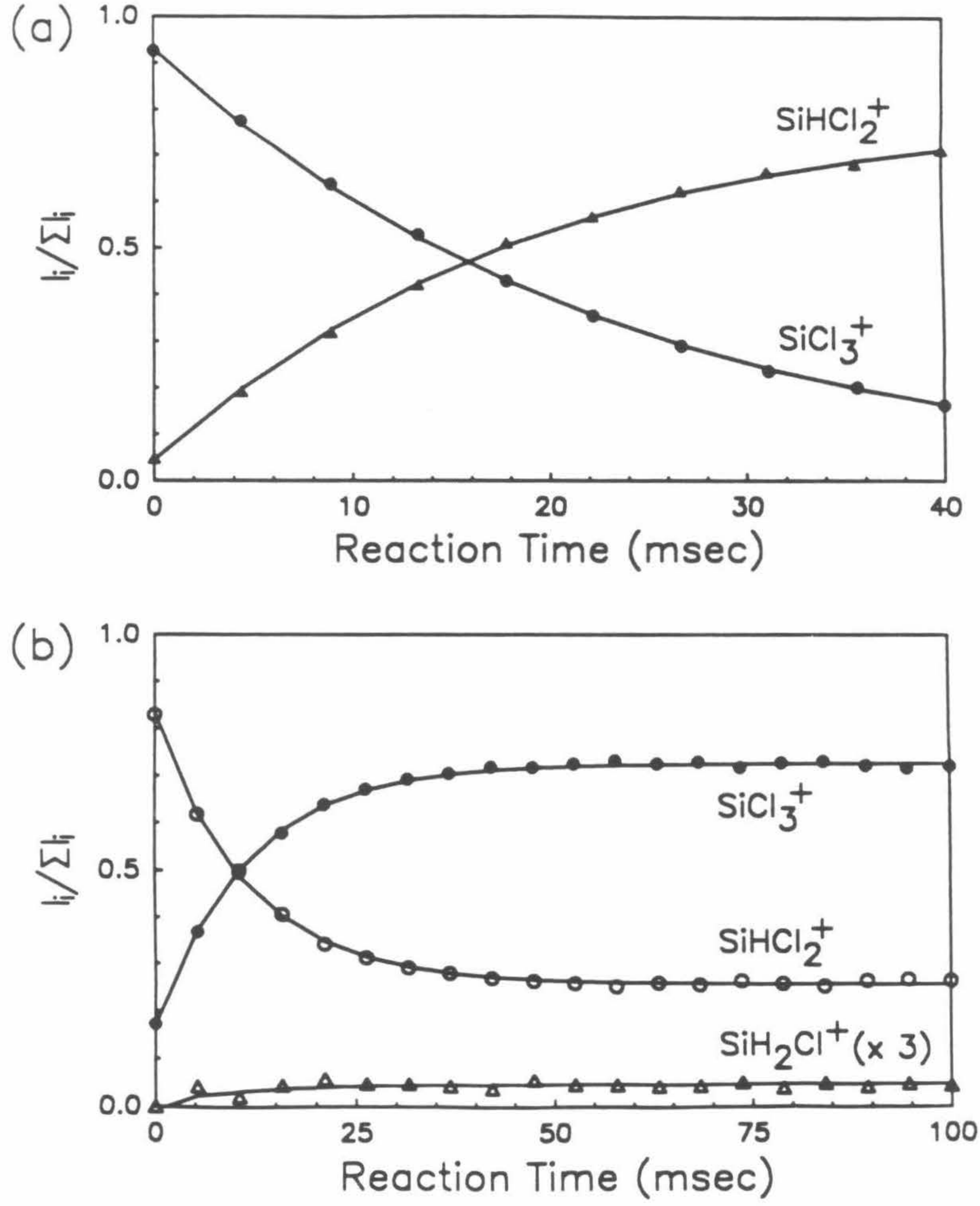
Equilibrium constants, K_{eq}, were determined by separately measuring the rate constants for the forward and backward processes since parallel and/or sequential reactions were present in all cases. For example, in reaction 7, isolation of $SiCl_3^+$ in $SiHCl_3$

$$SiCl_3^+ + SiHCl_3 \rightleftarrows SiHCl_2^+ + SiCl_4 \qquad (7)$$

permitted the determination of the forward rate constant. Isolation of $SiHCl_2^+$ in a 1:1.8 mixture of SiH_4 and $SiCl_4$ enabled the reverse rate constant to be determined. The experimentally observed and numerically simulated temporal variation of ion abundances for these two reactions are shown in Figures 3a and 3b respectively.

The principal errors in the rate constants (estimated to be up to ± 20%) arise from uncertainties in pressure measurement. Additional

Figure 3. Temporal variation of ion abundances following (a) the isolation of $SiCl_3^+$ in $SiHCl_3$ at a pressure of 4.8×10^{-6} torr, and (b) the isolation of $SiHCl_2^+$ in a 1:1.8 SiH_4-$SiCl_4$ mixture at a total pressure of 4.9×10^{-6} torr. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics.


(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
0
10
20
30
40
Reaction Time (msec)
$SiHCl_2^+$
$SiCl_3^+$
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
0
25
50
75
100
Reaction Time (msec)
$SiCl_3^+$
$SiHCl_2^+$
SiH_2Cl^+(x 3)

errors may be introduced by the mass dependent sensitivity of the instrument.[17] Reactions of the chlorosilyl ions with background water was also a problem. Even at a background pressure of 10^{-8} torr, the chlorosilyl ions were observed to react with water at long trapping times. These processes can be generalized by reaction 8, where x = 0-2.

$$SiH_xCl_{3-x}^+ + H_2O \rightarrow SiH_xCl_{2-x}OH^+ + HCl \qquad (8)$$

The product ion of reaction 8 undergoes further reactions with neutral water, chlorosilane, and silane molecules. However, by maintaining chlorosilane pressures in the range of 1.0-5 x 10^{-6} torr, the error introduced by the reactions of chlorosilyl ions with water molecules was minimized. Where necessary, the reactions of chlorosilyl ions with water molecules were taken into consideration in the simulation of the reaction kinetics.

Dichlorosilane and trichlorosilane were obtained from Petrarch Systems Incorporated. The dichlorosilane sample that was used contained a small amount of trichlorosilane impurity (≈7% as determined from the mass spectrum shown in Figure 1a) which could not be easily removed. Other chemicals were commercially obtained from other sources. All chemicals were subject to several freeze-pump-thaw cycles before use.

Results

Ion-molecule reactions. **SiH_2Cl_2.** The mass spectrum of SiH_2Cl_2 that was recorded at an electron impact energy of 14 eV is shown in Figure 1a. The principal ions are $SiHCl_2^+$ (67%), SiH_2Cl^+ (3%), $SiCl_2^+$ (22%), and $SiHCl^+$ (8%). Figure 2a shows the temporal variation of these ions. At long times the ions that remain in the cell are $SiHCl_2^+$ and SiH_2Cl^+ which react with background water by reaction 8. Isolation of these ions in SiH_2Cl_2 at pressures of 0.7-3.0 x 10^{-6} torr allowed reactions 9-12 to be identified.

$$SiHCl_2^+ + SiH_2Cl_2 \left[\begin{array}{ll} \rightarrow SiH_2Cl^+ + SiHCl_3 & (9) \\ \\ \rightarrow SiHCl_2^+ + SiH_2Cl_2 & (10) \end{array} \right.$$

$$SiH_2Cl^+ + SiH_2Cl_2 \left[\begin{array}{ll} \rightarrow SiH_2Cl^+ + SiH_2Cl_2 & (11) \\ \\ \rightarrow SiHCl_2^+ + SiH_3Cl & (12) \end{array} \right.$$

Reactions 9 and 11 are formally Cl^- transfer reactions, while reactions 10 and 12 formally represent H^- transfer processes. Both reactions 9 and 12 are operative when either $SiHCl_2^+$ or SiH_2Cl^+ is initially isolated in a neutral background of SiH_2Cl_2. This fact is taken into consideration in performing numerical simulations of experimentally observed temporal variation of ion abundances (shown in Figure 4). The rate constants of these reactions as well as those of other reactions are reported in Table 1.

Figure 4. Temporal variation of ion abundances following the isolation of (a) $SiHCl_2^+$ and (b) SiH_2Cl^+ in 2.2×10^{-6} and 1.7×10^{-6} torr of SiH_2Cl_2 respectively. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics.

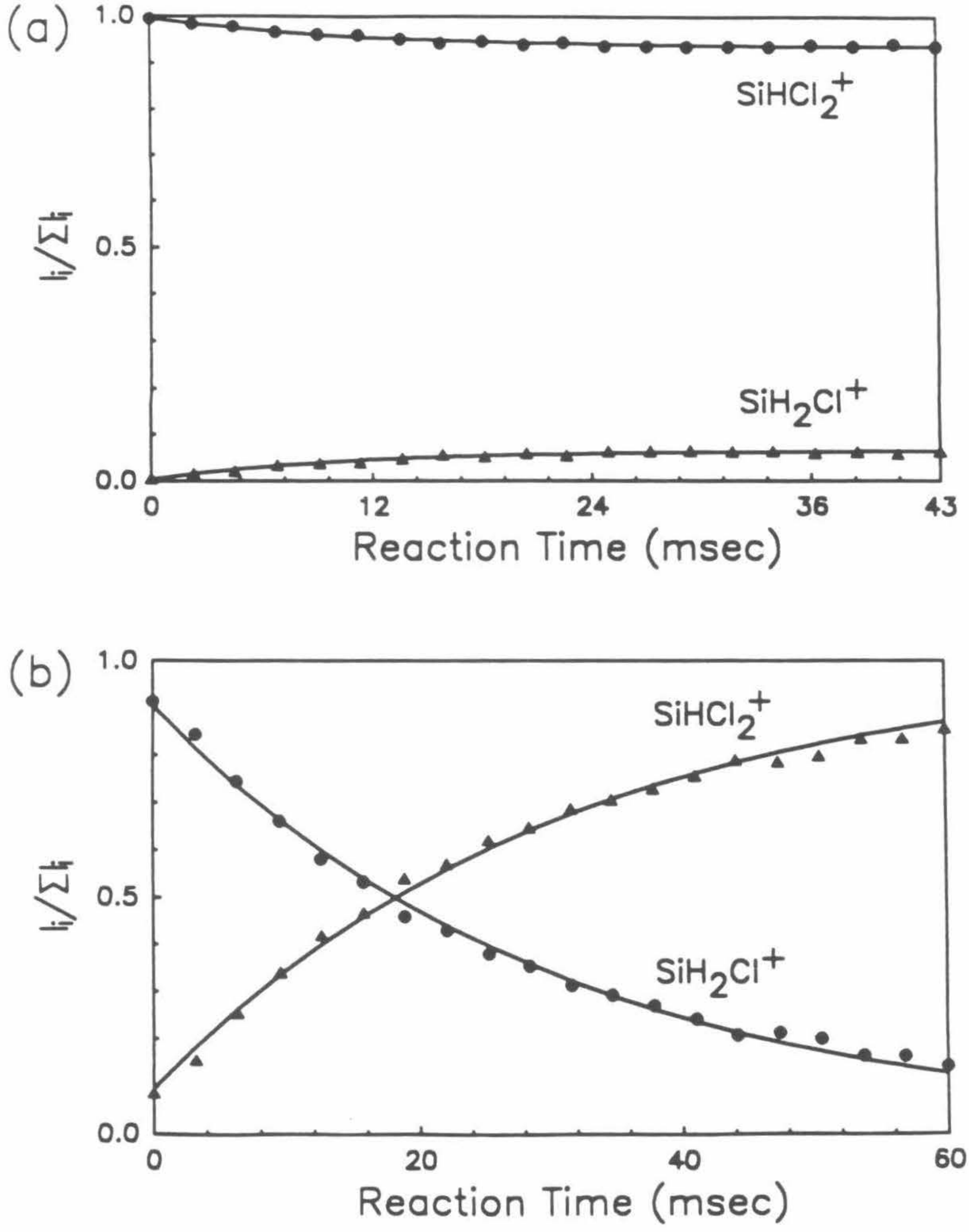

(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$SiHCl_2^+$
SiH_2Cl^+
0
12
24
36
43
Reaction Time (msec)
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$SiHCl_2^+$
SiH_2Cl^+
0
20
40
60
Reaction Time (msec)

Table 1. Rate constants of ion-molecule reactions.

Species / Mixture	Reaction	Reaction Type	k^a	k/k^b_{ADO}
SiH_2Cl_2	$SiHCl_2^+ + SiH_2Cl_2 \rightarrow SiH_2Cl^+ + SiHCl_3$	Cl^- transfer	1.0	0.08
	$\rightarrow SiHCl_2^+ + SiH_2Cl_2$	H^- transfer	3.9	0.3
	$SiH_2Cl^+ + SiH_2Cl_2 \rightarrow SiHCl_2^+ + SiH_3Cl$	H^- transfer	7.6	0.6
$SiHCl_3$	$SiCl_3^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiCl_4$	Cl^- transfer	2.9	0.3
	$SiHCl_2^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiHCl_3$	Cl^- transfer	4.2	0.4
	$\rightarrow SiCl_3^+ + SiH_2Cl_2$	H^- transfer	0.25	0.02
$SiCl_4$	$SiCl_3^+ + SiCl_4 \rightarrow SiCl_3^+ + SiCl_4$	Cl^- transfer	2.6	0.3 (0.2)
	$SiCl_4^+ + SiCl_4 \rightarrow SiCl_4^+ + SiCl_4$	Electron transfer	4.8	0.6 (0.4)
SiH_2Cl_2-$SiHCl_3$	$SiCl_3^+ + SiH_2Cl_2 \rightarrow SiH_2Cl^+ + SiCl_4$	Cl^- transfer	1.0	0.09
	$\rightarrow SiHCl_2^+ + SiHCl_3$	H^- transfer	1.5	0.1
$SiHCl_3$-SiH_4	$SiCl_3^+ + SiH_4 \rightarrow SiHCl_2^+ + SiH_3Cl$	Disproportionation	2.1	0.2
	$\rightarrow SiH_2Cl^+ + SiH_2Cl_2$	Disproportionation	0.5	0.05
	$SiH_2Cl^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiH_2Cl_2$	Cl^- transfer	13.2	1.1
	$SiHCl_2^+ + SiH_4 \rightarrow SiH_2Cl^+ + SiH_3Cl$	Disproportionation	0.07	0.006
	$SiH_3^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiH_3Cl$	Cl^- transfer	16.5	1.0
	$\rightarrow SiCl_3^+ + SiH_4$	H^- transfer		
	$\rightarrow SiH_2Cl^+ + SiH_2Cl_2$	Disproportionation		
$SiCl_4$-SiH_4	$SiHCl_2^+ + SiCl_4 \rightarrow SiCl_3^+ + SiHCl_3$	Cl^- transfer	5 .8	0.6 (0.5)
	$SiH_2Cl^+ + SiCl_4 \rightarrow SiCl_3^+ + SiH_2Cl_2$	Cl^- transfer	17.3	1.5 (1.2)
	$\rightarrow SiHCl_2^+ + SiHCl_3$	Disproportionation	1.4	0.1 (0.1)
	$SiH_3^+ + SiCl_4 \rightarrow SiCl_3^+ + SiH_3Cl$	Cl^- transfer	17.0	1.1 (0.9)
	$\rightarrow SiHCl_2^+ + SiH_2Cl_2$	Disproportionation		
	$\rightarrow SiH_2Cl^+ + SiHCl_3$	Disproportionation		
SiH_2Cl_2-SiH_4	$SiH_3^+ + SiH_2Cl_2 \rightarrow SiH_2Cl^+ + SiH_3Cl$	Cl^- transfer	14.5	0.8
	$\rightarrow SiHCl_2^+ + SiH_4$	H^- transfer	7.0	0.4

---

[a] Rate constant in units of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}. [b] Defined as reaction efficiency. k_{ADO} is given by the average dipole orientation theory discussed in reference 18. The dipole constants of all the molecules, and the polarizabilities of all the molecules except $SiCl_4$ were obtained from reference 19. The polarizability of $SiCl_4$ was obtained from references 20 and 3b. The values of k/k_{ADO} shown in parentheses are based on the polarizability of $SiCl_4$ obtained from reference 3b. The large error limits in this latter value have not been taken into consideration.

Reactions 10 and 11 were studied by recording the temporal variation of reactant and product ion abundances upon isolation of the ^{35}Cl isotopomer of the reactant ion. Both these reactions are complicated by the occurrence of side reactions 9 and 12. From the experimentally observed temporal variation of the abundances of the isotopomers of $SiHCl_2^+$, it was garnered that reaction 10 occurs at a rate approximately half an order of magnitude faster than that at which reaction 9 occurs. In order to simplify the reaction kinetics, the temporal variation of the abundances of the isotopomers of $SiHCl_2^+$ were renormalized to reflect the occurrence of only reaction 10. Numerical simulations were performed accordingly.

From the experimentally observed variation of ion abundances upon isolation of the ^{35}Cl isotopomer of SiH_2Cl^+, it was seen that reactions 11 and 12 occur at comparable rates. Hence, it was not considered justifiable to obtain the rate constant of reaction 11 by following a procedure analogous to the one used to obtain the rate constant for reaction 10.

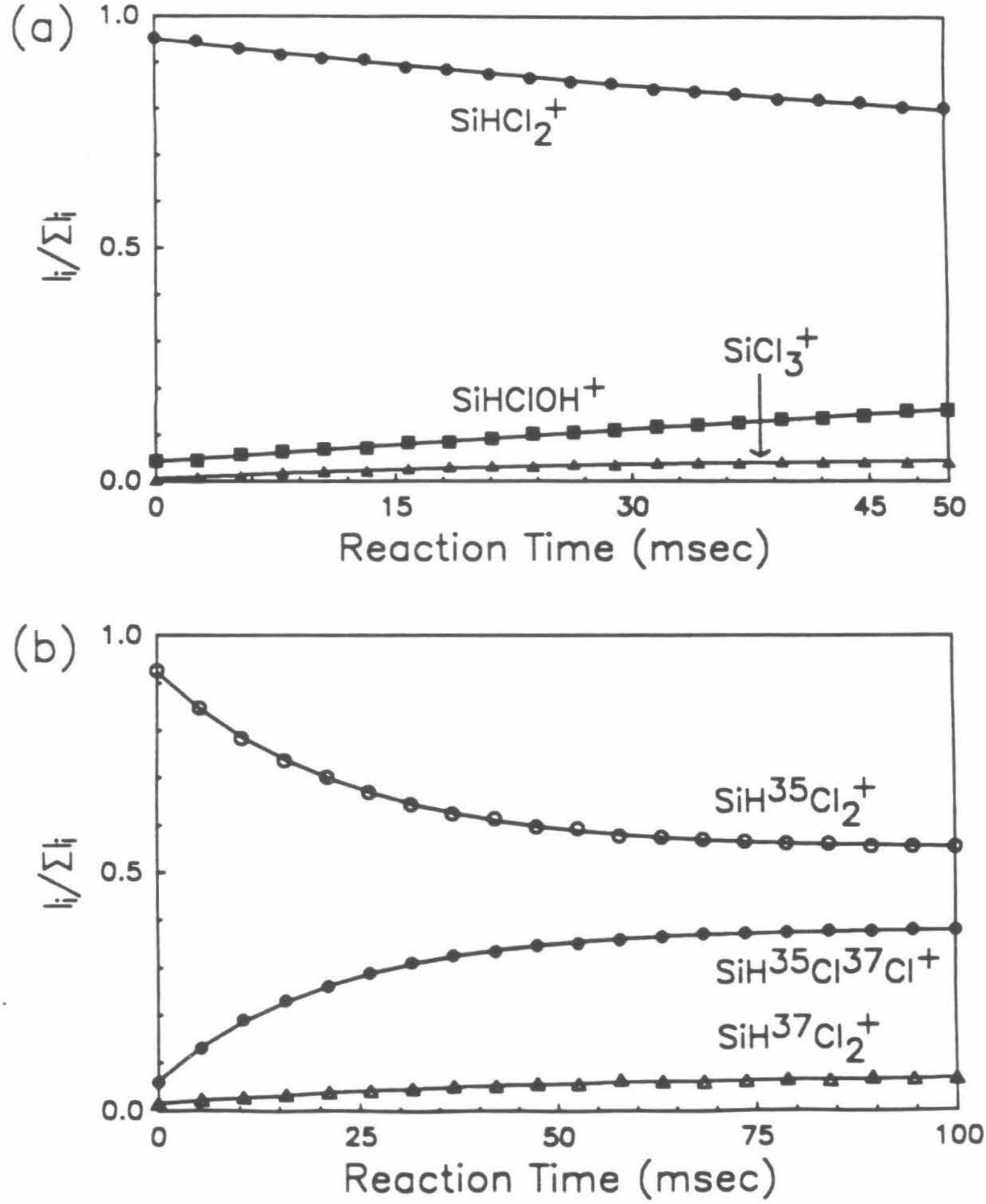
$SiHCl_3$. The mass spectrum of $SiHCl_3$ recorded at an electron impact energy of 14 eV is shown in Figure 1b. The principal ions are $SiCl_3^+$ (86%), $SiHCl_2^+$ (7%), and $SiCl_2^+$ (7%). Figure 2b shows the temporal variation of these ions. At long times the only ions that remain in the cell are $SiHCl_2^+$ and $SiCl_3^+$, which react with background water by reaction 8. Upon isolation of these ions in $SiHCl_3$ at pressures of $1.0\text{-}5 \times 10^{-6}$ torr, reactions 13-16 were identified.

