Intracluster Ion−Molecule Reactions of Dimer Cations of Phenylsilanes

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Intracluster ion−molecule reactions of dimer cations of various phenylsilanes were investigated in order to elucidate reaction mechanisms of phenylsilane cation reported in the gas-phase FT-ICR study. Two types of reactions, SiR_3 elimination and SiR_2^+ transfer, were observed. In the latter case, our observation strongly supported that a precursor of the reaction has a π-type complex configuration, $[C_6H_6{\cdot}SiR_2]^+$, which has been proposed before. On the contrary, in the former case, a dimer cation forms a reaction intermediate and then it dissociates preferentially to a larger exothermic channel.

I. Introduction

Since organic silicon compounds are known to exhibit different chemical properties compared with corresponding hydrocarbons, a pile of studies have accumulated in the field of synthetic chemistry, stereochemistry, physico-organic chemistry, photochemistry, and so on. Physical and chemical properties of cationic species of organic silicon compounds are also of great interest especially with respect to their role as intermediates of chemical reactions. Phenylsilane, $PhSiH_3$, is the simplest aromatic silicon compound. There are several reports on reactivities of its cationic species with neutral parent.[1−4] Nagano and others first investigated ion−molecule reactions of phenylsilane cation, $PhSiH_3^+$, in gas phase by using Fourier transform ion cyclotron resonance (FT-ICR) method, and found the following reactions;[1]

$$PhSiH_3^+ + PhSiH_3 \rightarrow C_{12}H_{13}Si^+ + SiH_3 \qquad (1a)$$

$$\rightarrow C_6H_{10}Si_2^+ + C_6H_6 \qquad (1b)$$

Rate constants of the reactions 1a and 1b were determined to be 1.7×10^{-10} and 3.2×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. They also investigated the reaction of $PhSiH_3^+$ with deuterated benzene, C_6D_6, and found that the following reaction takes place:

$$PhSiH_3^+ + C_6D_6 \rightarrow C_6D_6H_2Si^+ + C_6H_6 \qquad (2)$$

while the reaction corresponding to reaction 1a does not take place. Comparing the reactions 1b and 2, they concluded that a key process of the reactions is the transfer of the SiH_2^+ segment from the cation to the neutral species. They also proposed the existence of two isomers: one is a complex of SiH_2^+ with phenyl group, $C_6H_6{\cdot}SiH_2^+$, leading to the SiH_2^+ transfer reactions 1b and 2. The other was expected to be of $[C_6H_5{-}SiH_3]^+$ structure which undergoes reaction 1a. Recent ab initio study on the phenylsilane cation by Jarek and Shin concluded that the most stable form is a π-complex between SiH_2^+ with C_6H_6 and that there is an isomerization barrier of 14 kcal/mol between the $C_6H_6{\cdot}SiH_2^+$ and $[C_6H_5{-}SiH_3]^+$ configurations.[2]

Photoionization of a neutral dimer is a very efficient and suitable way of the generation of the reaction precursor of the ion−molecule reaction. If one initiates the ion−molecule reaction within a cluster by photoexcitation or collision, one can selectively observe the desired reaction and hence obtain a detailed information about a reaction mechanism. In our previous paper, we have reported a photoinitiated intracluster ion−molecule reaction of phenylsilane dimer cation, $(PhSiH_3)_2^+$.[3] The same ion−molecule reactions as those reported by the FT-ICR study[1] were observed in the photoexcitation of $(PhSiH_3)_2^+$ in the region of 6000−22000 cm^{-1}. In addition, we have found that the intracluster reactions are preferential for an isomer of the dimer cation having a parallel conformation of two phenyl rings which exhibits the charge-resonance (CR) transition. Recently, similar intracluster reactions of the phenylsilane dimer cation were also observed by Kosmidis and Philis.[4] The corresponding hydrocarbon, toluene, does not exhibit such ion−molecule reactions. Such a reactivity should be peculiar to aromatic silicon compounds. However, a clear interpretation for mechanisms of such ion−molecule reactions has not yet been made. In the course of the previous study, we found that the ion−molecule reactions of phenylsilane dimer cations occur very efficiently in a supersonic jet. In this paper, we report the intracluster ion−molecule reactions of dimer cations of various phenylsilanes. On the basis a comparison of possible reaction pathways among the ion−molecule reactions occurring in various dimer cations, we will discuss the mechanism of the ion−molecule reactions of phenylsilane cation.

