Intracluster Ion−Molecule Reactions of Phenylsilane Dimer Cation following the Charge Resonance Band Excitation

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Photoinitiated intracluster ion−molecule reactions of phenylsilane dimer cation have been investigated for the first time. The reaction products were the same as those reported in the gas-phase study. The photodepletion spectrum of the parent dimer ion and the action spectra of the reaction products were observed in the region of 6000−22 000 cm^{-1}. All the spectra exhibit an intense band appearing in near-IR region, which is associated with the charge resonance (CR) transition of the dimer ion. It was 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 CR transition.

Introduction

Since organic silicon compounds are known to exhibit different chemical properties compared with corresponding hydrocarbons, many studies have been performed in the field of synthetic chemistry, stereochemistry, physicoorganic chemistry, photochemistry, and so on. Recently, Nagano and others investigated ion−molecule reactions of phenylsilane cation $PhSiH_3^+$, occurring in gas phase, and found the following reactions:[1]

$$PhSiH_3^+ + PhSiH_3 \rightarrow C_6H_{10}Si_2^+ + C_6H_6 \qquad (1)$$

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

Rate constants of the reactions 1 and 2 were determined to be 3.2 × 10^{-10} and 1.7 × 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 the following reaction takes place:

$$PhSiH_3^+ + C_6D_6 \rightarrow C_6D_6H_2Si^+ + C_6H_6 \qquad (3)$$

while the reaction corresponding to reaction 2 does not take place. Comparing the reactions 1 and 3, they concluded that a key process of the reactions is the transfer of SiH_2^+ segment from the cation to the neutral species. They also proposed two isomers: one is a complex of SiH_2^+ with phenyl group, C_6H_6-SiH_2^+, leading to the SiH_2^+ transfer reactions 1 and 3. The other was expected to be of $[C_6H_5-SiH_3]^+$ structure, which undergoes reaction 2.

Although the isomer structures and reaction mechanisms are not well-known, these ion−molecule reactions are of particular interest with respect to cluster chemistry. In this work we report photoinduced intracluster ion−molecule reactions of phenylsilane dimer cation, $(C_6H_5SiH_3)_2^+$. By using clusters involving $PhSiH_3^+$ as reaction precursors, the intracluster ion−molecule reactions corresponding to the gas phase reactions were initiated by exciting the dimer cation with visible to near-infrared (IR) light. We have found for the first time that the reactions are efficiently induced by the excitation of the low-lying charge resonance (CR) transition of the dimer cation. In molecular clusters relative orientations or conformations among components are rather restricted by their structure, so that reactions are initiated from particular conformation between the reactants. We will discuss mechanisms of the intracluster reactions in respect to photoexcitations.

Experimental Section

A conventional molecular beam equipment combined with a time-of-flight (TOF) mass spectrometer was used for the experimental setup, which was described elsewhere. Commercial phenylsilane (Shin-Etsu Chemical Co.) was used without further purification. $PhSiH_3$ vapor seeded in He gas was supersonically expanded into a vacuum chamber through an orifice of a pulsed valve (General valve series 9). Clusters of $PhSiH_3$, including the dimer, were generated in the expansion. To avoid the formation of larger size clusters than the dimer, partial vapor pressure of $PhSiH_3$ in the seeded gas was controlled by regulating the temperature of a sample container to be 0 °C. The jet expansion was skimmed to prepare a molecular beam by a skimmer of 1 mm diameter and then introduced into an ionization region of the chamber. The dimer cations were produced by resonance-enhanced two photon ionization via the S_1 state of the neutral dimer. The ions produced were accelerated perpendicular to the molecular beam axis into a TOF spectrometer and detected by a channel electron multiplier (Murata). An output of XeCl excimer laser (Lambda Physik LEXtra 50) pumped dye laser (Lambda Physik Scanmate) 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. In the spectroscopic measurements, an output of a tunable optoparametric oscillator (Spectra Physics MOPO 730) was used for the excitation of the dimer ion. The excitation laser beam was used without focusing and counterpropagated collinearly with the ionization laser beam. The delay time between the ionization and the excitation laser pulses was maintained as 100 ns with the digital delay generator (SRS DG-535). To confirm the present results are not due to collisional effects, we have also carried out the collision-induced experiment in the free jet condition. The results will be given in a separate paper.[2]