$$\mathrm{SiCl_3^+ + SiHCl_3} \begin{cases} \rightarrow \mathrm{SiHCl_2^+ + SiCl_4} & (13) \\ \rightarrow \mathrm{SiCl_3^+ + SiHCl_3} & (14) \end{cases}$$

$$\mathrm{SiHCl_2^+ + SiHCl_3} \begin{cases} \rightarrow \mathrm{SiHCl_2^+ + SiHCl_3} & (15) \\ \rightarrow \mathrm{SiCl_3^+ + SiH_2Cl_2} & (16) \end{cases}$$

Reactions 13 and 15 are formally Cl^- transfer reactions, while reactions 14 and 16 formally represent H^- transfer processes. Isolation of either $SiCl_3^+$ or $SiHCl_2^+$ results in the occurrence of both reactions 13 and 16. Reaction 13 is about 20 times faster than reaction 16. The rate constant of reaction 16 was obtained from numerical simulations of the experimental data upon initial isolation of $SiHCl_2^+$. As evidenced by Figure 5a, it is important to take reaction 8 into consideration in the analysis of the results. The rate constant of reaction 16 is determined within an uncertainty of ± 25% as indicated by the 95% confidence limits of fits to experimental data. Reactions 14 and 15 were studied by isolating the ^{35}Cl isomers of $SiCl_3^+$ and $SiHCl_2^+$, respectively. Experimental investigations of both these reactions are complicated by the occurrence of side reactions 13 and 16. As the experimental variation of the ion abundances indicated that reaction 15 is an order of magnitude faster than reaction 16, it was possible to ignore side reactions. The rate constant for reaction 15

Figure 5. Temporal variation of ion abundances in $SiHCl_3$. (a) Isolation of $SiHCl_2^+$ in $SiHCl_3$ at a pressure of 2.9 x 10^{-6} torr. (b) Establishment of equilibrium amongst the isotopomers of $SiHCl_2^+$ following the isolation of the $SiH^{35}Cl_2^+$ isotopomer in $SiHCl_3$ at a pressure of 2.1 x 10^{-6} torr. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics.


(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$SiHCl_2^+$
$SiCl_3^+$
$SiHClOH^+$
0
15
30
45
50
Reaction Time (msec)
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$SiH^{35}Cl_2^+$
$SiH^{35}Cl^{37}Cl^+$
$SiH^{37}Cl_2^+$
0
25
50
75
100
Reaction Time (msec)

was obtained from numerical simulations of renormalized data sets which reflect the occurrence of only reaction 15. The experimentally observed and the numerically simulated variation of ion abundances are shown in Figure 5b. Experimental variation of ion abundances indicated that reactions 13 and 14 occur at comparable rates. Hence, it was not possible to obtain the rate constant of reaction 14 by following a procedure analogous to the one used to obtain the rate constant of reaction 15.

$SiCl_4$. The mass spectrum of $SiCl_4$ recorded at an electron impact energy of 14 eV is shown in Figure 1c. The principal ions are $SiCl_4^+$ (72%) and $SiCl_3^+$ (28%). Figure 2c shows the temporal variation of these ions. At neutral pressures of $1.0\text{-}2.0 \times 10^{-6}$ torr both $SiCl_3^+$ and $SiCl_4^+$ undergo isotopomer exchange reactions with $SiCl_4$, processes 17 and 18 respectively. Reaction 17 formally represents a Cl^- transfer

$$SiCl_3^+ + SiCl_4 \rightarrow SiCl_3^+ + SiCl_4 \tag{17}$$

$$SiCl_4^+ + SiCl_4 \rightarrow SiCl_4^+ + SiCl_4 \tag{18}$$

process, while reaction 18 presumably proceeds by electron transfer. $SiCl_3^+$ reacts with water by reaction 8, while the reaction of $SiCl_4^+$ with water is given by process 19. $SiCl_3OH_2^+$ does not react further

$$SiCl_4^+ + H_2O \rightarrow SiCl_3OH_2^+ + Cl \tag{19}$$

with either $SiCl_4$ or H_2O.

SiH_2Cl_2-$SiHCl_3$. Advantage was taken of the approximately 7% impurity of $SiHCl_3$ in SiH_2Cl_2 to generate $SiCl_3^+$ and study its reactions with SiH_2Cl_2 under conditions where its reactions with $SiHCl_3$ could be ignored. At neutral pressures of 1.0-2.0 x 10^{-6} torr $SiCl_3^+$ was seen to undergo both Cl^- and H^- transfer reactions with SiH_2Cl_2, reactions 20 and 21 respectively. In numerical simulations

$$SiCl_3^+ + SiH_2Cl_2 \left\{ \begin{array}{ll} \rightarrow SiH_2Cl^+ + SiCl_4 & \qquad (20) \\ \\ \rightarrow SiHCl_2^+ + SiHCl_3 & \qquad (21) \end{array} \right.$$

performed to extract rate constants for reactions 20 and 21, the occurrence of reactions 9 and 12 were also taken into account. Attempts were made at generating SiH_2Cl^+ in mixtures containing predominantly $SiHCl_3$ in order that its reactions with $SiHCl_3$ could be studied without interference from its reactions with SiH_2Cl_2. However, since SiH_2Cl_2 is not a copious source of SiH_2Cl^+ and the electron impact mass spectrum of SiH_2Cl_2 in the region of SiH_2Cl^+ is congested by the presence of $SiHCl^+$, reasonable abundances of translationally unexcited SiH_2Cl^+ could not be isolated. Observation of the reactions of SiH_2Cl^+ in equal concentrations of SiH_2Cl_2 and $SiHCl_3$ was not considered because of the complexity of competing processes in this system.

$SiHCl_3$-SiH_4. Initial isolation of SiH_3^+ and $SiCl_3^+$, respectively, in mixtures of SiH_4 and $SiHCl_3$ indicated that the ions SiH_3^+, SiH_2Cl^+, $SiHCl_2^+$ and $SiCl_3^+$ were participating in reaction processes. The formation of SiH_2Cl^+ in the reaction mixture suggested that a disproportionation reaction was occurring. In order to identify the various ion-molecule reactions occurring in this mixture, reactions occurring upon the initial isolation of each of the four ions at total neutral pressures in the range 0.7-5 x 10^{-6} torr were systematically studied. Isolation of $SiCl_3^+$ in a mixture containing predominantly SiH_4 enabled reactions 22 and 23 to be studied without interference from reactions 13, 16 and 24. Isolation of SiH_3^+, SiH_2Cl^+ and $SiHCl_2^+$ in 1:1-3:1 SiH_4-$SiCl_4$ mixtures allowed reactions 24-28 to be identified.

$$\mathrm{SiCl_3^+ + SiH_4} \begin{cases} \rightarrow \mathrm{SiH_2Cl^+ + SiH_2Cl_2} & (22) \\ \rightarrow \mathrm{SiHCl_2^+ + SiH_3Cl} & (23) \end{cases}$$

$$\mathrm{SiH_2Cl^+ + SiHCl_3 \rightarrow SiHCl_2^+ + SiH_2Cl_2} \qquad (24)$$

$$\mathrm{SiHCl_2^+ + SiH_4 \rightarrow SiH_2Cl^+ + SiH_3Cl} \qquad (25)$$

$$\mathrm{SiH_3^+ + SiHCl_3} \begin{cases} \rightarrow \mathrm{SiH_2Cl^+ + SiH_2Cl_2} & (26) \\ \rightarrow \mathrm{SiHCl_2^+ + SiH_3Cl} & (27) \\ \rightarrow \mathrm{SiCl_3^+ + SiH_4} & (28) \end{cases}$$

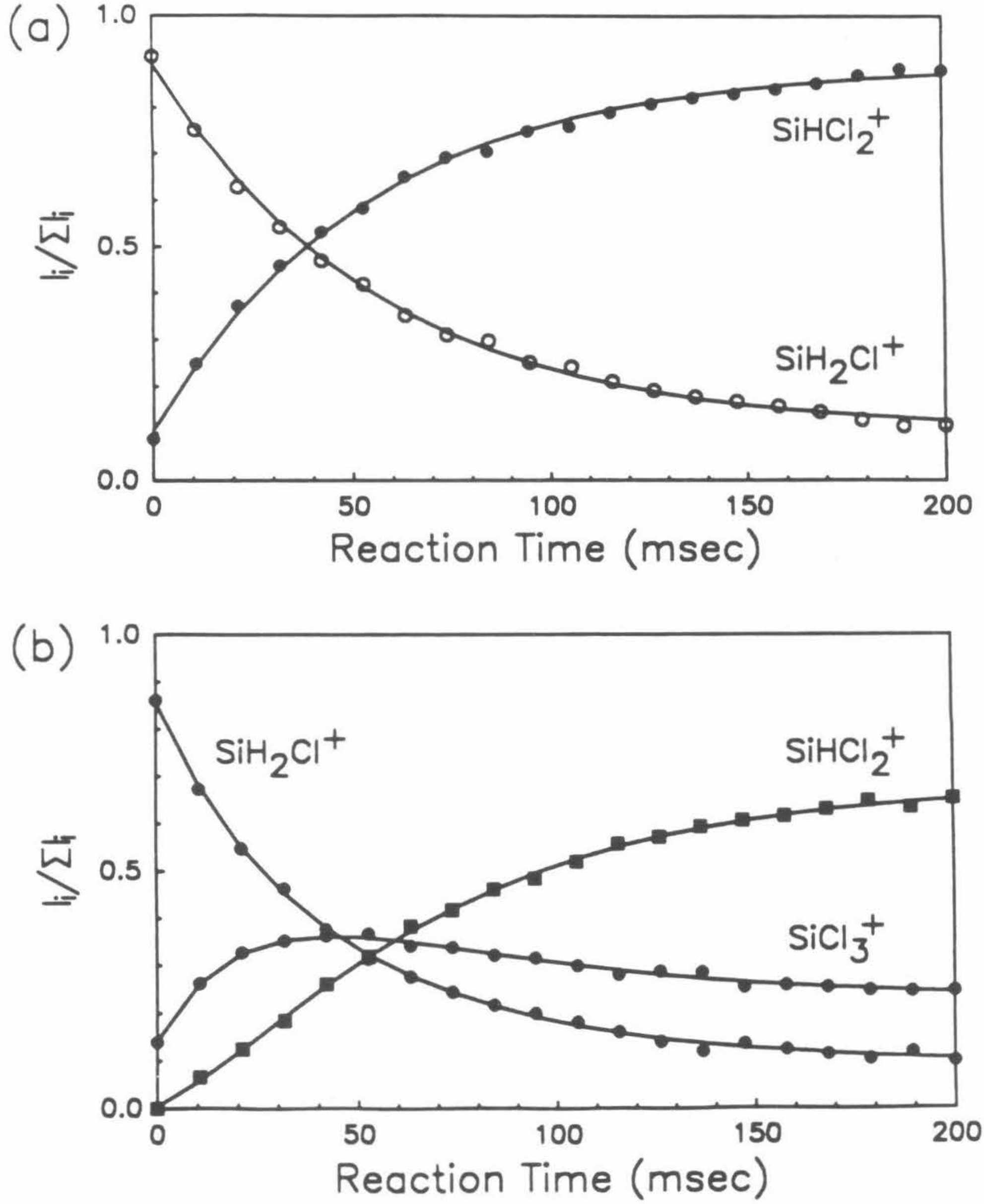
Despite performing experiments with different compositions of SiH_4-$SiHCl_3$ mixtures it was not possible to observe reaction 29 which formally involves a H^- transfer from $SiHCl_3$ to SiH_2Cl^+. The

$$SiH_2Cl^+ + SiHCl_3 \rightarrow SiCl_3{}^+ + SiH_3Cl \qquad (29)$$

experimentally observed and numerically simulated variation of ion abundances upon initial isolation of SiH_2Cl^+ in this mixture is shown in Figure 6a.

Reactions 22, 23, 25, and 26 are disproportionation reactions. They are so termed because they suggest a partitioning of atoms rather than the transfer of a basic moiety like Cl^- or H^- between the two Si centers of the reaction intermediate. Reaction 25 is very slow ($k = 0.07 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}) and is determined to an accuracy of ± 25%. Reactions 24 and 27 are formally Cl^- transfer reactions while reaction 28 formally represents a H^- transfer process. The reaction channels of $SiH_3{}^+$ with $SiHCl_3$ were identified by continuously ejecting either $SiCl_3{}^+$ or $SiHCl_2{}^+$. Isolation of $SiH_3{}^+$ followed by continuous ejection of $SiCl_3{}^+$ resulted in the production of both SiH_2Cl^+ and $SiHCl_2{}^+$. The initial rate of production of SiH_2Cl^+ is too high to be accounted for by reaction 25 alone. This indicates that reaction 26 must be occurring The initial rate of production of $SiHCl_2{}^+$ is much greater than the rate of production of SiH_2Cl^+, suggesting that $SiHCl_2{}^+$ is primarily produced by reaction 27.

Figure 6. Temporal variation of ion abundances following (a) the isolation of SiH_2Cl^+ in a 2:1 mixture of SiH_4-$SiHCl_3$ at a total pressure of 1.1 x 10^{-6} torr, (b) the isolation of SiH_2Cl^+ in a 4:1 mixture of SiH_4-$SiCl_4$ at a total pressure of 2.1 x 10^{-6} torr. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics.

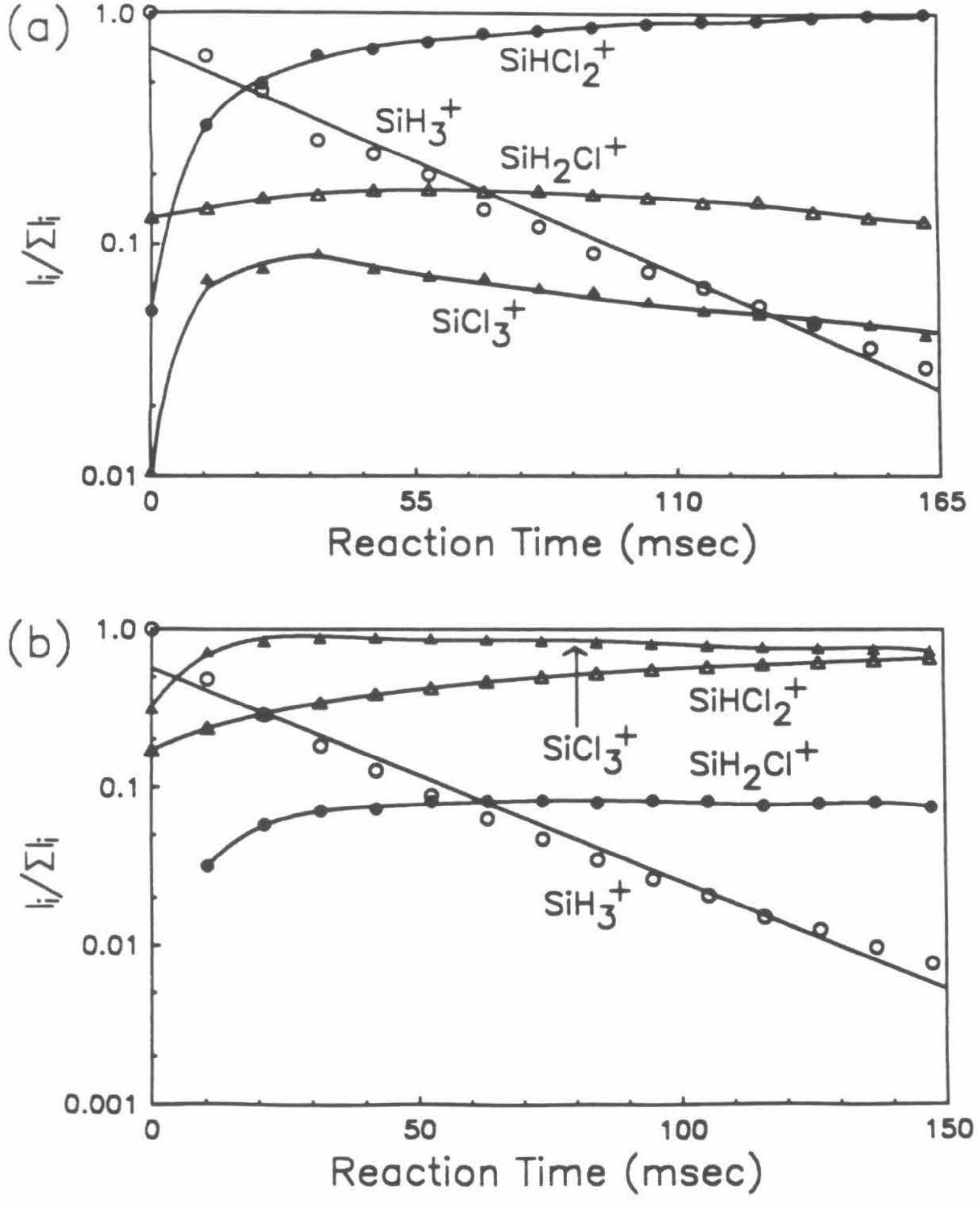

(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
0
50
100
150
200
Reaction Time (msec)
$SiHCl_2^+$
SiH_2Cl^+
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
SiH_2Cl^+
$SiHCl_2^+$
$SiCl_3^+$
0
50
100
150
200
Reaction Time (msec)

Isolation of SiH_3^+ followed by continuous ejection of $SiHCl_2^+$ resulted in the production of both $SiCl_3^+$ and SiH_2Cl^+. The production of $SiCl_3^+$ suggests that reaction 28 is operative. As noted before, under the experimental conditions employed, SiH_2Cl^+ does not yield $SiCl_3^+$ by a bimolecular process in this mixture. Rate constants for reactions 26, 27 and 28 have not been determined. The total rate constant for the reaction of SiH_3^+ with $SiHCl_3$ is determined from the slope of plots of log $[SiH_3^+]$ vs t as shown in Figure 7a. The Cl^- transfer process, represented by reaction 27, is the major product channel in the reaction of SiH_3^+ with $SiHCl_3$.

$SiCl_4$-SiH_4. Initial isolation of SiH_3^+ and $SiCl_3^+$, respectively, in mixtures of SiH_4 and $SiCl_4$ indicated that the ions SiH_3^+, SiH_2Cl^+, $SiHCl_2^+$ and $SiCl_3^+$ were participating in reaction processes. The presence of SiH_2Cl^+ and $SiHCl_2^+$ in the reaction mixture suggest that disproportionation reactions occur in this mixture as well. The reactions occurring upon initial isolation of SiH_3^+, SiH_2Cl^+, and $SiHCl_2^+$ at total neutral pressures in the range 1.0-2.0 x 10^{-6} were systematically studied. Upon isolation in 0.4:1-1.7:1 mixtures of $SiCl_4$ and SiH_4, $SiHCl_2^+$ was found to undergo reaction 30 as can be seen from Figure 3b. Isolation of SiH_2Cl^+ in 1:2-1:3 mixtures of $SiCl_4$ and

$$SiHCl_2^+ + SiCl_4 \rightarrow SiCl_3^+ + SiHCl_3 \qquad (30)$$

Figure 7. Temporal variation of ion abundances following the isolation of SiH_3^+ in (a) a 2.3:1 SiH_4-$SiHCl_3$ mixture at a total pressure of 0.9 x 10^{-6} torr, and (b) a 1.6:1 SiH_4-$SiCl_4$ mixture at a total pressure of 1.3 x 10^{-6} torr.