II. Experimental Section

A conventional supersonic jet equipment combined with a quadrupole mass (Q-mass) filter (Extranuclear Laboratories) was used. Commercial phenylsilanes (Shin-Etsu Chemical Co.) were used without further purification. Vapor of the compound seeded in He gas was supersonically expanded into a vacuum chamber through an orifice of a pulsed valve. Clusters of phenylsilanes, including the dimer, were generated in the expansion. To avoid the formation of larger size clusters than the dimer, partial vapor pressure of samples in the seeded gas was controlled by

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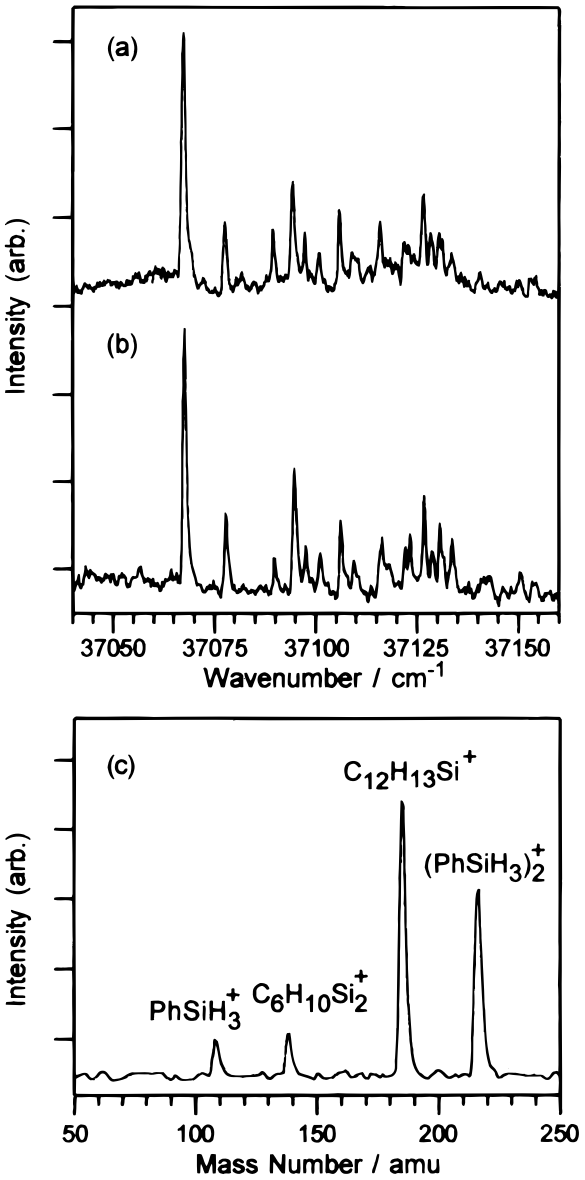

Figure 1. The RE2PI excitation spectra of $(PhSiH_3)_2$ monitoring (a) the parent cation and (b) the reaction product, $C_{12}H_{13}Si^+$. The mass spectrum in the 0_0^0 band excitation is also shown in c.

regulating the temperature of a sample container to be 0−10 °C. The jet expansion was introduced into an ionization region of the chamber without skimming. The dimer cations were produced by resonance-enhanced two photon ionization (RE2PI) via the S_1 state of the neutral dimer. An output of XeCl excimer laser (Lambda Physik EMG103) pumped dye laser (Lambda Physik FL2002) was frequency doubled by a KDP crystal and was used for ionization. The ionization laser beam was focused by a lens of $f = 500$ mm. The ions produced were repelled and accelerated by an electric field perpendicular to the axis of the jet stream. The repelled ions were analyzed with the Q-mass filter and detected by a channel electron multiplier (Murata). Ion current was preamplified, integrated by a digital Boxcar (EG&G Model 4420) and then processed by a personal computer.