Results and Discussion

Figure 1 shows the resonance enhanced two photon ionization (RE2PI) spectrum of the phenylsilane dimer. The 0−0 band of the S_1−S_0 transition was found to occur at 37 068 cm^{-1}, showing a low-frequency shifts of 112 cm^{-1} from the band

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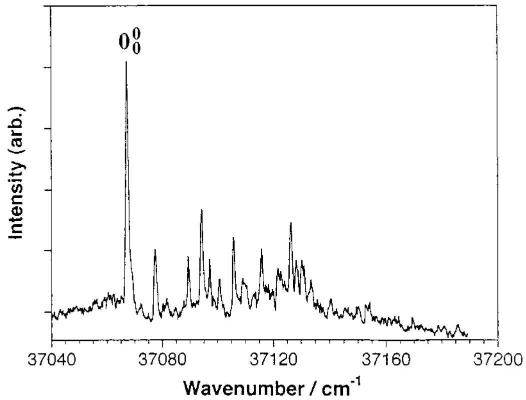

Figure 1. RE2PI spectrum of the phenylsilane dimer.

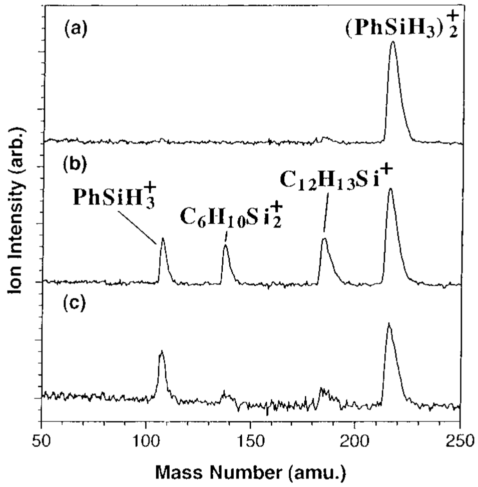

Figure 2. Time-of-flight mass spectra: (a) RE2PI mass spectrum of $(PhSiH_3)_2$. Only the ionization beam was irradiated. (b) and (c) The mass spectra after the photoexcitation of the $(PhSiH_3)_2^+$. The excitation energies were ca. 10 000 and 20 000 cm^{-1} for (b) and (c), respectively.

origin of the monomer.[3] Figure 2a shows the mass spectrum obtained by RE2PI with the 0−0 excitation of the dimer, representing that the dimer ion is preferentially created by the resonance ionization process. In contrast, three new species appeared and the dimer ion signal was reduced, when near-IR laser light was introduced into the region of ionization. Figure 2b reproduces the mass spectrum obtained after irradiation of the near-IR light with photon energy of ca. 10 000 cm^{-1}. The species with $m/z = 108$ amu is the monomer ion, $PhSiH_3^+$, which is one of the dissociation products[4] of the dimer ion. Other two species with $m/z = 138$ and 185 amu correspond to $C_6H_{10}Si_2^+$ and $C_{12}H_{13}Si^+$, respectively, which are the same reaction products found in the gas phase reaction study.[1] A linear laser power dependence of these products yield was also observed. These results indicate that the reactions similar to reactions 1 and 2 take place in $(C_6H_5SiH_3)_2^+$, as photoinduced intracluster ion−molecule reactions. It is noted that both intensities of the reaction products are comparable to the intensity of the dissociation product. In contrast, Figure 2c represents the mass spectrum obtained after the excitation by visible light with photon energy of ca. 22 000 cm^{-1}, which corresponds to the local excitation (LE) band of the dimer cation.[2] It is evident that the ion signal intensities of both the products are reduced compared to that of the dissociation product. The results represent that the yield of the photoinduced intracluster reactions substantially depend on the photon energy for the excitation of the dimer ion.