(a)
1.0
0.1
0.01
$I_i/\Sigma I_i$
0
55
110
165
Reaction Time (msec)
$SiHCl_2^+$
SiH_3^+
SiH_2Cl^+
$SiCl_3^+$
(b)
1.0
0.1
0.01
0.001
$I_i/\Sigma I_i$
0
50
100
150
Reaction Time (msec)
$SiHCl_2^+$
$SiCl_3^+$
SiH_2Cl^+
SiH_3^+

SiH_4 enabled reactions 31 and 32 to be identified. Figure 6b shows the

$$\mathrm{SiH_2Cl^+ + SiCl_4} \longrightarrow \begin{cases} \mathrm{SiHCl_2^+ + SiHCl_3} & (31) \\ \mathrm{SiCl_3^+ + SiH_2Cl_2} & (32) \end{cases}$$

experimentally observed and numerically simulated variation of ion abundances for this case.

Isolation of SiH_3^+ in a 1:1.5 mixture of $SiCl_4$ and SiH_4 enabled reactions 33-35 to be studied. Reactions 30, 32, and 35 are formally

$$\mathrm{SiH_3^+ + SiCl_4} \longrightarrow \begin{cases} \mathrm{SiH_2Cl^+ + SiHCl_3} & (33) \\ \mathrm{SiHCl_2^+ + SiH_2Cl_2} & (34) \\ \mathrm{SiCl_3^+ + SiH_3Cl} & (35) \end{cases}$$

Cl^- transfer reactions while reactions 31, 33, and 34 are disproportionation reactions. Identification of the reactions of SiH_3^+ with $SiCl_4$ was accomplished by following a procedure similar to the one used to identify the reactions of SiH_3^+ with $SiHCl_3$. Isolation of SiH_3^+ followed by continuous ejection of $SiCl_3^+$ resulted in the production of both $SiHCl_2^+$ and SiH_2Cl^+. The initial rate of production of SiH_2Cl^+ is much greater than that if it would have been produced by reaction 25 alone. Also, the initial rate of production of $SiHCl_2^+$ is greater than that of SiH_2Cl^+. From these two observations it is concluded that reaction processes 33 and 34 are both operative.

Isolation of SiH_3^+ followed by continuous ejection of SiH_2Cl^+ resulted in the production of both $SiHCl_2^+$ and $SiCl_3^+$. The greater initial rate of production of $SiCl_3^+$ compared to that of $SiHCl_2^+$ indicates that reaction 35 must be operative. This process, which represents Cl^- transfer from $SiCl_4$ to SiH_3^+, is the major product channel in the reaction of SiH_3^+ with $SiCl_4$. Rate constants for reactions 33, 34 and 35 have not been determined. The total rate constant for the reaction of SiH_3^+ with $SiCl_4$ is determined from the slope of plots of log $[SiH_3^+]$ vs t as shown in Figure 7b.

The efficiencies of ion-molecule reactions, given by k/k_{ADO} where k_{ADO} is the ion-molecule collisional rate calculated using the average dipole orientation theory,[18] are listed in Table 1. The value of 1.5 for the efficiency of reaction 32 suggests that the experimental rate constant may be erroneous by at least 35%. The value of k_{ADO} (which reduces to $k_{Langevin}$ for non-polar molecules[18]) for the collision of SiH_2Cl^+ with $SiCl_4$ was calculated using $\alpha(SiCl_4) = 11.27$ Å^3 obtained from reference 20. As stated by the authors this value was most likely derived from available literature values of molar refractions extrapolated from the visible region to $\lambda = \infty$. As such it is difficult to determine the uncertainties associated with this value. Polarizabilities of other non-polar molecules such as CF_4 and SF_6 listed in reference 20 are lower than more recent values obtained from highly reliable dielectric constant measurements[21,22] by 27% and 32% respectively. Weber and Armentrout[3b] obtained $\alpha(SiCl_4) =$ 18 (+ 13, - 9) Å^3 from experimentally measured total reaction crosssections for the process $Si^+ + SiCl_4$ at center of mass kinetic energies below ~ 0.6 eV by assuming unit reaction efficiency. Ion-molecule reaction efficiencies (ignoring error limits) calculated using this latter value for reactions involving $SiCl_4$ are listed in parentheses. Such a procedure leads to a value of 1.2 for the efficiency of reaction 32, which suggests that within experimental uncertainty reaction 32 proceeds at the collisional rate. Reaction 31 is the other product channel in the reaction of SiH_2Cl^+ with $SiCl_4$. Owing to the considerable uncertainty in the value of $\alpha(SiCl_4)$ and the possibility of the Langevin theory in placing an upper limit on these type of ion-molecule reaction rates, we estimate the uncertainty in the experimentally determined rate constants of reactions 31 and 32 to be up to ± 30 %.

SiH_2Cl_2-SiH_4. Isolation of SiH_3^+ in 1:1-1:4 mixtures of SiH_4 and SiH_2Cl_2 at total neutral pressures of $1.0\text{-}2.0 \times 10^{-6}$ enabled the identification of reactions 36 and 37.

$$SiH_3^+ + SiH_2Cl_2 \left\{ \begin{array}{ll} \rightarrow SiH_2Cl^+ + SiH_3Cl & \qquad (36) \\ \\ \rightarrow SiHCl_2^+ + SiH_4 & \qquad (37) \end{array} \right.$$

Reaction 36 is formally a Cl^- transfer reaction while reaction 37 formally represents a H^- transfer process. In simulations performed to obtain the rate constants of reactions 36 and 37 the occurrence of reactions 9 and 12 were taken into consideration.

Chloride and hydride affinities of the chlorosilyl ions. From the rate constants of the reactions of chlorosilyl ions with chlorosilanes, the value of the equilibrium constant, $K_{eq} = k_f/k_r$, is determined for reaction 38 where R_1^+ and R_2^+ belong to the set of ions SiH_2Cl^+,

$$R_1^+ + R_2X \rightleftarrows R_2^+ + R_1X \tag{38}$$

$SiHCl_2^+$ and $SiCl_3^+$ when X is Cl, and where R_1^+ and R_2^+ belong to the set of ions $SiHCl_2^+$ and $SiCl_3^+$ when X is H. From the value of K_{eq} the standard free energy change of reaction 38, $\Delta G^o_{298.15}$, is determined using equation 39. The standard entropy change of

$$\Delta G = - RT \ln K_{eq} \tag{39}$$

reaction 38, $\Delta S^o_{298.15}$, is given by equation 40 where $\Delta S^o_{ion\ 298.15}$ is

$$\Delta S^o_{298.15} = \Delta S^o_{ion\ 298.15} + \Delta S^o_{neut\ 298.15} \tag{40}$$

equal to the difference in standard entropies of the product and reactant ions and $\Delta S^o_{neut\ 298.15}$ is equal to the difference in standard entropies of the product and reactant neutral molecules. $\Delta S^o_{ion\ 298.15}$ is calculated using standard expressions[23] for differences in translational, rotational, and vibrational entropies of the two ions. The chlorosilyl ions are assumed to be planar, and bond lengths and bond angles are based on bond lengths and bond angles respectively of neutral chlorine substituted singlet silylene radicals.[24] The vibrational frequencies of the ions are assumed to be the same as those of the corresponding neutral chlorosilyl radical.[26] $\Delta S^o_{neut\ 298.15}$ is calculated using available literature values of the standard entropies of neutral chlorosilanes.[29] $\Delta H^o_{298.15}$ for reaction 38 is calculated using equation 41. This provides us with quantitative

$$\Delta H^o_{298.15} = \Delta G^o_{298.15} + T\Delta S^o_{298.15} \tag{41}$$

differences between the values of the Cl^- affinity of SiH_2Cl^+, $SiHCl_2^+$ and $SiCl_3^+$, and the quantitative difference between the H^- affinity of $SiHCl_2^+$ and $SiCl_3^+$ as listed in Table 2.

Quantitative differences between the values of the Cl^- affinity of SiH_3^+ and the chlorosilyl ions as well as those between the values of the H^- affinity of SiH_2Cl^+ and either $SiHCl_2^+$ or $SiCl_3^+$ have not been obtained because reactions of chlorosilyl ions with SiH_3Cl were not examined. However, since SiH_3^+ abstracts Cl^- from SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$ at close to collisional rates the Cl^- affinity of SiH_3^+ can be taken to be greater than those of the chlorosilyl ions. The non-observation of reaction 29 suggests that the H^- affinity of $SiCl_3^+$ is greater than that of SiH_2Cl^+. Neither $SiHCl_2^+$ nor $SiCl_3^+$ abstracts H^- from SiH_4 under the experimental conditions employed in the present studies. While this prevents the determination of quantitative differences between the values of the H^- affinity of SiH_3^+

Table 2. Chloride and Hydride transfer reaction enthalpies[a].

Reaction	$\Delta G^o = -RT\ln K_{eq}$	$T\Delta S^o$	ΔH^o
$SiH_2Cl^+ + SiHCl_3 \rightleftarrows SiHCl_2^+ + SiH_2Cl_2$	−1.5 ± 0.2	0.5	−1.0 ± 0.2
$SiH_2Cl^+ + SiCl_4 \rightleftarrows SiCl_3^+ + SiH_2Cl_2$	−1.7 ± 0.3	1.0	−0.7 ± 0.3
$SiHCl_2^+ + SiCl_4 \rightleftarrows SiCl_3^+ + SiHCl_3$	−0.4 ± 0.2	0.5	0.1 ± 0.2
$SiCl_3^+ + SiH_2Cl_2 \rightleftarrows SiHCl_2^+ + SiHCl_3$	−1.1 ± 0.3	0.2	−0.9 ± 0.3

---

[a] All data in units of kcal mol^{-1} at T = 298.15 K.

and either $SiHCl_2^+$ or $SiCl_3^+$, it suggests that the H^- affinity of SiH_3^+ is greater than that of either $SiHCl_2^+$ or $SiCl_3^+$.

On the basis of these observations, the ordering of the Cl^- and H^- affinities of the chlorosilyl ions are given by sequences 42 and 43 respectively.

Chloride Affinities: $SiH_3^+ > SiH_2Cl^+ > SiHCl_2^+ \approx SiCl_3^+$ (42)

Hydride Affinities: $SiH_3^+ > SiCl_3^+ > SiHCl_2^+, SiH_2Cl^+$ (43)

Even though SiH_2Cl^+ is observed to abstract H^- from SiH_2Cl_2 (reaction 12), the non-observation of the reverse process prevents the H^- affinities of SiH_2Cl^+ and $SiHCl_2^+$ from being ordered.

Discussion

Ionic chain reactions and thermochemistry of neutral species. The net effect of the occurrence of both reactions 13 and 16 in $SiHCl_3$ is to disproportionate two molecules of $SiHCl_3$ into one molecule of $SiCl_4$ and one molecule of SiH_2Cl_2 as shown in reaction 44. Such a process is known as an ionic chain reaction[25] and has been

$$2SiHCl_3 \rightarrow SiCl_4 + SiH_2Cl_2 \qquad (44)$$

previously observed in CH_2F_2[6]. In this system, two molecules of CH_2F_2 disproportionate to give one molecule of CHF_3 and one molecule of CH_3F as shown in reaction 45. The two elementary steps

$$2CH_2F_2 \rightarrow CHF_3 + CH_3F \qquad (45)$$

comprising reaction 45 are both exothermic and involve F^- and H^- abstraction from CH_2F_2 by CHF_2^+ and CH_2F^+ respectively. The reaction enthalpies of the two elementary steps comprising reaction 44, namely reactions 13 and 16, are -0.1 ± 0.2 and 0.9 ± 0.3 kcal mol^{-1} respectively. Within experimental uncertainty reaction 13 is thermoneutral, while reaction 16 is endothermic by at least 0.6 kcal mol^{-1}. This latter reaction is observable under low pressure conditions such as those employed in these experiments because its endothermicity is not high enough to preclude its observation over typical ICR experimental time scales (10 - 1000 msec).

The enthalpy of reaction 44 given by the sum of the enthalpies of reactions 13 and 16 is 0.8 ± 0.5 kcal mol^{-1}. This indicates that the difference in successive heats of formation of neutral chlorosilanes from SiH_2Cl_2 to $SiCl_4$ decreases by 0.8 ± 0.5 kcal mol^{-1} as the extent of chlorine substitution is increased.

The enthalpies of reaction 44 calculated from various available sets of thermochemical data are listed in Table 3. The value calculated from the BPP[31] data set is in considerable disagreement with the value determined in the present work. The accuracies of neutral heats of formation calculated by BPP have been criticized previously.[26,32] The enthalpy of reaction 44 obtained from the FS[28] data set is in reasonable agreement with the present experimental result in that it could be higher than the latter value by as little as 0.9 kcal mol^{-1}. The values of the enthalpy of reaction 44 calculated from the the JANAF Tables[29] and the CATCH Tables[30] are in agreement with the present experimental result provided the large uncertainties associated with neutral heats of formation are taken into account. The mean value of the enthalpy of reaction 44 calculated from the HM[27] data set is in excellent agreement with the present experimental result. None the less, on the basis of the experimental determination of the enthalpy of reaction 44, it is not possible to comment on the actual values of the heats of formation of the three neutral chlorosilane species involved in the reaction.

Reaction 46, which is a chain reaction observed in SiH_2Cl_2,

$$2SiH_2Cl_2 \rightarrow SiHCl_3 + SiH_3Cl \qquad (46)$$

comprises the elementary steps 9 and 12. Reaction 9 is endothermic by 1.0 ± 0.2 kcal mol^{-1}. The enthalpy of reaction 12 has not been determined. The enthalpies of reaction 46 calculated from the available data sets are shown in Table 3. The value of 6 kcal mol^{-1} derived from the BPP data set is likely to be erroneous because even if reaction 12 is endothermic, it is unlikely to be endothermic by more than 0.2 ± 0.2 kcal mol^{-1} [33], leading to the overall endothermicity of

Table 3. Heat of formation of neutral chlorosilanes and enthalpy of chain reactions.

molecule / reaction	(ΔH^o_f or ΔH^o_{rxn})[a]					
	HM[b]	FS[c]	JANAF[d]	CATCH[e]	BPP[f]	This Work
SiH_4	8.2 ± 1.0	---	8.2 ± 0.5	8.3 ± 0.3	8.3	---
SiH_3Cl	−32.0 ± 1.1	−32.4 ± 2.5	−33.9 ± 2.0	−48.0 ± 5.0	−38.0	---
SiH_2Cl_2	−74.4 ± 1.1	−75.3 ± 2.0	−76.6 ± 3.0	−80.0 ± 10.0	−79.8	---
$SiHCl_3$	−117.1 ± 1.1	−119.3 ± 1.5	−118.6 ± 1.0	−115.2 ± 0.3	−115.2	---
$SiCl_4$	−158.4 ± 1.0	−158.4 ± 0.3	−158.4 ± 0.3	−158.4 ± 0.2	−145.7	---
$2SiH_2Cl_2 \rightarrow SiHCl_3 + SiH_3Cl$	−0.3 ± 4.4	−1.1 ± 2.7[g]	0.7 ± 9.0	−3.2 ± 25.3	6.4	≤ 1.2 ± 0.4[h]
$2SiHCl_3 \rightarrow SiCl_4 + SiH_2Cl_2$	1.5 ± 4.2	4.9 ± 2.7[g]	2.2 ± 5.3	−8 ± 10.8	4.9	0.8 ± 0.5[i]

---

[a] kcal mol^{-1} at 298.15 K. [b] Ref. 27; [c] Ref. 28; [d] Ref. 29; [e] Ref. 30; [f] Ref. 31. [g] Based on the summation of the enthalpies of reactions involving the relevant neutral chlorosilanes determined in reference 28. [h] See text for a discussion of how this value was obtained.

[i] Experimentally determined.

reaction 46 being 1.2 ± 0.4 kcal mol^{-1} at most. Uncertainties associated with neutral heats of formation in all the other data sets make it impossible to calculate the enthalpy of reaction 46 (and thereby the enthalpy of reaction 12) to an accuracy that would be useful in determining the relative ordering of the H^- affinities of SiH_2Cl^+ and $SiHCl_2^+$.

Relative heats of formation of the chlorosilyl ions. The X^- affinities of the chlorosilyl ions can be used in conjunction with the heats of formation of neutral chlorosilanes and equation 47 to obtain the relative heats of formation of the chlorosilyl ions. The heats of formation of neutral chlorosilanes determined theoretically by Ho

$$D(R^+ \cdots X^-) = \Delta H_f\, R^+ + \Delta H_f\, X^- - \Delta H_f\, RX \qquad (47)$$

and Melius (the HM data set) are in good agreement with experimentally determined values.[26,27] The enthalpy of reaction 44 calculated on the basis of these values is in excellent agreement with the value determined in this work. For these reasons the HM data set is used to obtain the values of the relative heats of formation of the chlorosilyl ions as shown in Table 4. The heat of formation of $SiHCl_2^+$ relative to that of $SiCl_3^+$ was determined from the enthalpy of the Cl^- transfer and H^- transfer reactions to be 41.2 ± 2.3 kcal mol^{-1} and 41.8 ± 2.5 kcal mol^{-1} respectively. The value of 41.5 ± 2.8 kcal mol^{-1} listed in Table 4 is the average of these two values. The heat of

Table 4. Heats of formation of $SiH_nCl_{3-n}^+$.

Ion (A^+)	$\{\Delta H^o_f(A^+) - \Delta H^o_f(SiCl_3^+)\}$[a]	$\Delta H^o_f(A^+)$
$SiCl_3^+$	0.0	99.8 ± 1.6[c]
$SiHCl_2^+$	41.5 ± 2.7	141.3 ± 4.4[d]
SiH_2Cl^+	84.7 ± 2.4	184.5 ± 4.0[d]
SiH_3^+	135.3 ± 2.8[b]	235.1 ± 1.2[e]

[a] kcal mol^{-1} at 298.15 K. Unless otherwise stated neutral heats of formation required for calculating this quantity were taken from reference 27 (HM data set) and this quantity was calculated on the basis of equation 47. [b] Calculated using the values of $\Delta H^o_f(SiH_3^+)$ given in ref. 34 and $\Delta H^o_f(SiCl_3^+)$ given in ref. 4. [c] Ref. 4. [d] Based on relative heats of formation of the chlorosilyl ions and the value of $\Delta H^o_f(SiCl_3^+)$ given in ref. 4. [e] Ref. 34.

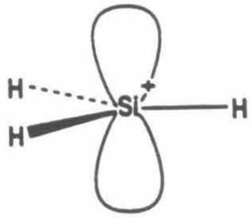
formation of SiH_2Cl^+ relative to that of $SiCl_3^+$ was determined from the enthalpy of the relevant Cl^- transfer reaction to be 84.7 ± 2.4 kcal mol^{-1}. The heat of formation of SiH_3^+ relative to that of $SiCl_3^+$ calculated from the literature values of the heats of formation of SiH_3^+ [34] and $SiCl_3^+$ [4] is 135.3 ± 2.8 kcal mol^{-1}.

It is of interest to consider the electronic structures of the chlorosilyl ions in order to understand the effects successive chlorine substitution on these ions. The effect of single atomic substitution in SiH_3^+ has been considered theoretically.[35-37] In particular, Cl substitution results in the stabilization of the cation through π donation and forward σ polarization effects[36] as shown in Figure 8b and explained in detail below. The SiH_3^+ ion, which has been studied both experimentally[38] and theoretically,[39] is found to be planar with the Si center containing an empty p orbital perpendicular to the plane of the ion as shown in Figure 8a. Such a structure is similar to the one envisaged for CH_3^+.[40,41] The effect of single substitution and, in particular, the effects of multiple substitution in CH_3^+ have been theoretically studied.[42-46] These studies provide us with a starting point for examining the effects of successive Cl substitution in SiH_3^+.

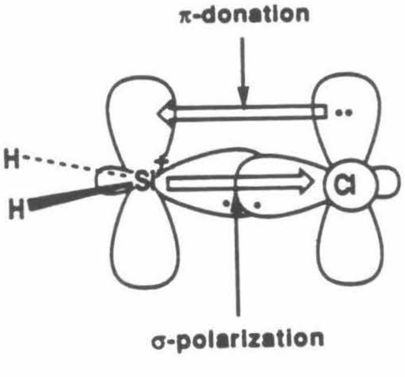
In SiH_2Cl^+ a π system is formed by the 3p orbitals of Si and Cl which are both perpendicular to the plane of the molecule. This is referred to as π donation. The σ bond formed between Si and Cl is polarized towards the Cl atom. The overlap of the 3p orbitals of Si and Cl, which governs the extent of π donation and σ bond

Figure 8. (a) Schematic representation of SiH_3^+. Figure shows an empty Si 3p orbital perpendicular to the plane of the molecular ion. (b) Schematic representation of SiH_2Cl^+. The π donation and the forward σ polarization effects are illustrated.