III. Results

1. Intracluster Ion−Molecule Reaction of the Phenylsilane Dimer Cation. Figure 1a shows a RE2PI spectrum of $(PhSiH_3)_2$ monitoring a species of $M = 216$, the parent cation $(PhSiH_3)_2^+$, in the vicinity of its origin band 0 of the S_1-S_0 transition. The strong 0_0^0 band is located at 37068 cm^{-1}. A mass spectrum in the photoionization at the 0_0^0 band was shown in Figure 1c. Peaks those correspond to the species of $M = 138$ and 185 clearly appeared in the mass spectrum in addition to those of monomer and dimer cations. The species of $M = 185$ and 138 were assigned as $C_{12}H_{13}Si^+$ and $C_6H_{10}Si_2^+$, respectively, since the mass number of these species were the same as those of the products of ion−molecule reaction 1a and b. They were also identified in our previous study on the CR band excitation of $(PhSiH_3)_2^+$. Since the excitation spectra monitoring $C_{12}H_{13}Si^+$, shown in Figure 1b, and $C_6H_{10}Si_2^+$ were identical to that monitoring $(PhSiH_3)_2^+$, it is evident that those species are generated after the photoionization of $(PhSiH_3)_2$. Thus, we can express these collision-induced intracluster reaction as

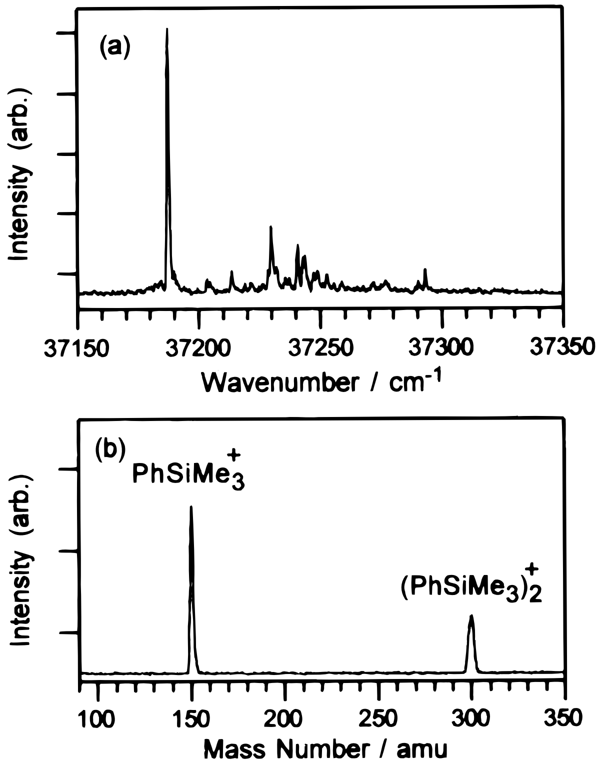

Figure 2. The RE2PI (a) excitation and (b) mass spectra of $(PhSiMe_3)_2$. The mass spectrum was measured at the 0_0^0 band ionization.

$$(PhSiH_3)_2^+ \rightarrow C_{12}H_{13}Si^+ + SiH_3 \qquad (2a)$$

$$\rightarrow C_6H_{10}Si_2^+ + C_6H_6 \qquad (2b)$$

The RE2PI mass spectrum of $(PhSiH_3)_2$ in a skimmed molecular beam condition was also observed. As shown in Figure 2a of ref 3, ion signals of the reaction products were very weak. In the previous study, similar intracluster reactions were initiated by the photoexcitation at the CR band. It was suggested that an energy activation process is necessary to initiate the reaction. In the present study, considering the difference in the experimental condition between the previous and present study, collisions of the parent dimer cation with He gas is the most probable candidate of the activation process. In the present experiment, the photoionization creates the dimer cation at the center of a corn-shaped jet stream of the carrier gas of He. Since the supersonic jet was not skimmed, the dimer cations are subjected to collide with He when it crosses the jet stream. Thus, it is suggested that the collision is the main activation process. However, the detailed interpretation of the

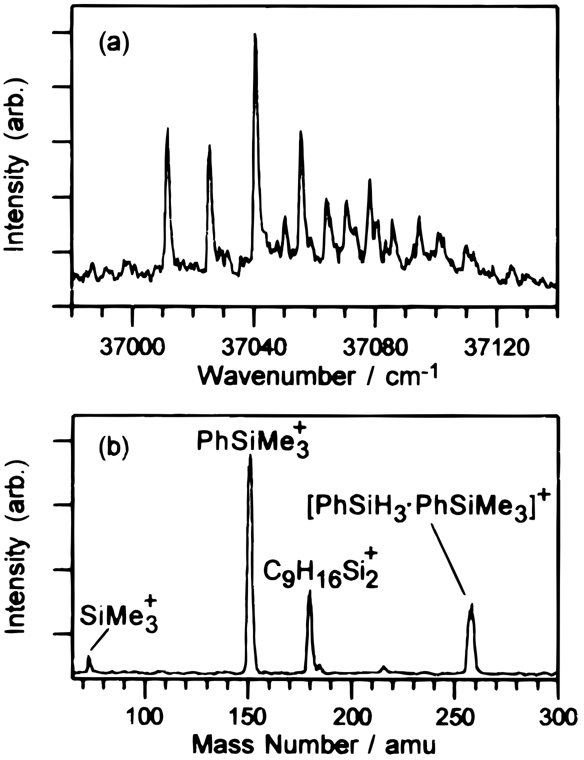

Figure 3. The RE2PI (a) excitation and (b) mass spectra of $PhSiH_3 \cdot PhSiMe_3$. The mass spectrum was measured at the 0_0^0 band ionization.