To investigate the photon energy dependence of the product yields, we observed the action spectra with respect to each product species by monitoring the ion signal of the individual ions. In Figure 3 are reproduced the depletion spectrum a of the dimer ion, the action spectrum b of the reaction product $C_{12}H_{13}Si^+$, and the spectrum c of the dissociation product, $C_6H_5SiH_3^+$. A quite similar yield spectrum of the other product, $C_6H_{10}Si_2^+$, was also obtained, but it is not shown in the figure. The depletion spectrum a corresponds to the absorption spectrum of $(C_6H_5SiH_3)_2^+$, if the destruction yield of the dimer ion is assumed to be constant with respect to the excitation energy. Despite of a poor signal-to-noise ratio, it is evident that the depletion spectrum exhibits an intense band with a maximum at 10 000 ± 1000 cm^{-1}, and a weak rise in the higher energy region than 16 000 cm^{-1}, in particular at around 22 000 cm^{-1}. In the spectrum b, the former band is pronounced, but there is no rise in the high energy region. In the spectrum c, on the other hand, the enhancement in higher energy region than 22 000 cm^{-1} is evident as well as the intense band in near-IR region. It is noticed that the low energy side of the intense band of the spectrum c is much steeper than the corresponding band in other spectra a and b. This steep onset of the appearance of $PhSiH_3^+$ may be related to the presence of a potential barrier to the dissociation.

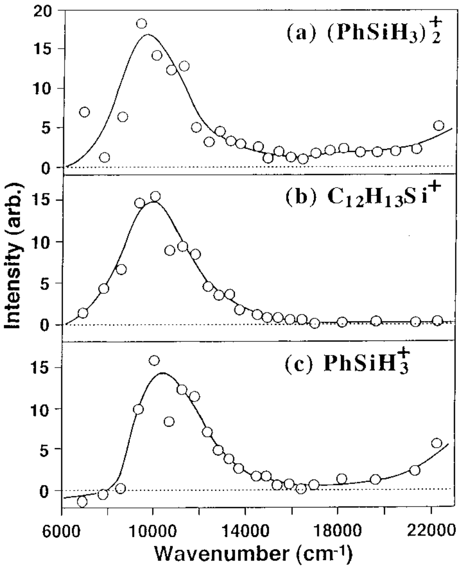

Figure 3. (a) Photo depletion spectrum of the $(PhSiH_3)_2^+$. (b) Action spectrum of the reaction products, $C_{12}H_{13}Si^+$. (c) Dissociation yield spectrum of the monomer ion.

Such an extremely broad feature of the absorption band occurring in near-IR region is known to be due to a charge resonance (CR) transition, which is well-known for dimer cations of aromatic molecules. CR transitions of the benzene dimer and the toluene dimer cations exhibit their maximum at 11 000 and 10 200 cm^{-1}, respectively.[5,6] In this respect, it is reasonable to assign the observed band with its maximum at ca. 10 000 cm^{-1} as a CR transition of $(PhSiH_3)_2^+$. On the other hand, the band appearing in the energy region of 22 000 cm^{-1} can be associated with a transition of the cationic moiety, that is, the LE of $PhSiH_3^+$. Also in the case of the benzene and toluene dimer cations, LE bands have been known to occur at 22 700 and 22 720 cm^{-1}, respectively.[6,7] The LE band of aromatic molecular ions, including the phenylsilane dimer cation, is expected to occur in the similar energy region, since the transition is associated with excitation of an electron from an occupied π orbital to the vacant π orbital of the ions.