(a)



(b)



polarization, is maximum for a planar geometry of the ion. As both the π donation and σ bond polarization effects are stabilizing, SiH_2Cl^+ favors a planar geometry.[36] Further substitution of another H atom by a Cl atom results in the cation $SiHCl_2^+$. In a planar configuration of this ion two π systems, one perpendicular to the plane of the molecule and one parallel to the plane of the molecule, are formed. Since the π system which is perpendicular to the plane of the molecule contains four electrons, two electrons occupy a bonding orbital and two occupy a non-bonding orbital. However, greater stabilization of the positively charged Si center in $SiHCl_2^+$ compared to that in SiH_2Cl^+ is not likely to be achieved, unless increased σ bond polarization reduces the bond distance and makes possible increased overlap between the 3p orbitals. The other π system formed in this ion is the in-plane π system which is formed by the two in-plane non σ bonding orbitals of the Cl atoms. This π system contains a fully occupied bonding and a fully occupied anti-bonding orbital and its net effect is destabilizing. Substitution of all the H atoms by Cl results in the cation $SiCl_3^+$, which in a planar configuration forms two π systems- one perpendicular and one parallel to the plane of the ion. The π system perpendicular to the plane of the ion contains one bonding, two non-bonding, and one anti-bonding orbital. Six electrons are accommodated in these orbitals, two in bonding and four in non-bonding orbitals. Greater stabilization of the positive Si center in $SiCl_3^+$ compared to that in SiH_2Cl^+ or $SiHCl_2^+$ is unlikely unless the σ bond polarization reduces the bond distance and makes possible increased overlap between the 3p orbitals when compared to that in either SiH_2Cl^+ or $SiHCl_2^+$. Opposing the shortening of the bond length due to σ bond polarization in the cation is the destabilization caused by the fully occupied in-plane π system which contains a bonding, a non-bonding, and an anti-bonding orbital.

The effects of successive chlorine substitution on the stability of SiH_3^+ can be gauged by the magnitude and sign of the enthalpy of reactions 48 and 49. The enthalpy of reaction 48 is calculated from the relative heats of formation of ions given in Table 4 is 7.4

$$2SiH_2Cl^+ \rightarrow SiH_3^+ + SiHCl_2^+ \tag{48}$$

$$2SiHCl_2^+ \rightarrow SiCl_3^+ + SiH_2Cl^+ \tag{49}$$

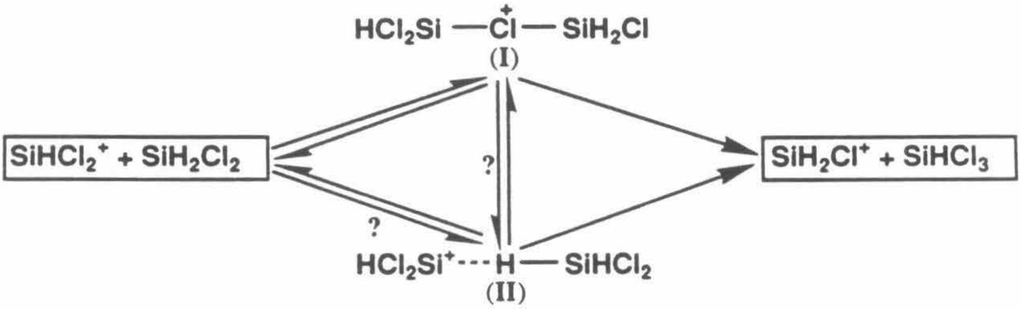
± 10.4 kcal mol^{-1}. Electronic structure considerations suggest that destabilizing interactions due to successive Cl substitution originate from $SiHCl_2^+$ onwards, while the magnitude of the stabilizing interactions are likely to remain largely unchanged. This would make reaction 48 more endothermic than reaction 49. Reaction 49 is made up of the elementary reaction steps 9 and 16. Summation of the enthalpies of reactions 9 and 16 leads to the enthalpy of reaction 49 being 1.9 ± 0.5 kcal mol^{-1}. The enthalpy of reaction 49 calculated from the relative heats of formation of the chlorosilyl ions determined in this study is 1.7 ± 8.0 kcal mol^{-1}. The mean of these two values are in excellent agreement with each other. Hence, it is likely that the relative heats of formation of the chlorosilyl ions determined in this study are reliable within the stated limits of uncertainty. However, the error limits are large enough to mask the effect of successive Cl substitution on the energetics of the chlorosilyl ions.

Reaction of silyl and chlorosilyl ions with chlorosilanes. It is of interest to understand the mechanisms of H^- and Cl^- transfer reactions and disproportionation reactions in chlorosilanes. The H^- and Cl^- transfer reactions in halomethanes are both known to involve halonium ion intermediates.[5,7,47,48] This fact is borne out by the fragmentation of $[H_3C-F-CH_3]^+$,[49] prepared by ion-molecule reactions, into CH_2F^+ and CH_4[5] and the observation of CD_2F^+ and CH_2F^+ as the only product ions in the "hydride transfer" reaction of CD_3^+ with CH_3F.[5] The fluoronium ion complex, $[H_3C-F-CH_3]^+$, can be formed during a collision of CH_3^+ with CH_3F due to electron donation from the fluorine lone pair electrons into the empty orbital of the positive carbon center. In order for $[H_3C-F-CH_3]^+$ to fragment into products that are indicative of H^- transfer from CH_3F to CH_3^+ it is necessary for the transition state structure involved in the fragmentation process to permit intramolecular H atom transfer to one of the two methyl groups. Intramolecular transfer of the bridging fluorine atom to one of the two methyl groups followed by fragmentation would lead to the thermoneutral fluoride transfer process.

In analogy with the halomethanes, chlorosilyl and silyl ions are likely to form chloronium ion intermediates in collisions with neutral chlorosilanes. It is important to ascertain whether the fragmentation of this collision complex is responsible for H^- and Cl^- transfer reactions and disproportionation reactions, or whether some of these reactive processes are due to the rearrangement of this complex into a different complex followed by fragmentation.

Consider first reactions that are indicative of H^- and Cl^- transfer processes. For purposes of clarity, reaction 9 is chosen as an example. The reaction mechanisms are depicted in Scheme I. The strong propensity for electron donation of the chlorine lone pair electrons of SiH_2Cl_2 into the empty Si orbital of $SiHCl_2^+$ is likely to result in the formation of a chloronium ion intermediate complex, $[HCl_2Si-Cl-SiH_2Cl]^+$ (**I**). While it is not clear what multiply bridged structures this complex may support, a structure involving a single bridging chlorine atom is reasonable.[49] We argue against a multiply bonded structure involving simultaneously a bridging H and a bridging Cl atom because of difference in sizes and in bonding characteristics of these two species. The unimolecular fragmentation of this complex through a transition state structure, analogous to the one in dialkylhalonium ions, could result in product channels that are indicative of Cl^- and H^- transfer from SiH_2Cl_2 to $SiHCl_2^+$. Cl^- and H^- transfer processes may be viewed as intramolecular transfer of a Cl and H atom respectively to the $SiHCl_2$ group in this complex followed by its fragmentation.

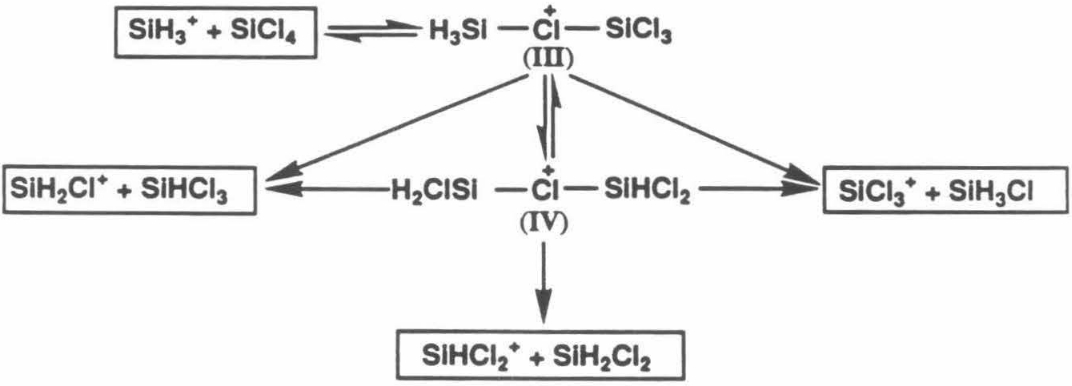
Scheme I


HCl2Si —Cl⁺— SiH2Cl
(I)
SiHCl2⁺ + SiH2Cl2
?
?
SiH2Cl⁺ + SiHCl3
HCl2Si⁺ --- H — SiHCl2
(II)

Rearrangement of intermediate complex **I** into intermediate complex **II**, $[HCl_2Si \cdots H - SiHCl_2]^+$, would be energetically allowed as intermediate complex **II** is likely to be energetically more stable than the asymptotic limit of $SiHCl_2^+ + SiH_2Cl_2$. Complex **II** could also be formed directly during a collision of the reactants. Intramolecular transfer of Cl^- and H^- within complex **II** to a $SiHCl_2^+$ group followed by its fragmentation would result in the Cl^- and H^- transfer processes, reactions 9 and 10, respectively. However, it is unclear if complex **II** would be sufficiently bound to play a role in the Cl transfer reaction, process 9. Isotopic labelling experiments could be useful in clarifying this. For example, if SiD_2Cl^+ is the only product ion in the Cl^- transfer reaction of $SiHCl_2^+$ with SiD_2Cl_2 then it is likely that complex **II** does not participate in the reaction process. The possible equilibrium between complexes **I** and **II** alluded to in Scheme I could lead to isotopic scrambling.

Also interesting, and perhaps more revealing in terms of the reaction potential energy surface are ion-molecule reactions that involve disproportionation channels. Consider, for example, the reaction of SiH_3^+ with $SiCl_4$ which results in three product channels represented by processes, 33, 34, and 35. The reaction mechanisms are depicted in Scheme II. In a collision of the reactants the chloronium ion intermediate complex, $[H_3Si - Cl - SiCl_3]^+$ (**III**), is likely to be formed. Intramolecular transfer of Cl to the SiH_3 group in intermediate complex **III** followed by its fragmentation would lead to reaction 35. Intramolecular transfer of H to the $SiCl_3$ group in

Scheme II


$SiH_3^+ + SiCl_4$
$H_3Si-\overset{+}{Cl}-SiCl_3$
(III)
$SiH_2Cl^+ + SiHCl_3$
$H_2ClSi-\overset{+}{Cl}-SiHCl_2$
(IV)
$SiCl_3^+ + SiH_3Cl$
$SiHCl_2^+ + SiH_2Cl_2$

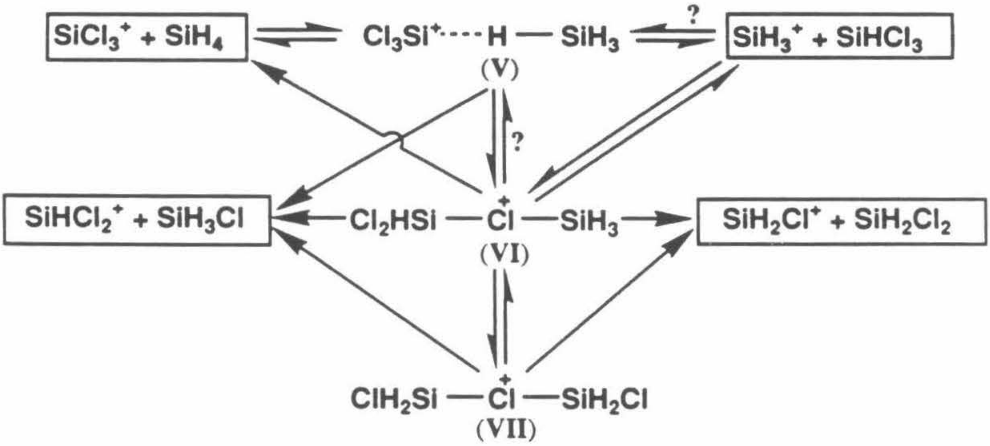
intermediate complex **III** followed by its fragmentation would lead to reaction 33. For reaction process 34 to occur, rearrangement of **III** is necessary. The chloronium ion intermediate, $[H_2ClSi - Cl \text{--} SiHCl_2]^+$ (**IV**), could be a viable intermediate for reaction 34. Intramolecular transfer of Cl to the SiH_2Cl group in intermediate complex **IV** followed by its fragmentation would result in reaction process 34. Intermediate complex **IV** could be formed from intermediate complex **III** through the recombination (assisted by exit channel angular momentum barriers and ion-dipole interactions) of its fragments SiH_2Cl^+ and $SiHCl_3$. The involvement of hydrogen bridged intermediate complexes of the type $[H_2ClSi \cdots H - SiCl_3]^+$ in these reactions cannot be ruled out *a priori* . However, if it is ascertained that intermediate complex **II** is not involved in reaction process 9 then this may be taken to be indicative of the fact that hydrogen bridged complexes are not sufficiently bound to play a role in these reaction processes.

Reaction of chlorosilyl ions with silane. In reactions involving chlorosilyl ions with silanes the formation of a hydrogen bridged complex, for example, intermediate complex $[Cl_3Si \cdots H - SiH_3]^+$(**V**) in the case of the collision of $SiCl_3{}^+$ with SiH_4,could essentially be the first step in the reaction process. The mechanisms of the reactions of $SiCl_3{}^+$ with SiH_4, represented by reaction processes 22 and 23, are depicted in Scheme III. Intramolecular transfer of Cl to the SiH_3 group in intermediate complex **V** followed by its fragmentation would result in reaction 23. For reaction process 22 to occur rearrangement of this complex is necessary. Rearrangement of complex **V** into the intermediate complex, $[HCl_2Si-Cl-SiH_3]^+$ (**VI**) and fragmentation of **VI** following intramolecular H transfer to the $SiHCl_2$ group would lead to reaction 22. Rearrangement of complex **VI** into intermediate complex, $[ClH_2Si-Cl-SiH_2Cl]^+$ (**VII**), followed by fragmentation of **VII** as shown in Scheme III could also lead to reactive processes.

From the discussion presented above, it is clear that for reactions that cannot be explained in terms of intramolecular Cl or H atom transfer to one of the two Si centers of the collision complex followed by its fragmentation, we propose reaction mechanisms wherein rearrangement(s) of the collision complex enable the reactants to explore all thermodynamically accessible product channels. In ion-molecule reactions involving neutral chlorosilanes it is very likely that the intermediates are primarily chloronium ions. The characterization of these intermediates requires further experimentation.

It would be interesting to compare product distributions arising from the collision of different ion-neutral pairs such that the total number of H, Cl, and Si atoms and the total energy available to the reacting partners are the same. A reaction involving the same number of H, Cl, and Si atoms as in the reaction of $SiCl_3^+$ with SiH_4 is the reaction of SiH_3^+ with $SiHCl_3$. The product channels of this latter reaction are represented by processes 26, 27, and 28. As can be seen

Scheme III


$SiCl_3^+ + SiH_4$
$Cl_3Si^+ \cdots H - SiH_3$
(V)
?
$SiH_3^+ + SiHCl_3$
?
$SiHCl_2^+ + SiH_3Cl$
$Cl_2HSi - \overset{+}{Cl} - SiH_3$
(VI)
$SiH_2Cl^+ + SiH_2Cl_2$
$ClH_2Si - \overset{+}{Cl} - SiH_2Cl$
(VII)

from Scheme III, the intermediate ions involved in this latter reaction process may be the same as the ones involved in the reaction of $SiCl_3^+$ with SiH_4. Isotopic labelling of the reactants could provide useful information in determining the nature of some of the intermediate ions. Unfortunately, such experiments are difficult to perform in FT-ICR instruments like the one employed in these studies. Firstly, it is almost impossible to systematically control the total energy of the reacting partners. Secondly, in certain cases, multiple bimolecular collisions which occur during typical ICR time scales may smear out any useful information. Experiments performed using ion-beam techniques[50] could be more helpful. Another possibility is to selectively prepare some of the chloronium ion intermediates through ion-molecule reactions or through collisional stabilization at higher pressures, and induce fragmentation through lowest energy pathways. Collision induced dissociation[51] (CID) may be a useful technique in such studies.

Reactions of the tetrachlorosilane ion with water and with tetrachlorosilane. Reactions 18 and 19 are additional interesting processes. While reaction 19 is observed because of the presence of trace amounts of water, reaction 18 represents the reaction of the tetrachlorosilane ion with tetrachlorosilane. The most likely process by which reaction 18 proceeds is through electron transfer from the neutral to the ion. If the reaction proceeded through the transfer of atomic species, then this would require either: (i) Cl atom exchange between the ion and the neutral or (ii) transfer of a Cl^- species from the neutral to the ion and a transfer of a Cl atom from the ion to the neutral. Both these processes are fairly complicated and may involve energetically unfavorable intermediates.

Reaction 19 is interesting in that it results in the loss of a Cl atom instead of a HCl molecule. This suggests that the O-H bond dissociation energy of $SiCl_3OH_2^+$ is greater than the HCl bond strength.

Conclusions

Ion-molecule reactions of silyl and chlorosilyl ions with chlorosilanes, and of the chlorosilyl ions with silane have been reported and discussed for the first time. These reactions are interesting in that H^- and Cl^- transfer reactions and disproportionation processes are competitive. Further, some of the disproportionation reactions seem to proceed through rearrangement of the collision complex formed by the reactants. The systematic characterization of these reaction processes would be aided by the observation and analysis of product distributions resulting from (i) the reactions of isotopically and energetically selected ions with neutrals, and (ii) the lowest energy fragmentation channels of chloronium ion intermediates prepared possibly through ion-molecule reactions or by collisional stabilization at higher pressures.

Trends in the Cl^- and H^- affinities of the chlorosilyl ions have been identified. Where possible the relative Cl^- and H^- affinities have been quantitatively determined. In certain other cases, the preferred direction of the Cl^- and H^- transfer reactions has been used to order the Cl^- and H^- affinities of the chlorosilyl ions.

Acknowledgements

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Chapter III

FT-ICR Spectrometric Studies of Ion-Molecule Reactions in Monochlorosilane

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Abstract

Gas-phase positive ion chemistry in SiH_3Cl is examined by the technique of Fourier Transform Ion Cyclotron Resonance Spectrometry. Reaction pathways and rate constants for the reactions of $SiH_nCl_{3-n}^+$ (n = 1-3) with SiH_3Cl have been obtained. The difference in the H^- affinities of SiH_2Cl^+ and $SiHCl_2^+$ has been determined to be 1.5 ± 0.3 kcal mol^{-1}. Within experimental uncertainty the values of the H^- affinities of the chlorosilyl ions lie within 1.8 kcal mol^{-1} of each other and decrease in the order $SiH_2Cl^+ \approx SiCl_3^+ > SiHCl_2^+$. The ionization potential of SiH_2Cl has been determined to be 7.68 ± 0.24 eV and its heat of formation at room temperature has been determined to be 7.46 ± 1.6 kcal mol^{-1}. Protonated SiH_3Cl is generated by proton transfer from CH_5^+ and is observed to be stable at room temperature under the time-scales of our experiment. It reacts with SiH_3Cl to yield the disilylchloronium ion, $(SiH_3)_2Cl^+$.

Introduction.

The recognition of the importance of fundamental knowledge in improving chlorosilane plasma processing technology has, in recent years, stimulated a number of fundamental experimental studies on the chlorosilanes. These include studies of electron-molecule interactions by transmission electron momentum spectrometry,[1,2] studies of negative ion formation by dissociative electron attachment,[2,3] and studies of ion-molecule reactions by guided ion beam techniques[4] and Fourier transform ion cyclotron resonance (FT-ICR) spectrometry.[5] Energetic environments such as those found in plasma reactors support ion-molecule processes.[6] Hence, direct examination of these processes is of primary importance. Even though SiH_3Cl is not commonly used in plasma processing owing likely to its commercial unavailability, we have chosen to examine ion-molecule reactions in this system in order to get a comprehensive picture of the ion chemistry of the chlorosilanes.