activation process has not yet made. Hereafter, these processes will be called reactions, while the merely evaporation of neutral monomer is called the fragmentation.

2. Intracluster Ion−Molecule Reactions of Various Phenylsilanes. To our knowledge, there is no report in which species other than monomer and dimer cation is observed in the RE2PI mass spectrum of the toluene dimer. Thus, it is readily expected that the intracluster reaction is a prominent feature of aromatic silicon compounds. In the FT-ICR study, the reaction between $PhSiH_3^+$ and C_6D_6 was also observed.[1] Its reaction rate constant was reported to be 1.0×10^{-10} cm^3 molecule^{-1} s^{-1}. This value is about a half of the rate of the reaction between $PhSiH_3^+$ and $PhSiH_3$. Thus, it would be expected that the similar intracluster reaction may occur in the case of $(PhSiH_3 \cdot C_6D_6)^+$ or $(PhSiH_3 \cdot PhCH_3)^+$ heterodimer cation. However, we could not observe appreciable amount of the reaction products expected for the case. From this fact one of the necessary condition for the collision-induced intracluster reaction is that both reactants must contain Si atom. To acquire the detailed information about the reaction mechanism and also the molecular structure of the reaction products, we have examined several homo- and heterodimer of phenylsilanes.

A. $(PhSiMe_3)_2^+$ *and* $(PhSiH_3 \cdot PhSiMe_3)^+$. Figure 2 shows the S_1-S_0 excitation spectrum of the homodimer $(PhSiMe_3)_2$ and the mass spectrum obtained by RE2PI at the 0_0^0 band. The mass spectrum clearly indicates that intracluster reaction does not occur, but only the fragmentation to the neutral monomer takes place. This result suggests that there is another necessary condition for the reaction to occur, since the $(PhSiMe_3)_2^+$ satisfies the above-mentioned condition on the existence of Si atom. Next, we concerned with the heterodimer $(PhSiH_3 \cdot PhSiMe_3)$; the S_1-S_0 excitation spectrum and mass spectrum are shown in Figure 3. In contrast to the case of the homodimer, the intracluster reaction takes place for the heterodimer. The observed reactions are