It is well-known that the upper state of such an intense CR transition is inherently dissociative. Then, the excitation to the upper state of $(PhSiH_3)_2^+$ easily leads to the dissociation products, that is, $PhSiH_3^+$ with the neutral $PhSiH_3$; the mass spectrum of the former species was actually observed as shown in Figure 2b. Although the excitation results in the direct dissociation of the dimer ion, the time scale required for the process seems to be not so fast that the intracluster ion−molecule reactions take place during the dissociation. In the case of the benzene dimer cation, Ohashi and Nishi reported that about 10% of the available energy, at most, is released into the translation degree of freedom of the fragments, and they assumed that the time for the dissociation is comparable or even longer than the time of molecular rotation.[8] In the case of $(PhSiH_3)_2^+$, we assume the similar time scale for the dissociation as in the case of the benzene dimer cation, although no reaction is involved in the latter. The intracluster ion−molecule reaction of the former cation proceeds during the time scale of the dissociation, as the products were actually observed in this work. In other words, the reaction proceeds on the electronic ground potential energy surface after the rapid internal conversion from the CR state. In contrast, the spectrum b of Figure 3 represents an quite interesting feature in considering mechanisms of the intracluster ion−molecule reaction; the spectrum shows that the yield of the reaction does not increase with the excitation energy. Despite the fact that the excitation energy of the LE band is twice as large as that of the CR band, the reaction yield of the latter is much more pronounced. Again in the case of the benzene dimer cation, the dissociation takes place after internal conversion from the upper state of the LE band, so that large amount of the available energy converts into internal excitations of the dissociation fragments. The same seems to be true for $(PhSiH_3)_2^+$, because internal conversion is usually very fast compared to the dissociation process of such a heavy moiety. If the reaction as well as the dissociation of $(PhSiH_3)_2^+$ proceeds statistically from the upper state of the LE band, the reaction products should also be comparable with the dissociation product, as it is found in the case of the CR excitation, shown in Figure 2b. The mass spectrum, given in Figure 2c, shows much smaller yield of the reaction products than the dissociation product, representing that the upper state of the LE band is not well-communicated with the reaction process. Therefore, we have concluded that the intracluster ion−molecule reaction coordinates are more preferentially interacting with the upper state of the CR transition than that of the LE band. Similar dependence was observed in the case of naphthalene cluster cations.[9]

The presence of the characteristic CR transition indicates that the dimer cation has a parallel conformation of the two phenyl rings, as it is known in the case of $(C_6H_6)_2^+$. Because the CR interaction in dimer cations depends strongly on overlaps of π-orbitals between the aromatic rings, the parallel conformation is essential for the dimer cation to be substantially stabilized. Since $PhSiH_3$ has a dipole moment, the antiparallel conformation would be more feasible for the dimer cation. However, further details of the geometrical structure, such as their relative orientation of silyl groups, are not determined in the present work. In this respect, we could not predict the presence of isomers which may lead to different reaction products. As seen in Figure 2b, the relative intensity of $C_6H_{10}Si_2^+$ versus $C_{12}H_{13}Si^+$ is about unity, it seems to suggest for the yields of both the photoinduced intracluster reactions corresponding to reactions 1 and 2 to be the same, while the rate constant of reaction 1 has been known to be large as twice as that of reaction 2. The difference in reaction yields or rate constants between the intracluster and the gas-phase reactions is of quite interesting in respect of stereochemical point of view. However, there are two possible reasons for this difference. The FT-ICR study revealed that two isomers of $PhSiH_3^+$ are generated at the low-energy electron impact ionization and that these isomers react with $PhSiH_3$ differently.[1] If two isomers of $(PhSiH_3)_2^+$, each one of which corresponds to the isomer of $PhSiH_3^+$, were generated at the two-photon ionization or the CR exictation, the relative product ratio reflects the relative population between these isomers as well as the reaction rate for each path. On the other hand, if there is no isomer of $(PhSiH_3)_2^+$, the relative products ratio contains the information about the stereochemical effect on the intracluster reaction. If we could determine more details of geometrical structure of the dimer ion, or if we may find isomers having different conformations, we may be able to discuss the intracluster reaction processes on the basis of stereochemistry in molecular level.

Conclusion

We reported here the photoinitiated intracluster ion−molecule reactions of phenylsilane dimer cation. The reaction products were the same as those reported in the gas phase study. It should be noted that product yield is much dependent on the excitation photon energy. The CT band excitation produces intracluster-reaction products whereas the LE band does not.

References and Notes

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