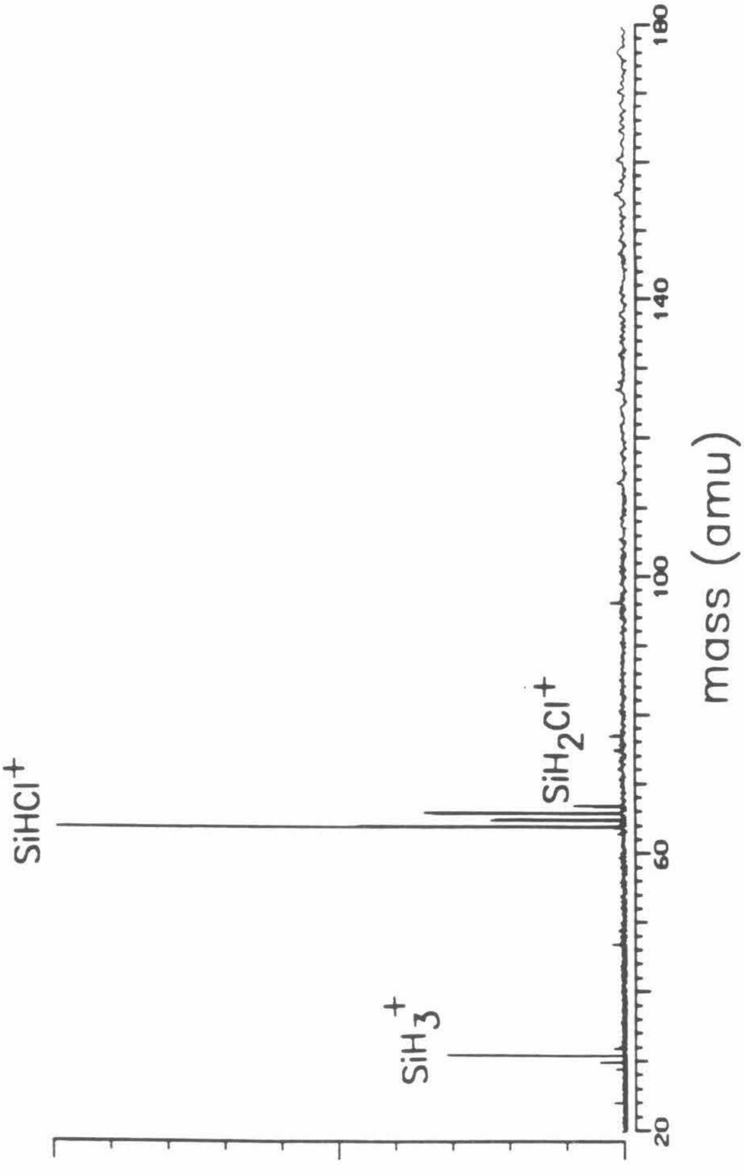
Recent studies of ion-molecule reactions in the chlorosilanes, SiH_nCl_{4-n} (n = 0-2), by FT-ICR spectrometry[5] in our laboratory indicate that the ion chemistry of the chlorosilanes differs from that of the halomethanes in significant ways. H^- transfer, Cl^- transfer and disproportionation reactions involving chlorosilyl ions and neutral chlorosilanes occur competitively. In contrast, exothermic H^- transfer reactions involving fluoromethyl ions and neutral fluoromethanes are slow when compared to exothermic F^- transfer reactions involving these reactants.[7] Disproportionation reactions have not been reported to occur in the halomethanes. The values and the ordering of the relative stabilities of the chlorosilyl ions display striking differences from those of the halomethyl ions. From a fundamental chemical perspective, therefore, the formation, stability, and reactivity of ionic species derived from the chlorosilanes in comparison with analogous species derived from the halomethanes is of potential interest. One such species is protonated SiH_3Cl. Protonated CH_nF_{4-n} (n= 2-4) can be easily generated by reactions of the parent ion with the parent neutral.[8] In SiH_3Cl, the parent ion is not observed under the sensitivity of our instrument as is evident from the mass spectrum of the compound shown in Figure 1. However, protonated SiH_3Cl may be generated by proton transfer from a highly acidic species such as CH_5^+. A similar technique has been previously used to generate protonated SiH_4.[9]

In this paper, we report a systematic study of the kinetics and pathways of bimolecular ion-molecule reactions in SiH_3Cl using Fourier transform ion cyclotron resonance spectrometry.[10] We complete the ordering of the H^- affinities of the chlorosilyl ions by determining the relative H^- affinities of SiH_2Cl^+ and $SiHCl_2^+$ using a procedure similar to the one outlined in reference 5. We generate protonated SiH_3Cl and examine its reactions with SiH_3Cl.

Experimental Section.

The experimental aspects of FT-ICR spectrometry have been discussed previously in the literature.[10b] Only details relevant to

Figure 1. FT-ICR mass spectrum of SiH_3Cl at a pressure of 1.5 x 10^{-7} Torr following a 3 msec, 20 eV electron beam pulse. The principal peaks are $SiHCl^+$ (64 and 66 amu), SiH_2Cl^+ (65 and 67 amu) and SiH_3^+ (31 amu). Isotopomers of these ions due to the isotopes of Si may also be present but are not resolved.


SiHCl$^+$
SiH_3^+
SiH_2Cl^+
20
60
100
140
180
mass (amu)

these experiments are outlined in this section. The FT-ICR spectrometer used to conduct these experiments comprises a 1-inch cubic trapping cell located between the poles of a Varian 15-inch electromagnet maintained between 0.8-1 T for these experiments. Data collection is accomplished with an Ion-Spec 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 (type 390 HA-00001SP5) capacitance manometer.

Ions were formed by electron impact ionization of neutral molecules or through ion-molecule reactions. The energy of ionizing electrons was in the range of 14-20 eV. Reactant ions were selectively isolated in the cell by ejecting unwanted ions using the technique of double resonance[11] and/or frequency sweep excitation.[12] Non-resonant translational excitation of reactant ions was minimized by using the lowest possible levels of radio-frequency fields during ion ejection. The shortest possible frequency sweep excitation pulses were used during ion detection.

Interrelations of reactant and product ions in a complicated reaction scheme involving consecutive and/or parallel reactions were facilitated by continuously ejecting all the isotopomers of a particular ion and observing changes in the reaction processes. The identified reaction scheme was used to perform a pseudo-first-order reaction kinetics simulation[13] of the experimentally observed temporal variation of reactant and product ion abundances. The reported rate constants are averages of several different sets of experimental data taken at different pressures of neutral gases. In reactions where ions have isotopomers, the isotopomer abundances of each ion were summed to give single ion abundances. The temperature was assumed to be 298.15 K.

Equilibrium constants, K_{eq}, for various reactions reported in this study were obtained by separately measuring the rate constants for the forward and reverse processes as parallel and/or sequential reactions were present. The principal errors in the rate constants (estimated to be up to ±20%) arise from uncertainties in pressure measurement. Additional errors may be introduced by the mass dependent sensitivity of the instrument[14] and the day to day variations of the Baratron Constant. Reactions of silyl and chlorosilyl ions with background water[5] was also a problem. Where possible these reactions were included in the simulation of the reaction kinetics. Nonetheless, owing to the complexity of ion-molecule reactions in this system, in most cases only the major reaction channels were considered. The non-inclusion of minor reaction channels in the simulation of the reaction kinetics contributes additionally to the error in the rate constants.

SiH_3Cl was kindly provided by Professor Ring's laboratory at San Diego State University and was used after repeated distillation and freeze-pump-thaw cycles. As can be seen from the mass spectrum shown in Figure 1 contamination from SiH_4 or higher chlorosilanes is negligible.

Results and Discussion.

A. Reactions of $SiH_nCl_{3-n}^+$ (n = 1-3) with SiH_3Cl and their Thermochemical Implications. Isolation of SiH_3^+, SiH_2Cl^+ and $SiHCl_2^+$ in SiH_3Cl at pressures of (0.4-1) x 10^{-6} Torr enabled reactions 1 to 4 to be studied.

$$\mathrm{SiH_3^+ + SiH_3Cl \rightarrow SiH_2Cl^+ + SiH_4} \qquad (1)$$

$$\mathrm{SiH_2Cl^+ + SiH_3Cl} \begin{cases} \rightarrow \mathrm{SiH_2Cl^+ + SiH_3Cl} & (2) \\ \rightarrow \mathrm{SiHCl_2^+ + SiH_4} & (3) \end{cases}$$

$$\mathrm{SiHCl_2^+ + SiH_3Cl \rightarrow SiH_2Cl^+ + SiH_2Cl_2} \qquad (4)$$

The rate constants and enthalpies of these reactions are summarized in Table 1. Reactions 1, 2 and 4 are H^- transfer reactions while reaction 3 is a disproportionation reaction. Figure 2 illustrates the temporal variation of ion abundances following the isolation of SiH_3^+ in SiH_3Cl. Calculation of the enthalpy of reaction 1 using the heats of formation of the relevant species shown in Table 2 indicates that reaction 1 is exothermic by 10.4 ± 7.3 kcal mol^{-1}. Reaction 2 is thermoneutral. As shown in Table 1, the enthalpies of reactions 3 and 4 are obtained to be -2.9 ± 0.3 and 1.5 ± 0.3 kcal mol^{-1} respectively.

Table 1. Rate Constants of Ion-Molecule Reactions in SiH_3Cl.

Reaction	k[a]	k/k_{ADO}[b]	ΔH[c]
$SiH_3^+ + SiH_3Cl \rightarrow SiH_2Cl^+ + SiH_4$	9.8	0.6	-10.4 ± 7.3[d]
$SiH_2Cl^+ + SiH_3Cl \rightarrow SiHCl_2^+ + SiH_4$	2.2	0.2	-2.9 ± 0.3[e]
$SiHCl_2^+ + SiH_3Cl \rightarrow SiH_2Cl^+ + SiH_2Cl_2$	0.8	0.1	1.5 ± 0.3[e]
$CH_5^+ + SiH_3Cl \rightarrow SiH_3ClH^+ + CH_4$	~23.5	1.0	
$SiH_3ClH^+ + SiH_3Cl \rightarrow (SiH_3)_2ClH^+ + HCl$	~3.8	0.3	

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[a] Rate constant in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Rate constants are within an accuracy of ± 20%. [b] Defined as reaction efficiency. k_{ADO} is given by the average dipole orientation theory discussed in ref. 15. The polarizability and dipole moment of SiH_3Cl was obtained from ref. 16. [c] ΔH in kcal mol^{-1} at 298.15 K. [d] Calculated using thermochemical data summarized in Table 2. [e] Experimentally determined in this work. See text for details.

Figure 2. Temporal variation of ion abundances following the isolation of SiH_3^+ in a neutral background of SiH_3Cl maintained at a pressure of 0.6×10^{-6} Torr. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics.

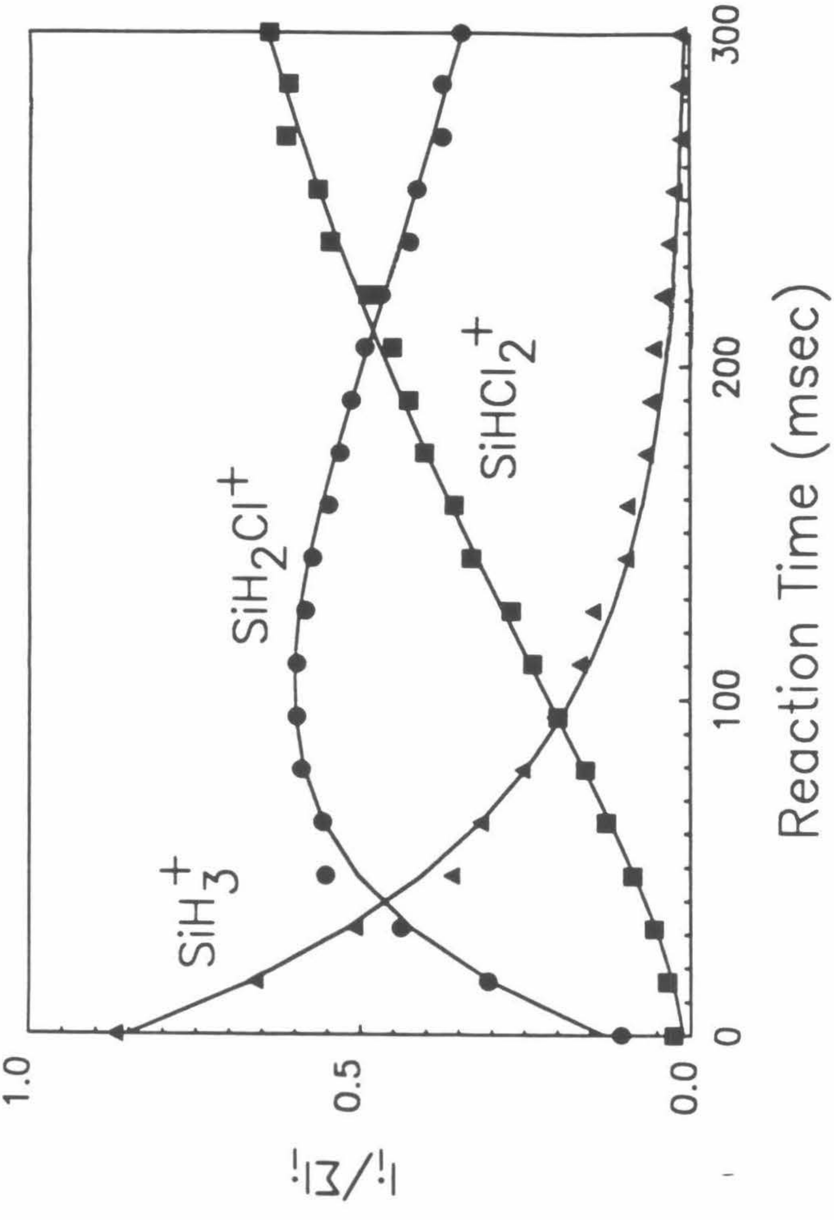

$I_i/\Sigma I_i$
1.0
0.5
0.0
0
100
200
300
Reaction Time (msec)
SiH_3^+
SiH_2Cl^+
$SiHCl_2^+$

Table 2. Heats of Formation of Relevant Species.

Neutral Species	ΔH^o_f[a]	Ionic Species	ΔH^o_f[a]
SiH_4	8.2 ± 1.0[b]	SiH_3^+	235.1 ± 1.2[d]
SiH_3Cl	-32.0 ± 1.1[b]	SiH_2Cl^+	184.5 ± 4.0[e]
SiH_2Cl_2	-74.4 ± 1.1[b]	$SiHCl_2^+$	141.3 ± 4.4[e]
$SiHCl_3$	-117.1 ± 1.1[b]	$SiCl_3^+$	99.8 ± 1.6[f]
$SiCl_4$	-158.4 ± 1.0[b]	H^-	34.7[g]
SiH_2Cl	7.46 ± 1.6[c]		

[a] Units of kcal mol^{-1} at 298.15 K. [b] Reference 17. [c] This work. [d] Reference 18. [e] Reference 5. [f] Reference 4b. [g] Reference 19.

The reactions of the silyl and chlorosilyl ions with SiH_3Cl are likely to proceed through chloronium ion intermediates.[5] These complexes are Lewis acid-base complexes in which the lone pair chlorine electrons insert into the empty orbital of the positive silicon center of the $SiH_nCl_{3-n}^+$ (n=0-3) cation. For example, reaction 1 is likely to proceed through the formation of the disilylchloronium ion, $(SiH_3)_2Cl^+$, intermediate. The energetics of reaction 1 is schematically illustrated in Figure 3.

From the rate constant of reaction 4 obtained in this study and the rate constant of the reverse reaction obtained previously, $K_{eq} = k_f/k_r$ for process 5 is calculated to be 0.1(+0.6, -0.3). $\Delta G^o_{298.15}$, is determined using equation 6 to be 1.4 ± 0.3 kcal mol^{-1}. The standard

$$SiHCl_2^+ + SiH_3Cl \rightleftarrows SiH_2Cl^+ + SiH_2Cl_2 \tag{5}$$

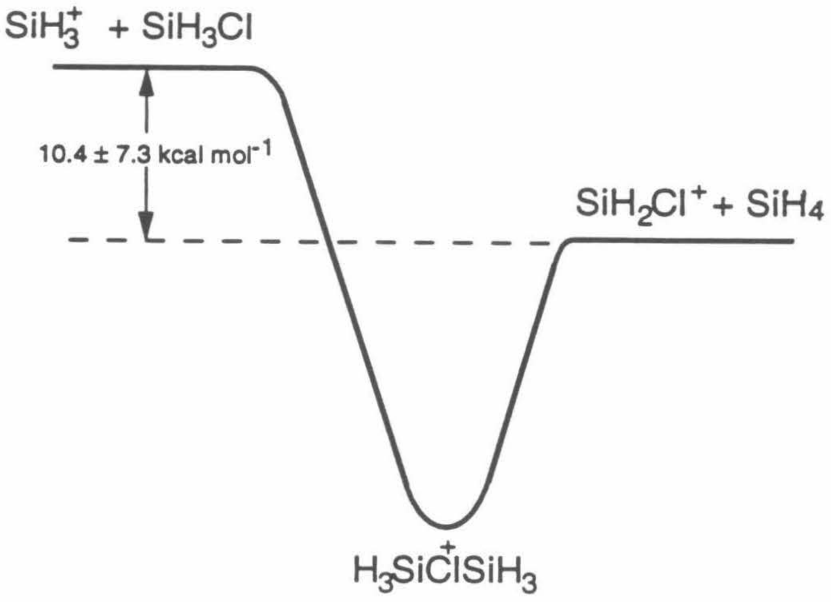
$$\Delta G = -RT \ln K_{eq} \tag{6}$$

entropy change for reaction 5, $\Delta S^o_{298.15}$, is calculated using equation 7 where $\Delta S^o_{ion,298.15}$ is equal to the difference in standard entropies of

$$\Delta S^o_{298.15} = \Delta S^o_{ion,298.15} + \Delta S^o_{neut,298.15} \tag{7}$$

the reactant and product ions and $\Delta S^o_{neut,298.15}$ is equal to the difference in the standard entropies of the product and reactant neutrals. $\Delta S^o_{ion,298.15}$ is calculated using standard expressions for the

Figure 3. Schematic representation of the energetics of reaction 1.


SiH_3^+ + SiH_3Cl
10.4 ± 7.3 kcal mol^{-1}
SiH_2Cl^+ + SiH_4
$H_3Si\overset{+}{Cl}SiH_3$

differences in translational, rotational, and vibrational entropies of the two ions.[20] The chlorosilyl ions are assumed to be planar and bond lengths and bond angles are based on neutral chlorine substituted singlet silylene radicals.[21] The vibrational frequencies of the ions are assumed to be the same as those of the corresponding neutral chlorosilyl radicals.[22] $\Delta S^{o}_{neut,298.15}$ is calculated using available literature values of the standard entropies of neutral chlorosilanes.[23] $\Delta H^{o}_{298.15}$ for reaction 5 is calculated using equation 8 to be 1.5 ± 0.3 kcal mol^{-1}. The H^{-} affinity of $SiHCl_2^+$ has been previously determined to be less than that of $SiCl_3^+$ by 0.9 ± 0.3 kcal

$$\Delta H^{o}_{298.15} = \Delta G^{o}_{298.15} + T\Delta S^{o}_{298.15} \tag{8}$$

mol^{-1}. If the value of the H^{-} affinity of $SiHCl_2^+$ is used as the datum, then the difference in the H^{-} affinity of SiH_2Cl^+ and that of $SiCl_3^+$ is found to be 0.6 ± 0.6 kcal mol^{-1}. This indicates that within experimental uncertainty the hydride affinities of $SiH_2Cl^+ \approx SiCl_3^+$. Previously the non-observation of reaction 9 in mixtures of SiH_4 and $SiHCl_3$ was taken to be indicative of the H^{-} affinity of $SiCl_3^+$ being

$$SiH_2Cl^+ + SiHCl_3 \rightarrow SiCl_3^+ + SiH_3Cl \tag{9}$$

greater than that of SiH_2Cl^+.[5] It is possible that in mixtures of SiH_4 and $SiHCl_3$ owing to other faster reaction processes, the occurrence of reaction 9 was not observable under the conditions in which the

Table 3. Ion-Molecule Reaction Enthalpies[a].