$$(PhSiH_3 \cdot PhSiMe_3)^+ \rightarrow SiMe_3^+ + C_{12}H_{13}Si \tag{3a}$$

$$\rightarrow C_9H_{16}Si_2^+ + C_6H_6 \tag{3b}$$

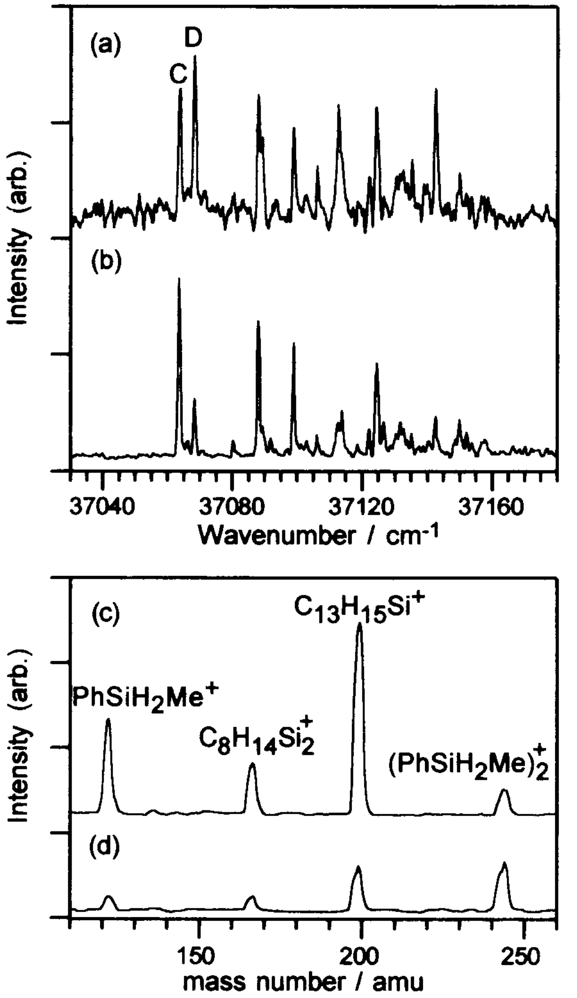

Figure 4. The RE2PI excitation spectra of $(PhSiH_2Me)_2$ monitoring (a) the parent cation and (b) the reaction product $C_{13}H_{15}Si^+$. The mass spectra c and d were measured in the ionization at the C and D bands, respectively.

Thus, the results lead us to propose the condition that at least one Si−H bond is inherently necessary for the reaction to be induced. It was confirmed that $SiMe_3^+$ was not a simple fragment from the $PhSiMe_3^+$ moiety but the reaction products of the dimer cation, because the $SiMe_3^+$ intensity was found to be much weaker even at the 0_0^0 band excitation of $PhSiMe_3$ monomer in our experimental condition.

B. $(PhSiH_2Me)_2^+$ *and* $(PhSiHMe_2)_2^+$. Another valuable information was obtained by the observation of the intracluster reaction of $(PhSiH_2Me)_2^+$ and $(PhSiHMe_2)_2^+$. These dimers satisfy the necessary condition for the reaction as proposed above. In Figures 4 and 5, the S_1-S_0 excitation and mass spectra for each dimer are shown, respectively. In both cases, we could observe the intracluster reaction products.

$$(PhSiH_2Me)_2^+ \rightarrow C_{13}H_{15}Si^+ + SiH_2Me \tag{4a}$$

$$\rightarrow C_8H_{14}Si_2^+ + C_6H_6 \tag{4b}$$

$$(PhSiHMe_2)_2^+ \rightarrow C_{14}H_{17}Si^+ + SiHMe_2 \tag{5a}$$

$$\rightarrow C_{10}H_{18}Si_2^+ + C_6H_6 \tag{5b}$$

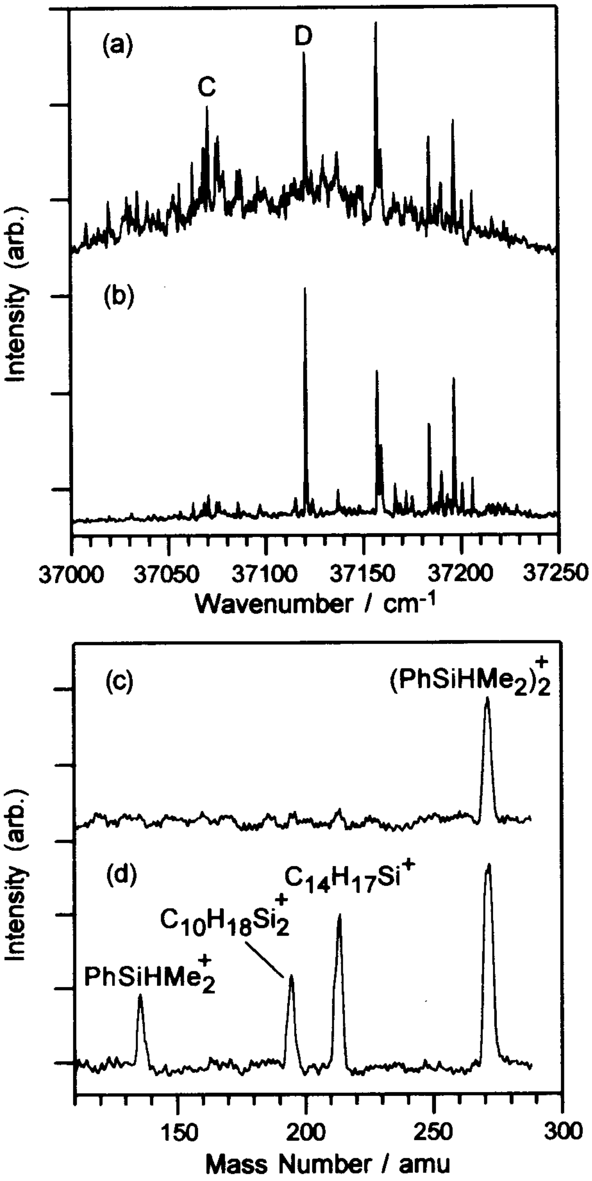

Figure 5. The RE2PI excitation spectra of $(PhSiHMe_2)_2$ monitoring (a) the parent cation and (b) the reaction product $C_{14}H_{17}Si^+$. The mass spectra c and d were measured in the ionization at the C and D bands, respectively.

The action spectra monitoring one of the reaction products are also shown for each dimer, Figure 4b and 5b, respectively.

The band D in Figure 4a appears with similar intensity in the excitation spectrum, whereas its intensity is much weaker than that of the band C in the action spectrum (Figure 4b). This difference indicates that there are two isomers in the jet and that the species responsible for the band C is much reactive than the species for the band D. We have confirmed the existence of the two isomer in the case of $(PhSiH_2Me)_2^+$ by hole-burning spectroscopy of the S_1-S_0 transition.

In the case of $(PhSiHMe_2)_2^+$, although we have not yet carried out the hole burning spectroscopy, it is apparent that there is two species in the jet from the action spectrum shown in Figure 5b. In addition, mass spectra in Figure 5c and d clearly exhibit the difference in reactivity between these two species. One of the species that exhibits the ion−molecule reaction is assigned as the dimer, since the red shift of the 0_0^0 band from that of the monomer is reasonable compared with those of the other dimers. Less reactive species should be an isomer of the dimer or a large size cluster.

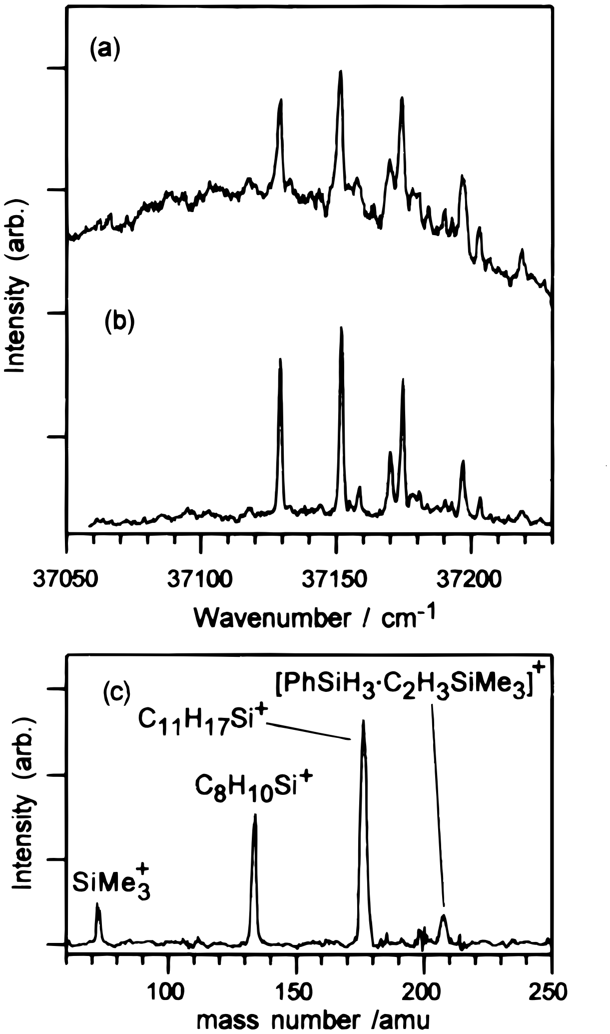

Figure 6. The RE2PI excitation spectra of $(PhSiH_3{\cdot}C_2H_3SiMe_3)$ monitoring (a) the parent cation and (b) the reaction product $C_{11}H_{17}Si^+$. The mass spectrum by RE2PI at the 0_0^0 band excitation is also shown in c.

C. $(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$. To elucidate a role of the phenyl π-system, a heterodimer $(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$ was also examined. The excitation and mass spectra are shown in Figure 6. The mass spectrum shown in Figure 6c indicates the occurrence of the ion−molecule reaction in this system. A broad and structureless background in the excitation spectrum shown in Figure 6a is due to a contribution of a fragmentation of large size clusters. The action spectrum monitoring the reaction products has no such a broad background (see Figure 6b). The reactions observed in this system are

$$(PhSiH_3{\cdot}C_2H_3SiMe_3)^+ \rightarrow C_{11}H_{17}Si^+ + SiH_3 \tag{6a}$$

$$\rightarrow SiMe_3^+ + C_8H_{11}Si \tag{6b}$$

$$\rightarrow C_8H_{10}Si^+ + HSiMe_3 \tag{6c}$$

In this case, the C_6H_6 elimination type 1b reaction was not observed.