Reaction	$\Delta G^o = -RT \ln K_{eq}$	$T\Delta S^o$	ΔH^o
$SiHCl_2^+ + SiH_3Cl \rightleftarrows SiH_2Cl^+ + SiH_2Cl_2$	1.4 ±0.3	0.1	1.5 ± 0.3
$SiH_2Cl^+ + SiH_3Cl \rightleftarrows SiHCl_2^+ + SiH_4$	-2.0 ± 0.3	-0.9	-2.9 ± 0.3

[a] All data in units of kcal mol^{-1} at T = 298.15 K.

experiments were carried out. The present results support the H^- affinities of the chlorosilyl ions to be ordered as shown in sequence 10. The H^- affinities of the chlorosilyl ions lie within a range of

$$\text{Hydride Affinities:} \quad SiH_3^+ > SiH_2Cl^+ \approx SiCl_3^+ > SiHCl_2^+ \tag{10}$$

1.8 kcal mol^{-1}.

Reaction 3 is the only disproportionation reaction whose forward and reverse rate constants have been measured. The reverse reaction, previously observed to occur in mixtures of SiH_4 and $SiHCl_3$, has a rate constant of 0.07×10^{-10} cm^3 $molecule^{-1}$ sec^{-1}.[5] The enthalpy of reaction 3 calculated by a procedure similar to the one used to calculate the enthalpy of reaction 4 is -2.9 ± 0.3 kcal mol^{-1}. Summation of reactions 3 and 4 leads to reaction 11, which indicates

$$2SiH_3Cl \rightarrow SiH_4 + SiH_2Cl_2 \tag{11}$$

that the chlorosilyl ions, SiH_2Cl^+ and $SiHCl_2^+$ catalytically disproportionate SiH_3Cl. Reaction 11 is known as an ionic chain reaction.[24] Ionic chain reactions have been previously observed in CH_2F_2[8], $SiHCl_3$[5] and SiH_2Cl_2.[5] Summation of the enthalpies of reactions 3 and 4 leads to the enthalpy of reaction 11 being equal to -1.4 ± 0.6 kcal mol^{-1}. From the heats of formation of the chlorosilanes listed in Table 2, the enthalpy of reaction 11 is calculated to be -2.2 ± 3.1 kcal mol^{-1}. The enthalpy of the chain reaction 12 (observed

$$2SiH_2Cl_2 \rightarrow SiH_3Cl + SiHCl_3 \qquad (12)$$

previously in pure SiH_2Cl_2^{5}) could not be calculated because the enthalpy of reaction 4 had not been previously measured. It is calculated to be 0.5 ± 0.5 kcal mol^{-1}.

B. Thermochemical Properties of SiH_2Cl. From the thermochemical data listed in Table 1, the hydride affinity of SiH_2Cl^+, $DH^o_{298.15}(SiH_2Cl^+—H^-)$, is calculated to be 251.2 ± 5.1 kcal mol^{-1}. The homolytic bond dissociation energy of SiH_2Cl^+ with hydrogen, $DH^o_{298.15}(SiH_2Cl—H)$, has been theoretically determined to be 92.2 kcal mol^{-1}.[22] From the thermodynamic cycle shown below equation

$$\begin{tikzcd}
R^+ + X^- \arrow[r, "-DH^0_{298.15}(R^+\text{--}X^-)"] & RX \arrow[d, "DH^0_{298.15}(R\text{--}X)"] \\
R^+ + X \arrow[u, "-EA(X)"] & R + X \arrow[l, "IP(R)"']
\end{tikzcd}$$

$$IP(R) = D(R^+—H^-) - D(R—H) + EA(H) \qquad (13)$$

13 is derived. From equation 13 the ionization potential of SiH_2Cl, $IP(SiH_2Cl)$, is calculated to be 7.68 ± 0.24 eV. Using the value of $IP(SiH_2Cl)$ calculated in this work and the value of

$\Delta H_{f,298.15}(SiH_2Cl^+)$ = 184.5 ± 4.0 kcal mol^{-1} listed in Table 2, $\Delta H_{f,298.15}(SiH_2Cl)$ is calculated to be 7.46 ± 1.6 kcal mol^{-1}. This value is in excellent agreement with the value of 7.8 ± 3 kcal mol^{-1} for $\Delta H_{f,298.15}(SiH_2Cl)$ that has been obtained theoretically.[22]

The ionization potential of SiH_3, IP(SiH_3), is reported in the literature to be 8.14 ± 0.01 eV.[25] IP(SiH_2Cl) is seen to be less than IP(SiH_3) by 0.68 ± 1.7 eV. Ionization of SiH_nCl_{3-n} (n = 0-3) radicals corresponds to the removal of an unpaired electron from a silicon 3p orbital. In SiH_3 the orbital that the unpaired electron occupies does not interact with the other filled orbitals of the radical. Removal of this unpaired electron results in an empty 3p orbital in the positively charged silicon center of the SiH_3^+ cation. This empty 3p orbital does not interact with any other orbital of the SiH_3^+ cation. In SiH_2Cl the unpaired electron in the 3p silicon orbital is destabilized due to interactions with the chlorine lone pair orbitals. Removal of this unpaired electron results in an empty 3p orbital in the positively charged silicon center of the SiH_2Cl^+ cation.. This empty 3p orbital is stabilized through interactions with the lone pair chlorine orbitals in the SiH_2Cl^+ cation. A π bond is created between the empty 3p silicon orbital and the lone pair electrons of Cl atom with a concommitant polarization of the Si-Cl σ bond towards the chlorine atom. These effects are known as the π donation and the forward σ polarization effects and are schematically illustrated in Figure 8 of Chapter 2. It is because the 3p orbital in the SiH_2Cl radical is destabilized relative to the orbital in SiH_3 and the 3p orbital in the SiH_2Cl^+ cation is stabilized relative to the orbital in SiH_3^+ that the ionization potential of SiH_2Cl is less than that of SiH_3.

C. Preparation and Reactivity of Protonated SiH_3Cl. Isolation of CH_5^+ in mixtures of CH_4 and SiH_3Cl results in the production of SiH_3ClH^+ through reaction 14. SiH_3ClH^+ is observed to

$$CH_5^+ + SiH_3Cl \rightarrow SiH_3ClH^+ + CH_4 \tag{14}$$

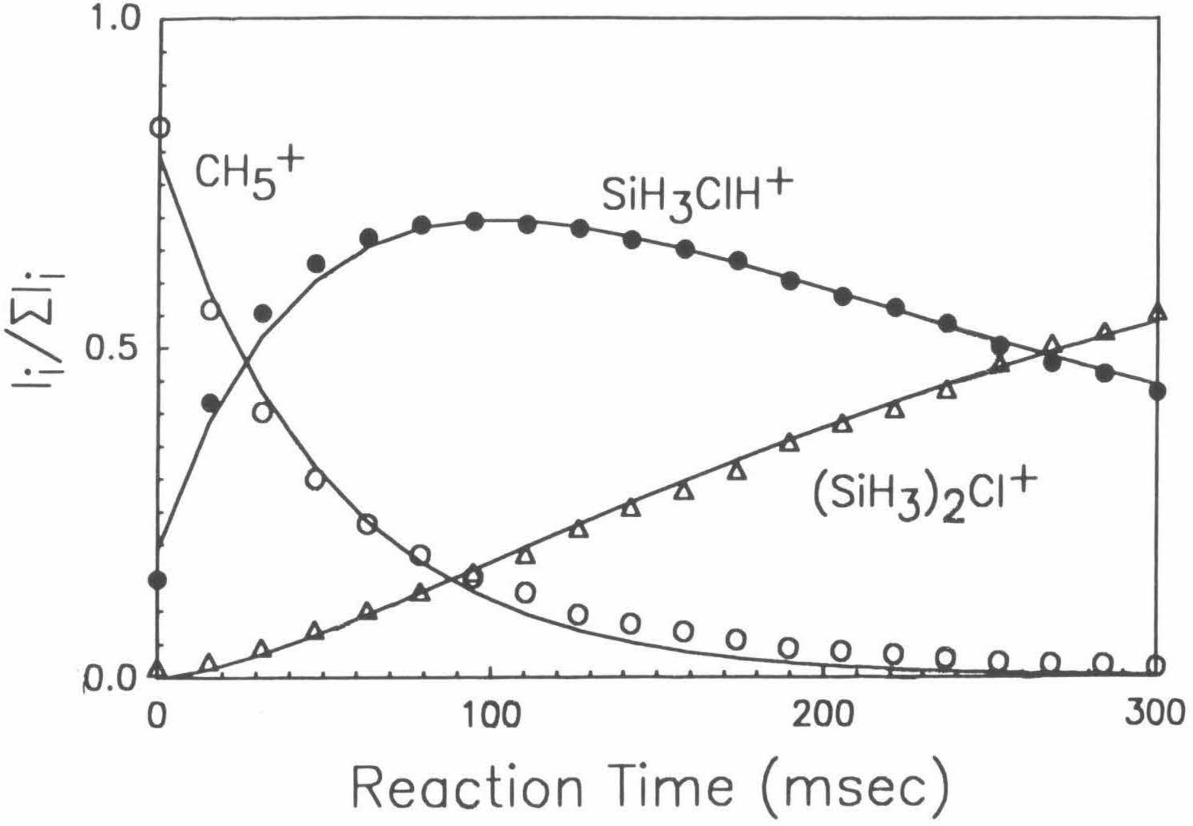
react further with SiH_3Cl to yield the disilylchloronium ion, $(SiH_3)_2Cl^+$, as indicated by process 15. Isolation of $(SiH_3)_2Cl^+$ in

$$SiH_3ClH^+ + SiH_3Cl \rightarrow (SiH_3)_2Cl^+ + HCl \tag{15}$$

SiH_3Cl at long times indicates that it is unreactive. Reactions analogous to process 15 leading to the formation of dialkylhalonium ions have been reported previously in halomethanes.[8,26] These reactions have been proposed to occur through a tight four center transition state.[26] From Table 1 it can be seen that the rate constant of reaction 15 is less than half the collision frequency. This would support the proposition that reaction 15 also occurs through a tight four center transition state.

Formation of the fluoronium ion, $[(CH_3)_3Si]_2F^+$ has been previously observed[27] to occur through reaction 16. The anologous

Figure 4. Temporal Variation of ion abundances following the isolation of CH_5^+ in a 6:1 mixture of CH_4 and SiH_3Cl maintained at a total pressure of 1.8×10^{-6} Torr. Points are from experiment; solid lines are from numerical simulation of the reaction kinetics. Other ions arising from reactions with impurities have been ignored.


1.0
0.5
0.0
$I_i/\Sigma I_i$
0
100
200
300
Reaction Time (msec)
CH_5^+
SiH_3ClH^+
$(SiH_3)_2Cl^+$

$$(CH_3)_3Si^+ + (CH_3)_3SiF \rightarrow [(CH_3)_3Si]_2F^+ \qquad (16)$$

process in SiH_3Cl would be reaction 17. This reaction is not observed

$$SiH_3^+ + SiH_3Cl \rightarrow (SiH_3)_2Cl^+ \qquad (17)$$

to occur because under the conditions of our experiments the chloronium ion, $(SiH_3)_2Cl^+$, is sufficiently energized to fragment into either SiH_3^+ and SiH_3Cl or into the products indicated in process 1. $[(CH_3)_3Si]_2F^+$ has a sufficiently long lifetime for it to be stabilized by collisions and/or by infra red emission. Hence, it is observed to be stable under the time-scales of typical ICR experiments (1-1000 msec).

Conclusions.

The reactions of the ions $SiH_nCl_{3-n}^+$ ($n = 1$-3) with SiH_3Cl have been reported for the first time. The H^- affinities of the chlorosilyl ions have been quantitatively determined and precisely ordered. Protonated SiH_3Cl has been generated at room temperature and is observed to react with SiH_3Cl to yield the disilylchloronium ion, $(SiH_3)_2Cl^+$.

Acknowledgments.

This work was supported by Grant CHE-91-08318 from the National Science Foundation. The assistance of Kathleen L. Walker in making available the SiH_3Cl sample used in these experiments is gratefully acknowledged.

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Chapter IV

Electron Impact Ionization of Phenylsilane. Evidence for the Formation of Phenylsilyl and Silacycloheptatrienyl Cations

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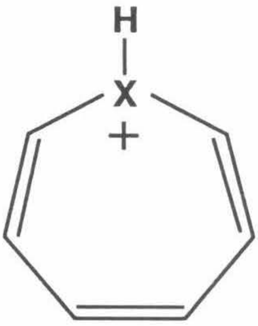
Abstract

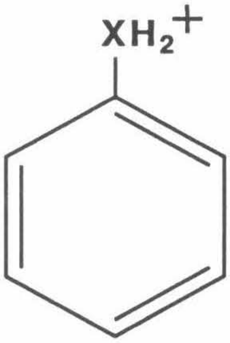
Fourier transform ion cyclotron resonance studies of the ion-molecule reactions of $C_6SiH_7^+$ (formed by electron impact ionization of phenylsilane) with the parent neutral indicate that it comprises reactive and unreactive populations. H^- abstraction from phenylsilane by CH_2F^+, CF_3^+ and $C_7H_7^+$ results in the formation of reactive $C_6SiH_7^+$ ions. This suggests that the reactive $C_6SiH_7^+$ isomer is the phenylsilyl cation. The variation with electron impact energy of the relative yields of reactive and unreactive $C_6SiH_7^+$ isomers from phenylsilane exhibits a behavior that is qualitatively similar to the relative yields of reactive (benzyl) and unreactive (cycloheptatrienyl) $C_7H_7^+$ isomers from toluene. This indicates that the unreactive $C_6SiH_7^+$ isomer maybe the silacycloheptatrienyl cation.

Since the original suggestion by Mayerson and co-workers[1] that hydrogen atom loss from the molecular toluene cation results in the formation of the cycloheptatrienyl cation (**Ia**), a number of studies[2] have attempted to elucidate the structure, energetics, and modes of formation of $C_7H_7^+$ isomers. It is now well understood that electron impact ionization of toluene yields both **Ia** and **IIa**. The relative yields of the two isomers is dependent on the internal energy content of the molecular toluene cation.[2a,f,i,j,m,n]



I

a: X = C
b: X = Si



II

a: X = C
b: X = Si

Interestingly, Fourier transform ion cyclotron resonance spectrometric studies[3] in our laboratory of the reactions of $C_6SiH_7^+$ (formed by electron impact ionization of phenylsilane) with the parent neutral indicate that this ion may be formed in two isomeric forms which are non-interconverting at room temperature. As can be seen from Figure 1a, the abundance of $C_6SiH_7^+$ decays initially and then becomes constant at longer times. The initial decay of $C_6SiH_7^+$ is due to reaction process 1. Isolation of $C_{12}SiH_{11}^+$ in neutral phenylsilane does not yield $C_6SiH_7^+$. Further, isolation of $C_6SiH_7^+$ at long times indicates that it is unreactive. These observations suggest that $C_6SiH_7^+$ consists of a reactive and an unreactive population of ions. In this communication, we provide evidence that suggests that

$$C_6SiH_7^+ + C_6H_5SiH_3 \rightarrow C_{12}SiH_{11}^+ + SiH_4 \qquad (1)$$

the unreactive and reactive $C_6SiH_7^+$ ions are two structurally distinct forms of the ion, namely, the silacycloheptatrienyl (**Ib**) and the phenylsilyl (**IIb**) cations.

Figure 1b shows the temporal variation of ion abundances following the isolation of CH_2F^+ in a 1: 6 mixture of phenylsilane and CH_3F at a total pressure of 0.9 x 10^{-7} Torr. Besides CH_2F^+, the other ions that participate in the reaction processes are $C_7H_7^+$, $C_6SiH_7^+$, and $C_{12}SiH_{11}^+$. Standard double resonance ion ejection techniques[4] enabled reaction processes 2-5 to be identified. $C_6SiH_7^+$ is eventually

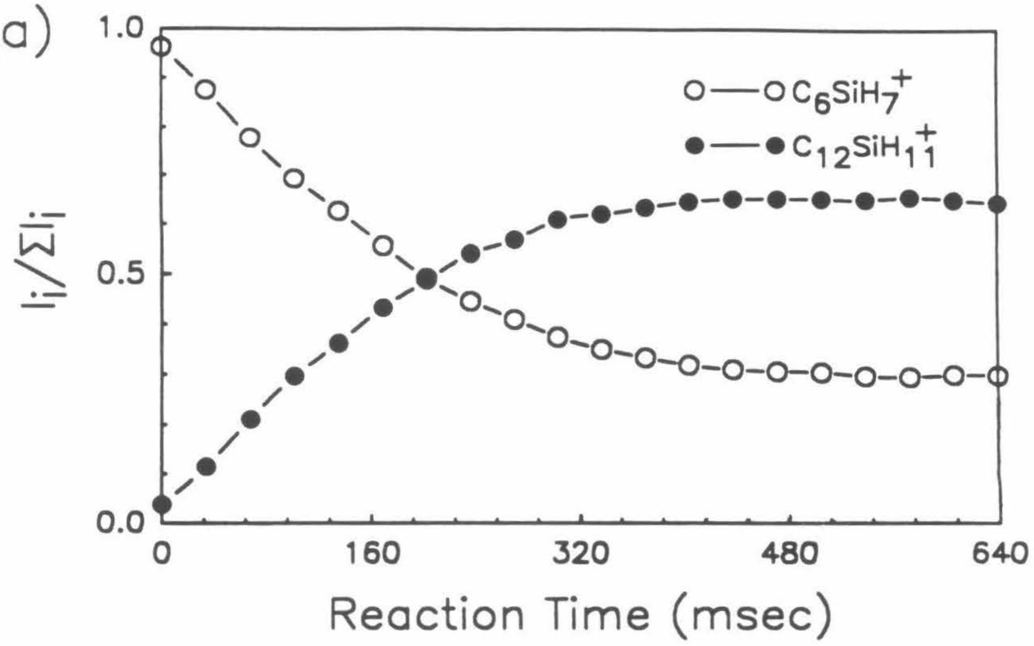
$$CH_2F^+ + C_6H_5SiH_3 \begin{cases} \rightarrow C_6SiH_7^+ + CH_3F & (2) \\ \\ \rightarrow C_7H_7^+ + SiH_3F & (3) \end{cases}$$

$$C_7H_7^+ + C_6H_5SiH_3 \rightarrow C_6SiH_7^+ + C_7H_8 \qquad (4)$$

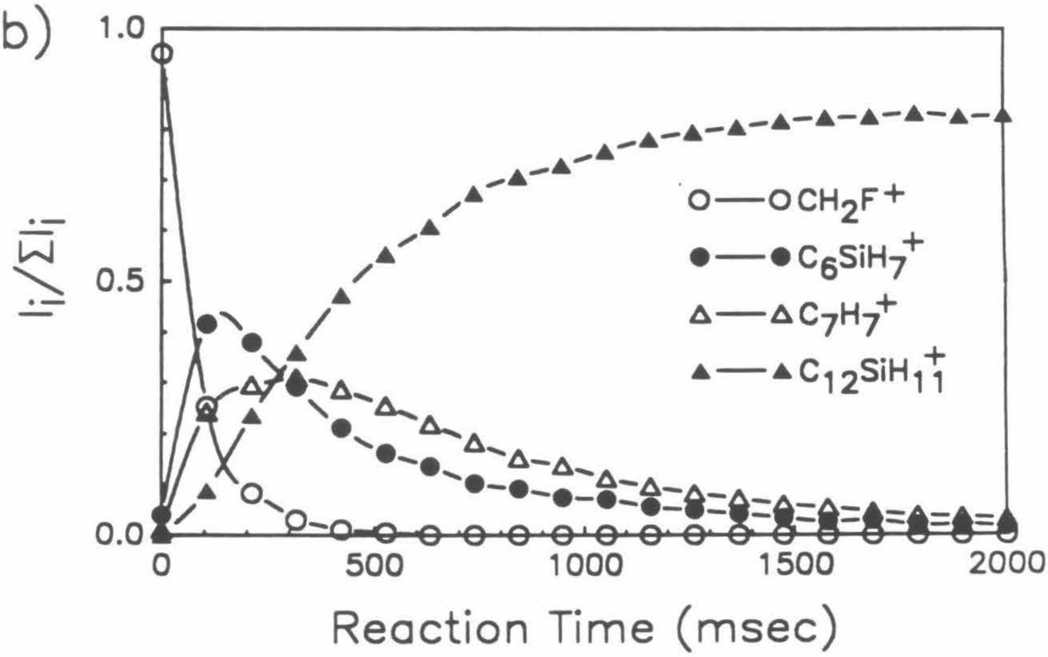
$$C_6SiH_7^+ + CH_3F \rightarrow C_7H_7^+ + SiH_3F \qquad (5)$$

Figure 1. (a) Temporal variation of ion abundances following the isolation of $C_6SiH_7^+$ in phenylsilane at a pressure of 2.8×10^{-8} Torr. The electron impact ionization energy was 20 eV. (b) Temporal variation of ion abundances following the isolation of CH_2F^+ in a 1: 6 mixture of phenylsilane and CH_3F at a total pressure of 0.9×10^{-7} Torr. The electron impact ionization energy was 30 eV. For purposes of clarity, in both the figures, minor products arising from side reactions are not shown. These ions are, however, included in the total ion count.