IV. Discussion

The reaction products observed in this study for each parent cation are summarized in Table 1 together with the band origin of the S_1-S_0 transition of the corresponding neutral dimers. As

TABLE 1: Band Origin of S_1−S_0 Transition of Neutral Dimer of Phenylsilanes and Ion−Molecule Reactions Observed in This Study

species	0_0^0/cm^{-1} [a]	reaction[b]
$(PhSiH_3)_2^+$	37068 (−112)	$C_{12}H_{13}Si^+$ [185] + SiH_3
		$(PhSiH_3{\cdot}SiH_2)^+$ [138] + C_6H_6
$(PhSiMe_3)_2^+$	37187 (−143)	no reaction
$(PhSiH_3{\cdot}PhSiMe_3)^+$	37012 (−168)	$SiMe_3^+$ [73] + $C_{12}H_{13}Si$
		$(PhSiMe_3{\cdot}SiH_2)^+$ [180] + C_6H_6
$(PhSiH_2Me)_2^+$	37064 (−171)[c]	$C_{13}H_{15}Si^+$ [199] + SiH_2Me
	37068 (−167)[c]	$(PhSiH_2Me{\cdot}SiHMe)^+$ [166] + C_6H_6
$(PhSiHMe_2)_2^+$	37120 (−185)	$C_{14}H_{18}Si^+$ [213] + $SiHMe_2$
$(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$	37129 (−51)	$C_{11}H_{17}Si^+$ [177] + SiH_3
		$SiMe_3^+$ [73] + $C_8H_{11}Si$
		$C_8H_{10}Si^+$ [134] + $SiHMe_3$

[a] A number in parenthesis is a value of the red shift of the 0_0^0 band of the dimer compared with that of the monomer or that of the $PhSiH_3$ monomer in the case of heterodimer. [b] A number in square brackets is a mass number of species observed in this study. [c] Two isomers were identified by a spectral hole-burning technique.

mentioned above, no clear interpretation of the activation process of the ion−molecule reaction has yet been made. Since our discussion is based on the branching of the possible reaction pathways; however, the unidentified activation process does not affect on our arguments. As mentioned before, the FT-ICR study reported two types of ion−molecule reactions of phenylsilane cation: SiH_3 (reaction 1a) or C_6H_6 (reaction 1b) elimination.[1] The intracluster reactions observed in this study are also classified into these types. In each case except for $(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$, two reaction pathways are identified and one of them corresponds to the SiR_3 elimination (reaction 1a) type and the other is the C_6H_6 (reaction 1b) elimination.

1. C_6H_6 Elimination. In the FT-ICR study, Nagano and coworkers considered that one of the isomer of phenylsilane cation has a π-type complex form, $[C_6H_6{\cdot}SiH_2]^+$, and that this isomer leads to the product associated with the SiH_2^+ transferred type reaction.[1] As a result, a C_6H_6 moiety is eliminated in the reaction. Our results support this mechanism as described below. In the case of methyl substituted phenylsilane dimers, $(PhSiH_2Me)_2^+$, $(PhSiHMe_2)_2^+$, and $(PhSiMe_3)_2^+$, the following five pathways are formally expected for the C_6H_6 or C_6H_5Me elimination reaction.