(a)


1.0
0.5
0.0
$I_i/\Sigma I_i$
0
160
320
480
640
Reaction Time (msec)
○—○ $C_6SiH_7^+$
●—● $C_{12}SiH_{11}^+$

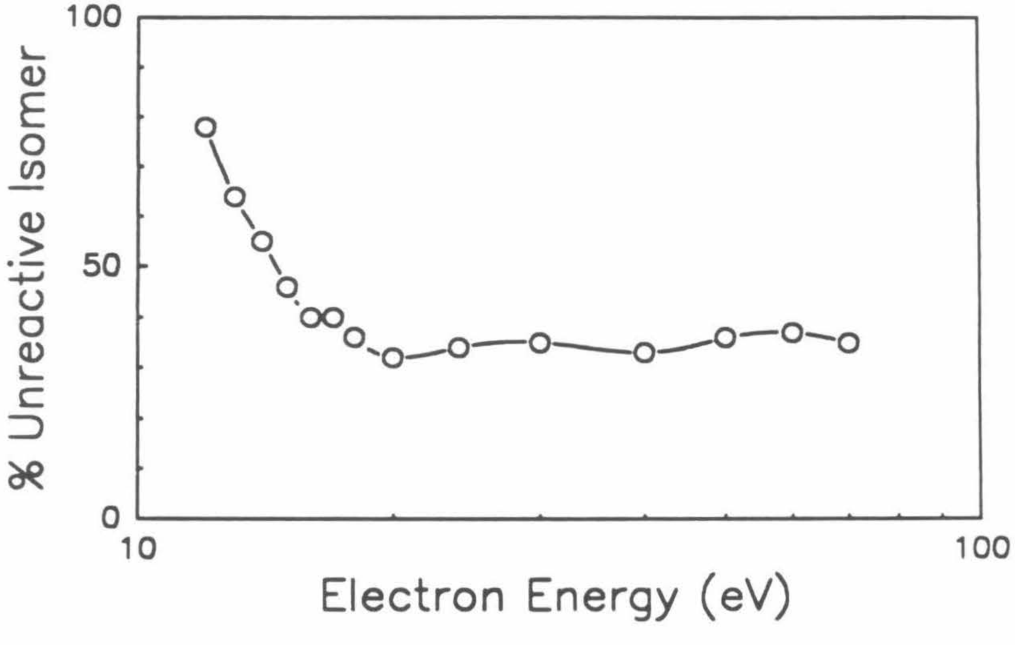
(b)


1.0
0.5
0.0
$I_i/\Sigma I_i$
0
500
1000
1500
2000
Reaction Time (msec)
○—○ CH_2F^+
●—● $C_6SiH_7^+$
△—△ $C_7H_7^+$
▲—▲ $C_{12}SiH_{11}^+$

depleted through reaction 1. Isolation of $C_6SiH_7^+$ produced by electron impact ionization of phenylsilane in the same mixture of phenylsilane and CH_3F indicates that the fraction of $C_6SiH_7^+$ which is unreactive with phenylsilane is unreactive with CH_3F as well, while the reactive fraction of $C_6SiH_7^+$ is seen to undergo both reactions 1 and 5. These observations strongly suggest that $C_6SiH_7^+$ generated by reaction 2 is the same reactive species generated from phenylsilane by electron impact. In a mixture of CF_4 and phenylsilane the reactive isomer of $C_6SiH_7^+$ is exclusively generated by the reaction channel of CF_3^+ with phenylsilane which is analogous to process 2. It is entirely reasonable that "soft" chemical ionization processes such as hydride abstraction (by CH_2F^+, $C_7H_7^+$ and CF_3^+) are likely to generate the phenylsilyl cation. We, therefore, propose that the reactive isomer of $C_6SiH_7^+$ is the phenylsilyl cation (**IIb**).

From Figure 2 it can be seen that the unreactive isomer of $C_6SiH_7^+$, which is the dominant product at electron energies below 14 eV, decreases monotonically until the ratio of the unreactive to reactive isomers attains a constant value of ~ 0.5 at electron energies greater than 20 eV. Such behavior is qualitatively similar to the analogous process in toluene (as studied by ion cyclotron resonance spectrometric techniques[2i,m]) where the ion analogous to the unreactive isomer of $C_6SiH_7^+$ is **Ia** ($\Delta H_f \approx 206$ kcal mol^{-1} [5]) while the ion analogous to the reactive isomer of $C_6SiH_7^+$ is **IIa** ($\Delta H_f \approx 217$ kcal mol^{-1} [5]). This leads us to propose that the unreactive isomer of $C_6SiH_7^+$ is the silacycloheptatrienyl cation (**Ib**). The greater yield of **Ib**

Figure 2. Variation of the percentage of the unreactive $C_6SiH_7^+$ isomer as a function of electron impact ionization energy (uncorrected) of phenylsilane at a pressure of 0.9 x 10^{-8} Torr. The fraction of the unreactive $C_6SiH_7^+$ isomer is defined as the ratio of the steady state (measured between 1500 - 2000 msec) abundance of $C_6SiH_7^+$ to the abundance of $C_6SiH_7^+$ measured 5 msec after the electron beam pulse. The width of the electron beam pulse was ~ 20 msec.


100
50
0
% Unreactive Isomer
10
100
Electron Energy (eV)

at low electron impact energies indicates that it is perhaps more stable than **IIb**. Further studies are in progress in our laboratory to quantitatively determine the relative stabilities of the $C_6SiH_7^+$ isomers and the energetics of their interconversion.

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(5) Average of the values listed in Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988** 17 (Suppl. No. 1).

Chapter V

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

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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^o_{298} of the H^- transfer reaction 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, $DH^{o}_{298}(PhSiH_2^{+}\text{–}H^{-})$, 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 $PhSiH_3^{+}$, $DH^{o}_{298}(PhSiH_2^{+}\text{–}H)$, to be 38 kcal mol^{-1}, and the ionization potential of the phenylsilyl radical, IP($PhSiH_2$), to be 6.89 eV.

Introduction.

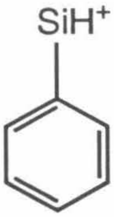
The gas phase ion chemistry of toluene has been extensively investigated[1] due primarily to the fact that electron impact ionization of toluene yields two (parent – H)$^+$ isomeric ions, namely, the benzyl and the cycloheptatrienyl cations. Interestingly, Fourier transform ion cyclotron resonance (FT-ICR) 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 and8) 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 has 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**, **2b** and **2c**), 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.

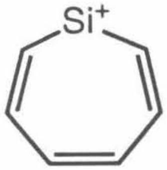
In this paper, we provide a full account of the gas phase chemistry of this interesting molecule. We report FT-ICR studies of the ion-

1

2a

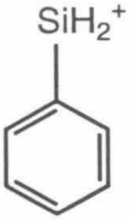


2b

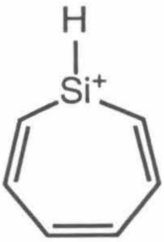


2c

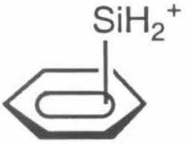
3a



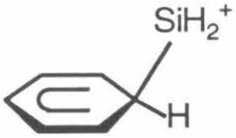
3b



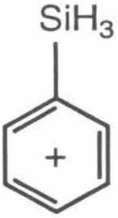
3c



4a



4b



4c

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, 1 or 2) transfer reactions from $C_6H_xSi^+$ (x = 6, 7 or 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, 2b, 2c**) for $C_6H_6Si^+$, two (**3b, 3c**) for $C_6H_7Si^+$ and two (**4a or 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 earlier studies of the methylsilanes in our laboratory[6] and with the carbon analogues of these compounds.

Experimental.

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-inch cubic trapping cell with trapping voltages of +1V located between the poles of a Varian 15-inch 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.

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

$$C_6H_5Si^+ + PhSiH_3 \left\{ \begin{array}{ll} \rightarrow C_{12}H_{13}Si_2^+ & (1) \\ \\ \rightarrow C_{12}H_{11}Si^+ + SiH_2 & (2) \end{array} \right.$$

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 $C_6H_6Si^+$ 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 $C_{12}H_{11}Si^+$ (Ph_2SiH^+), respectively. These reactions are indicated by processes 3 and 4. Reactions of $C_6H_8Si_2^+$ with phenylsilane

$$C_6H_6Si^+ + PhSiH_3 \left\{ \begin{array}{ll} \rightarrow C_6H_8Si_2^+ + C_6H_6 & (3) \\ \\ \rightarrow C_{12}H_{11}Si^+ + SiH_3 & (4) \end{array} \right.$$

were examined by this isolating this ion in phenylsilane. Two reaction channels 5 and 6 were identified. Reactions 3-6 account for the observed variation in ion abundances shown in Figure 1(b). $C_{12}H_{11}Si^+$ and $C_{12}H_{13}Si_2^+$ were not observed to react in the time range shown in Figure

1(b). Reactions following the isolation of $C_6H_6Si^+$ in phenylsilane and their rate constants are summarized in Sequence II of Figure 2.

$$C_6H_8Si_2^+ + PhSiH_3 \longrightarrow \begin{cases} C_{12}H_{11}Si^+ + Si_2H_5 & (5) \\ C_{12}H_{13}Si_2^+ + SiH_3 & (6) \end{cases}$$

Reactions of $C_6H_7Si^+$ (m/z = 107). Figure 1(c) shows the temporal variation of ion populations following the isolation of $C_6H_7Si^+$ in phenylsilane. Process 7 which leads to the production of $C_{12}H_{11}Si^+$ is the only reaction observed. The population of the $C_6H_7Si^+$ ion decreases

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

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.

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 1(d), 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,

$$C_6H_8Si^+ + PhSiH_3 \rightarrow C_6H_{10}Si_2^+ + C_6H_6 \qquad (8)$$

$$C_6H_8Si^+ + PhSiH_3 \rightarrow C_{12}H_{13}Si^+ + SiH_3 \qquad (9)$$

respectively. Continuous ejection 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 $C_{12}H_{13}Si^+$

$$C_6H_{10}Si_2^+ + PhSiH_3 \rightarrow C_6H_{12}Si_3^+ + C_6H_6 \qquad (10)$$

$$C_6H_{10}Si_2^+ + PhSiH_3 \rightarrow C_{12}H_{15}Si_2^+ + SiH_3 \qquad (11)$$

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

with phenylsilane. These reactions and their rate constants are summarized in Sequence IV of Figure 2. Upon isolation of m/z = 108 ($C_6H_8Si^+$), the peak corresponding to m/z = 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

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

produce $C_6H_{11}Si_2{}^+$ 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 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 period the intensity of $C_6H_9Si^+$ was not 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.

Reactions of $C_6H_6Si^+$. Upon isolation of $C_6H_6Si^+$ in phenylsilane/ benzene-d_6 mixtures the formation of an ion of m/z = 112 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 variation of

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

ions are shown in Figure 5 (a). 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

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

Si^+ transfer reaction. These reactions are summarized in Sequence I of Figure 3.

If there were a competitive process corresponding to reaction 4, involving $C_6D_6Si^+$ as the reactant, it would have produced $C_{12}H_{8-x}D_{3+x}Si^+$ ions ($x = 0$-3) with m/z = 186 - 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.

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 5(b). The formation of $C_6D_6H_2Si^+$ by process 18 involves the

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

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 and 215. The ion with m/z = 191 reacts to produce the ion with m/z = 215. If 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, then 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.

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

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

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

Reaction 19 is formally an SiH_2^+ transfer reaction. These reactions are summarized in Scheme II of Figure 3.

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 not formed 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_6H_6 is released, is not observed since an

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

ion of m/z = 221 is not formed. This 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 m/z = 138. Hence, the ion of m/z = 139 is $C_6H_{11}Si^+$, 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.

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. Figure 6a and b show the temporal variation of ion abundances following the isolation of $C_5H_{11}^+$ and $PhSiH_2^+$ ions, respectively, in 2-methylbutane/phenylsilane mixtures. Reaction 23 represents the

$$C_5H_{11}^+ + PhSiH_3 \rightleftarrows PhSiH_2^+ + C_5H_{12} \qquad (23)$$

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) x 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} and (1.0 ± 0.4) x 10^{-10} cm^3 $molecule^{-1}$ sec^{-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 reaction from phenylsilane to 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 affinity of the phenylsilyl cation, which is defined by equation

$$(CH_3)_3C^+ + (CH_3)_2(CH_3CH_2)CH \rightleftarrows (CH_3)_2CH_3CH_2)C^+ + (CH_3)_3CH \qquad (24)$$

25, is determined to be 229.8 ± 0.6 kcal mol^{-1}. Hydride transfer reactions

$$DH^{o}_{298}(PhSiH_2{}^{+}–H^{-}) = \Delta_fH^{o}_{298}(PhSiH_2{}^{+}) + \Delta_fH^{o}_{298}(H^{-}) - \Delta_fH^{o}_{298}(PhSiH_3) \quad (25)$$

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.

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 concomitant with a decrease in the abundance of the unreactive $C_6H_7Si^+$ ion. Above 20 eV, the fraction 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**).

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 $C_{12}H_{11}Si^+$ (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**, **2b** and **2c**. In the same report, they provide evidence for the existence of the $Si^+–C_6H_6$ complex ion (**2a**) by 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.

$C_6H_6–SiH_2^+$ 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 un-rearranged 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 SiH_2^+–C_6H_6 (**4a or 4b**). complexes are of interest. For the Si^+–C_6H_6 complex, theoretical calculations[5] suggest a structure in which the Si^+ ion does not locate 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 $C_6H_x Si^+$ (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**, **2b** and **2c** for $C_6H_6Si^+$, two structures **3b** and **3c** for $C_6H_7Si^+$ and two structures **4a**/**4b** and **4c** for $C_6H_8Si^+$.

B. Thermochemical Properties of $PhSiH_2^+$. The H^- affinity of $PhSiH_2^+$, $DH^o_{298}(PhSiH_2^+–H^-)$, 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 equation 26,

$$DH^o_{298}(PhSiH_2^+–H) = DH^o_{298}(PhSiH_2^+–H^-) + EA(H) - IP(PhSiH_3) \qquad (26)$$

therefore, the Si–H bond dissociation energy in $PhSiH_3^+$, $DH^o_{298}(PhSiH_2^+–H)$, 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. By using a value of 11.0 eV[18] for the appearance potential of SiH_4^+ 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 band width 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^+.

The ionization potentials of silyl, methylsilyl and phenylsilyl radicals are shown in Table 1 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 this empty orbital.[26-28] The formation of this π bond enables the σ bond between M^+ and the substituent to be concomitantly polarized towards the

Table 1. Thermodynamic quantities of silyl, methylsilyl, phenylsilyl radicals and their carbon analogues.[a]

R	IP(R)[b] eV	$DH^\circ_{298}(R^+-H^-)$ kcal mol^{-1} [c]	$DH^\circ_{298}(R-H)$ kcal mol^{-1}
SiH_3	8.17	261.4[d]	90.3[e]
CH_3SiH_2	7.53	245.9[f]	89.6[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 the physical quantities are at 298 K. [b] $IP(R) = DH^\circ_{298}(R^+-H^-) - DH^\circ_{298}(R-H) + EA(H)$. EA(H) = 0.754 eV (reference 17). [c] 1 kcal mol^{-1} = 4.1840 kJ mol^{-1} = 0.043360 eV. [d] Reference 19. [e] Reference 15. [f] Reference 6. [g] This work. [h] Reference 21.

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 $DH^o_{298}(R\text{–}H)$ for the silicenium radicals listed in Table 1 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 1, 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 1, 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 1, 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 $Ph\text{–}C^+$ bond distance in the benzyl cation is likely to be shorter than the $Ph\text{–}Si^+$ 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 1, 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 $DH^o_{298}(R^+–H^-)$. Additionally, in the case of the silicenium ions, within experimental uncertainty, $DH^o_{298}(R^+–H^-)$ correlates linearly with IP(R). This is because DH^o_{298}(R–H) is approximately the same in each of these radicals.

Acknowledgments.

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Figure 1. (a) Temporal variation 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 variation 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 intensity of $C_{12}H_{11}Si^+$ and $C_{12}H_{13}Si_2^+$. (c) Temporal variation 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 variation 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.

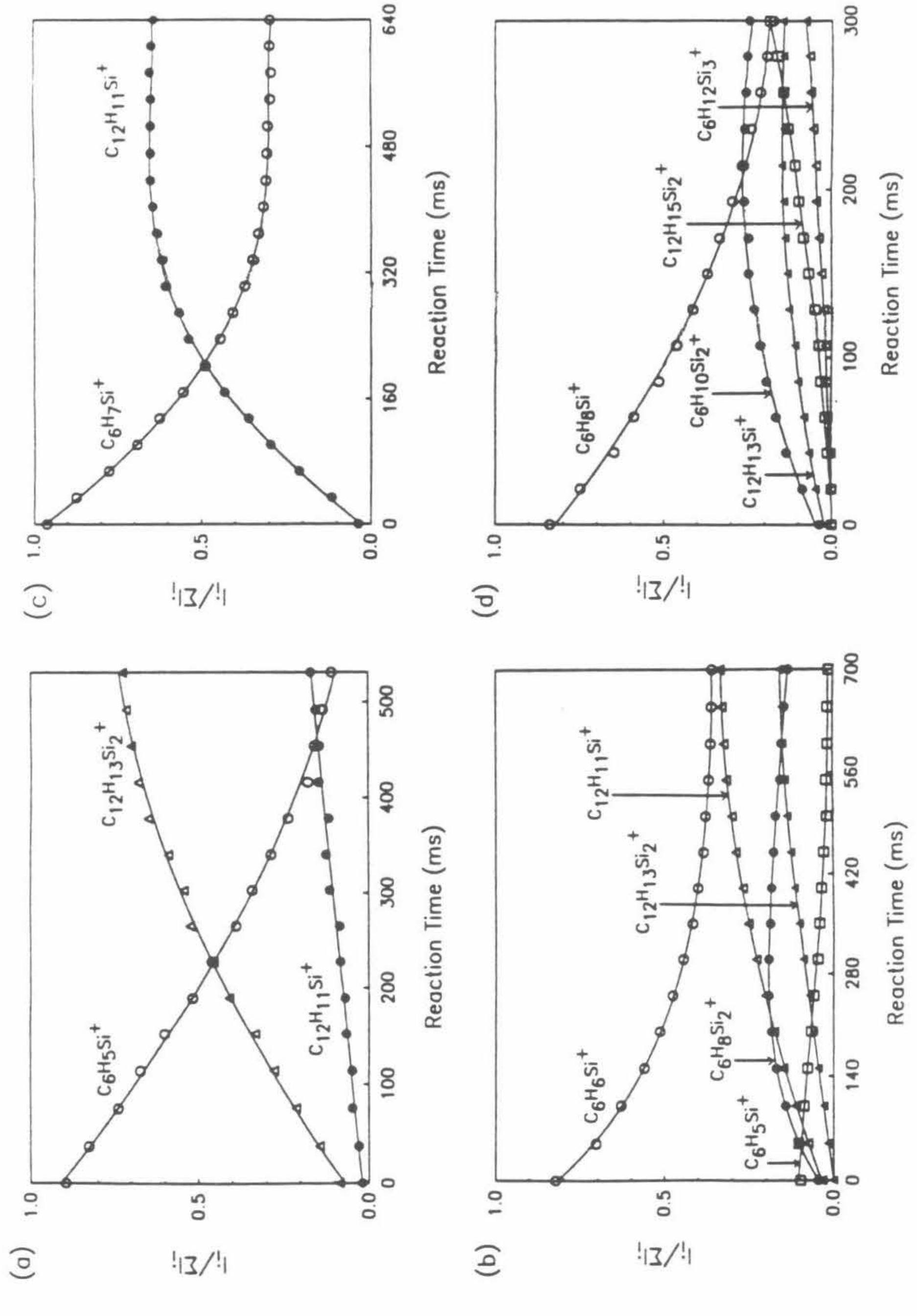
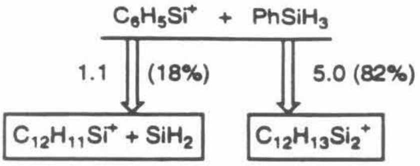

(a)
(b)
(c)
(d)
$I_i/\Sigma I_i$
1.0
0.5
0.0
Reaction Time (ms)
0
100
200
300
400
500
$C_6H_5Si^+$
$C_{12}H_{13}Si_2^+$
$C_{12}H_{11}Si^+$
0
140
280
420
560
700
$C_6H_6Si^+$
$C_{12}H_{11}Si^+$
$C_{12}H_{13}Si_2^+$
$C_6H_8Si_2^+$
$C_6H_5Si^+$
0
160
320
480
640
$C_6H_7Si^+$
$C_{12}H_{11}Si^+$
0
100
200
300
$C_6H_8Si^+$
$C_{12}H_{15}Si_2^+$
$C_6H_{12}Si_3^+$
$C_6H_{10}Si_2^+$
$C_{12}H_{13}Si^+$

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 mark have larger uncertainties owing to the complexities of ion-molecule reactions in these systems. Branching ratios are listed within parentheses.