$$(PhSiH_2Me)_2^+ \rightarrow (PhSiH_2Me{\cdot}SiHMe)^+ + C_6H_6 \quad (7a)$$

$$\rightarrow (PhSiH_2Me{\cdot}SiH_2)^+ + C_6H_5Me \quad (7b)$$

$$(PhSiHMe_2)_2^+ \rightarrow (PhSiHMe_2{\cdot}SiMe_2)^+ + C_6H_6 \quad (8a)$$

$$\rightarrow (PhSiHMe_2{\cdot}SiHMe)^+ + C_6H_5Me \quad (8b)$$

$$(PhSiMe_3)_2^+ \rightarrow (PhSiMe_3{\cdot}SiMe_2)^+ + C_6H_5Me \quad (9)$$

However, the reactions 7a and 8a were found to really occur only for the case of the C_6H_6 elimination, but not for the C_6H_5Me elimination. Since the reaction requires the SiR_2^+ transfer to the other moiety of the dimer, the binding between the SiR_2^+ segment and the aromatic ring is expected to be weak. These results are well explained by assuming that the reaction intermediate has a π-type complex configuration between C_6H_6 and SiR_2^+ segments such as as $[C_6H_6{\cdot}SiR_2]^+$. Thus, the C_6H_6 elimination reaction can be referred to the SiRtransfer alternatively. On the other hand, in the cases of reactions 7b and 8b, corresponding reaction intermediates are $[C_6H_5Me{\cdot}SiR_2]^+$. A methyl group attached to the phenyl ring seems to inhibit the formation of the π-type complex as well as the SiR_2^+ transfer, consequently. In Table 1, reaction products are denoted as $(PhSiR_3{\cdot}SiR_2^+)^+$, so that one can readily recognize that they are produced by the SiR_2^+ transfer reaction. In addition, in the case of $(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$, the SiH_2^+ transfer reaction does not occur. This means that the π-electrons of the phenyl ring efficiently accept the SiR_2^+ moiety, supporting that the structure of the intermediate is of the π-type complex.

Recent ab initio study by Jarek and Shin predicted that the most stable form of $C_6H_8Si^+$ is a π-type complex form, $[C_6H_6{\cdot}SiH_2]^+$.[2] A $[C_6H_5{-}SiH_3]^+$ type cation that is initially prepared can isomerize to $[C_6H_6{\cdot}SiH_2]^+$ with enough internal energy to surmount an isomerization barrier. This energy for isomerization should be supplied by a collision with He in our collision-induced reaction.

2. SiR_3 Elimination. In the case of the SiH_3 elimination type reaction, the product cation consists of one Si atom and five functional groups for reactions 2a, 4a, 5a, and 6a. The structure of these cations cannot be determined from our results. Possible structures of the reaction products are a "Wheland intermediate" type σ-complex or a π-type complex between the SiR_3^+ and phenyl ring. Lambert and co-workers suggested the existence of the "Wheland intermediate" type σ-complex between the SiEt and toluene solvent in solution.[5] The latter π-type complex is deduced from infrared spectroscopy of SiH_5^+, where its structure was determined as $SiH_3^+{\cdot}H_2$.[6] Spectroscopic studies such as vibrational and/or rotational ones are necessary to obtain the information about the structure of these species.

The production of $SiMe_3^+$ in reaction 3a should be a clue for the interpretation of the mechanism for this SiR_3 elimination type reactions. There is two possible mechanisms of reaction: (1) the product formation occurs after the SiR_3 moiety is eliminated or (2) the SiR_3 elimination occurs after the reaction intermediate is formed. In the case of $(PhSiH_3{\cdot}PhSiMe_3)^+$, reaction 3b indicates that a possible structure of this cation should be $PhSiH_3^+{\cdot}PhSiMe_3$. Thus, the following reaction is expected to occur:

$$PhSiH_3^+{\cdot}PhSiMe_3 \rightarrow C_{15}H_{19}Si^+ + SiH_3 \quad (10)$$

However, the $SiMe_3^+$ production path 3a occurs instead of this reaction. This fact can be interpreted based on the above mechanism 2. Since the heat of formation of $SiMe_3^+$ (145.8 kcal/mol[7]) is much smaller compared with that of SiH_3 (237 kcal/mol[8]), it is expected that the exothermicity of the $SiMe_3^+$ + $C_{12}H_{13}Si$ channel 3a is larger than that of the $C_{15}H_{19}Si^+$ + SiH_3 channel 10. This is the reason of the occurrence of the $SiMe_3^+$ + $C_{12}H_{13}Si$ channel. Thus, the reaction mechanism of the SiR_3 elimination is considered to be the dissociation of the reaction intermediate, and the lower energy channels are preferred as the dissociation path. In the case of $(PhSiH_3{\cdot}C_2H_3SiMe_3)^+$, all the three pathways should have similar exothermicities.

V. Conclusion

We have investigated intracluster ion−molecule reactions of dimer cations of various phenylsilanes in order to elucidate reaction mechanisms of phenylsilane cation. Similar types of reactions to those reported in the gas-phase FT-ICR study, SiR_3 elimination and SiR_2^+ transfer ones, were observed. On the basis of the possible reaction pathways, we could suggest the reaction mechanism for each type. In the latter case, our observation strongly supported that a precursor of this type of reaction has a π-type complex configuration, $[C_6H_6{\cdot}SiR_2]^+$, which has been proposed. On the contrary, in the former type of reaction, a dimer cation reacts and forms a reaction intermediate and then it dissociates preferentially to a larger exothermic channel.

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