Sequence I



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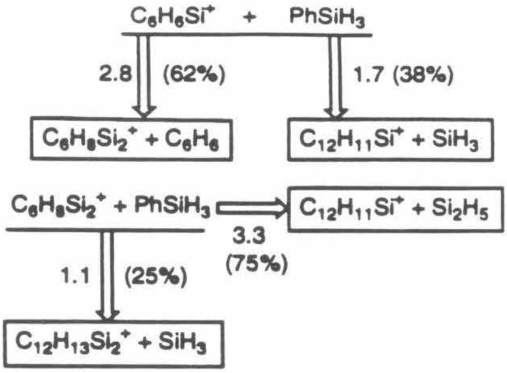

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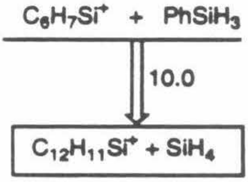

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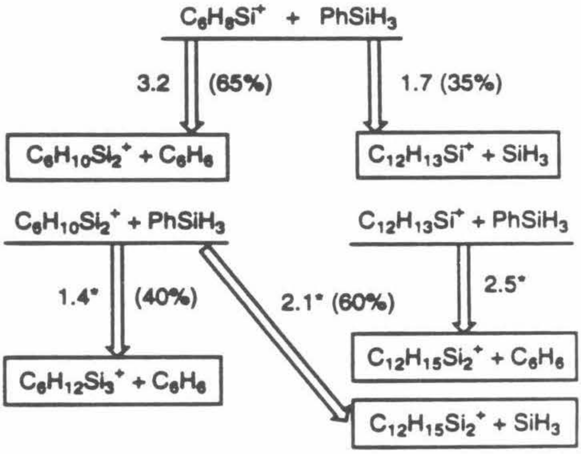


Figure 3. Schematic representation of reaction sequences following the isolation of individual $C_6H_6Si^+$ and $C_6H_8Si^+$ ions in phenylsilane/benzene-d_6 mixtures. Rate constants in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1} are reported for individual reactions. Rate constants are within an accuracy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

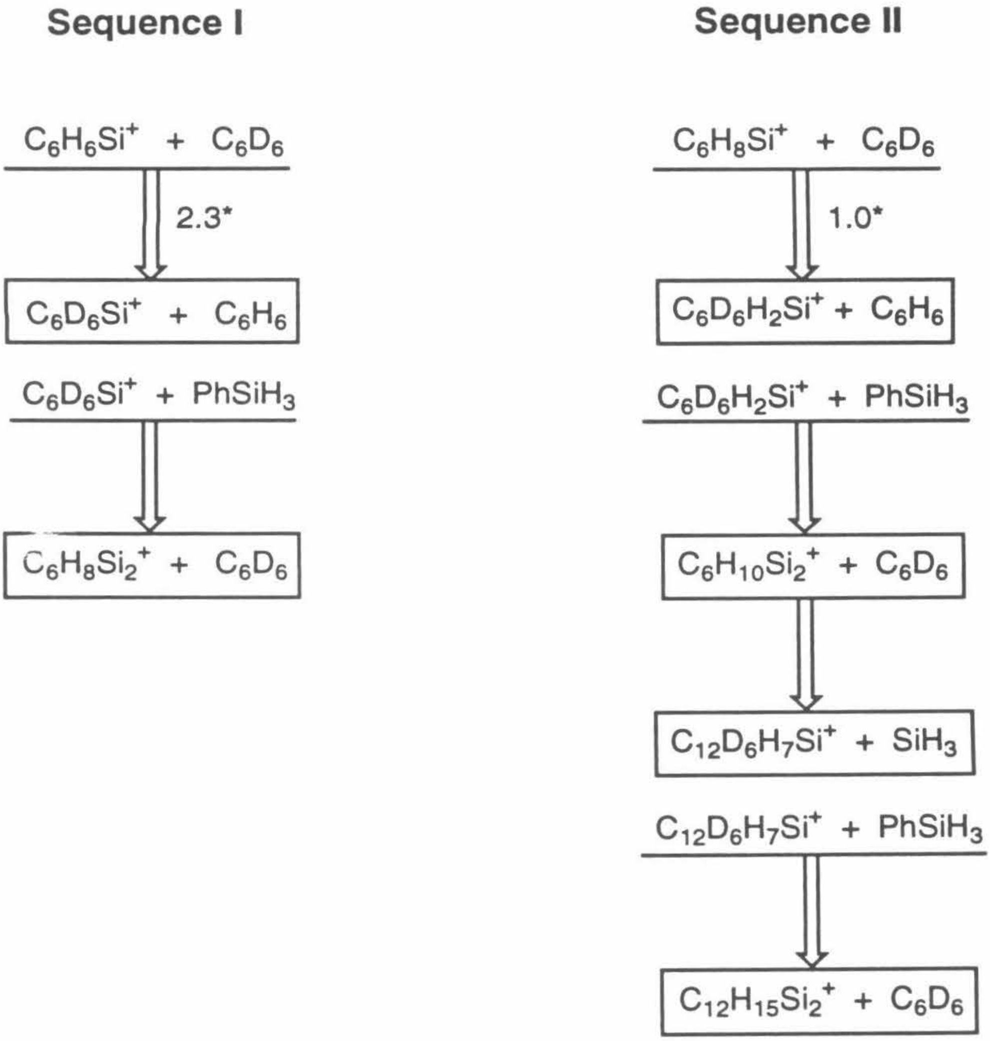

Sequence I
$C_6H_6Si^+ + C_6D_6$
2.3*
$C_6D_6Si^+ + C_6H_6$
$C_6D_6Si^+ + PhSiH_3$
$C_6H_8Si_2^+ + C_6D_6$
Sequence II
$C_6H_8Si^+ + C_6D_6$
1.0*
$C_6D_6H_2Si^+ + C_6H_6$
$C_6D_6H_2Si^+ + PhSiH_3$
$C_6H_{10}Si_2^+ + C_6D_6$
$C_{12}D_6H_7Si^+ + SiH_3$
$C_{12}D_6H_7Si^+ + PhSiH_3$
$C_{12}H_{15}Si_2^+ + C_6D_6$

Figure 4. Variation of the percentage 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 x 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.

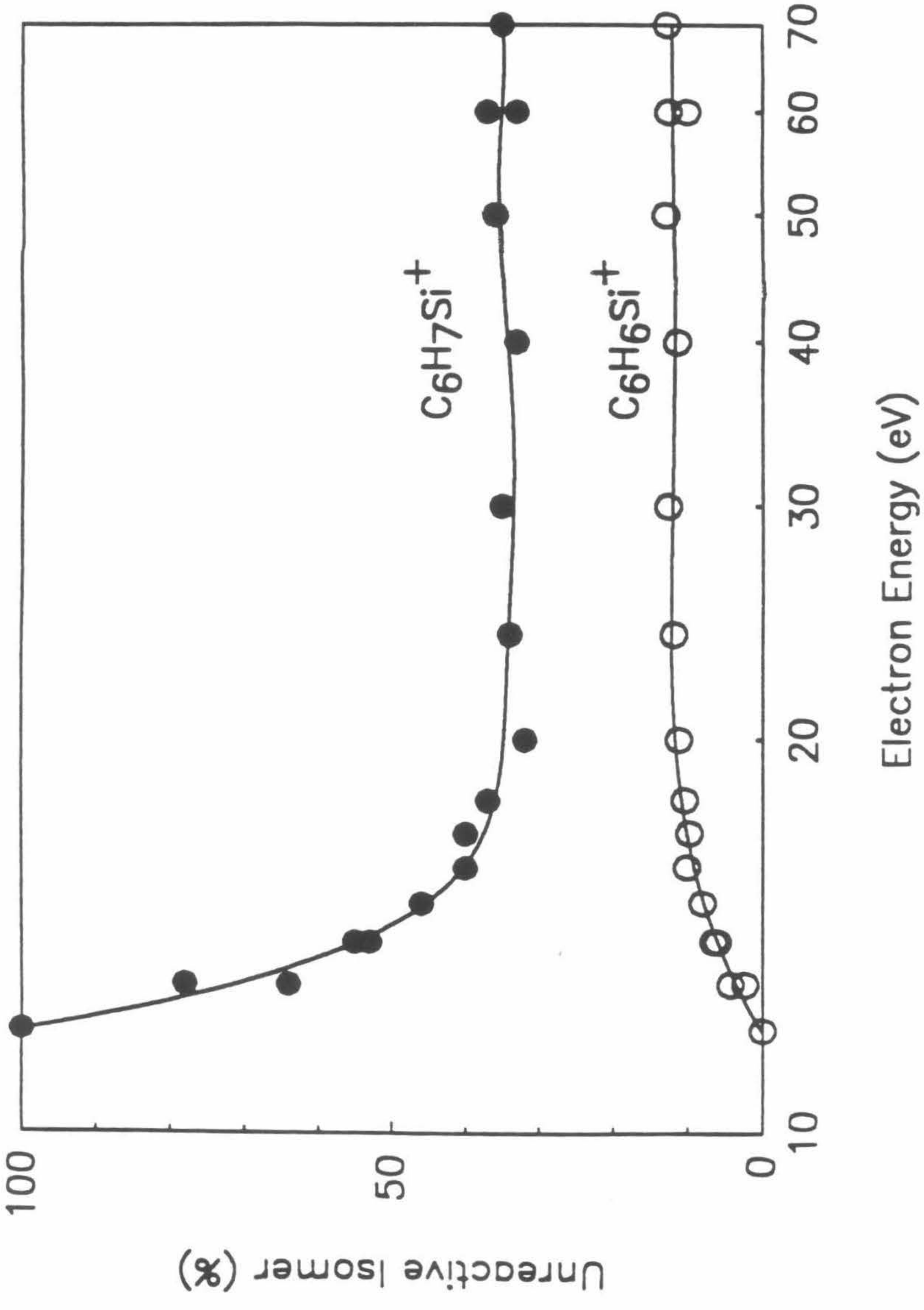

Unreactive Isomer (%)
100
50
0
Electron Energy (eV)
10
20
30
40
50
60
70
$C_6H_7Si^+$
$C_6H_6Si^+$

Figure 5. (a) Temporal variation 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 variation 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. The other ions are not included because the increase in abundance of $C_6H_{11}Si_2^+$ compensates for the decrease in abundance of $C_6H_9Si^+$.

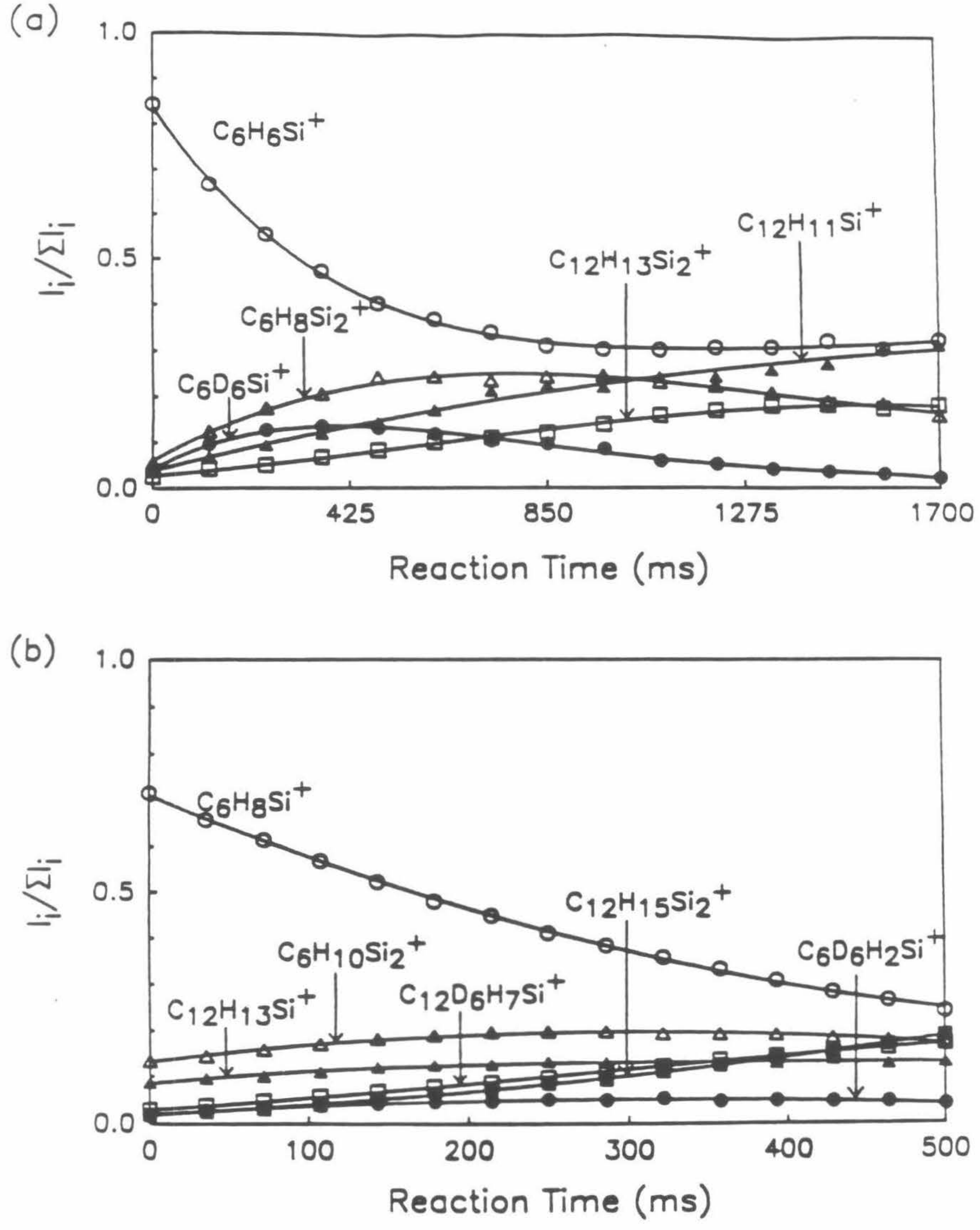
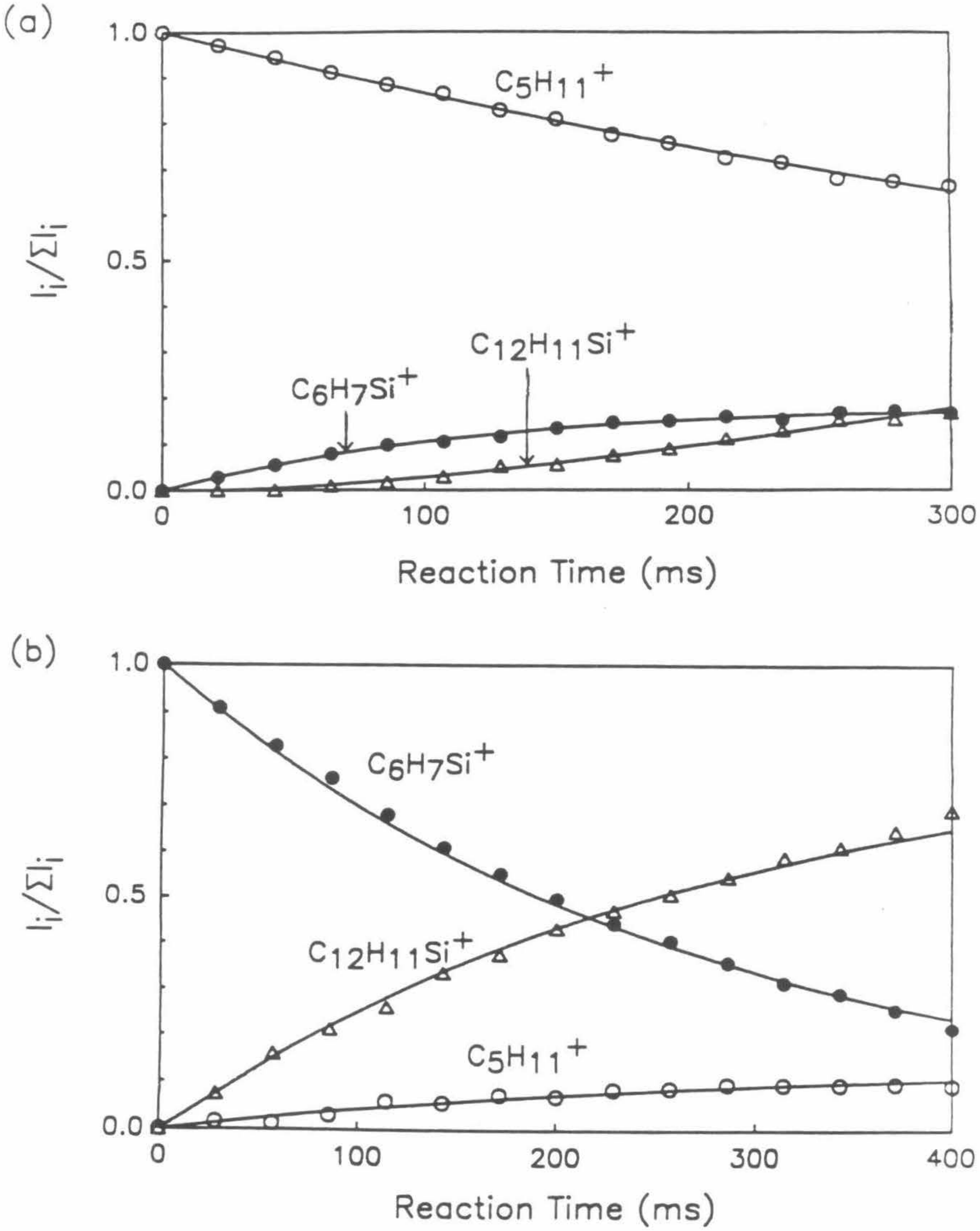

(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$C_6H_6Si^+$
$C_{12}H_{11}Si^+$
$C_{12}H_{13}Si_2^+$
$C_6H_8Si_2^+$
$C_6D_6Si^+$
0
425
850
1275
1700
Reaction Time (ms)
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$C_6H_8Si^+$
$C_{12}H_{15}Si_2^+$
$C_6H_{10}Si_2^+$
$C_6D_6H_2Si^+$
$C_{12}D_6H_7Si^+$
$C_{12}H_{13}Si^+$
0
100
200
300
400
500
Reaction Time (ms)

Figure 6. (a) Temporal variation 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 x 10^{-7} Torr. (b) Temporal variation 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 x 10^{-7} Torr. In both (a) and (b), points are from experiment; solid lines are from numerical simulation of the reaction kinetics.


(a)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$C_5H_{11}^+$
$C_{12}H_{11}Si^+$
$C_6H_7Si^+$
0
100
200
300
Reaction Time (ms)
(b)
1.0
0.5
0.0
$I_i/\Sigma I_i$
$C_6H_7Si^+$
$C_{12}H_{11}Si^+$
$C_5H_{11}^+$
0
100
200
300
400
Reaction Time (ms)