Microscopic Solvation Effects on Si-Si Bond Cleavage Reactions of Cluster Cation Radicals of (*p*-Cyanophenyl)pentamethyldisilane with Hydroxylic Molecules

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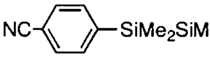
Facile Si-Si bond cleavage reactions of cation radicals of jet-cooled clusters of (*p*-cyanophenyl)pentamethyldisilane with H_2O or CH_3OH were found to occur via intracluster nucleophilic attack of a solvent molecule by means of resonance-enhanced two photon ionization mass spectrometry.

It is well-known that a facile Si-Si bond cleavage occurs in aryl- and alkyl-oligosilane cation radicals which are generated by electron-impact ionization (EI) in the gas phase[1] and by photochemical electron-transfer reactions in solution.[2] Whereas it is an interesting issue whether the Si-Si bond cleavage reactions occur spontaneously or through the nucleophilic attack by solvents, there has been only a little argument on this subject until now.[2e,h,i] The resonance-enhanced multiphoton ionization (REMPI) method combined with mass spectrometry has been demonstrated to be a useful technique in order to study the reactions of solvated cation radicals in a supersonic free jet expansion.[3,4] Using the REMPI technique, we have investigated the Si-Si bond cleavage reactions of (*p*-cyanophenyl)-pentamethyldisilane (CPDS) cluster cation radicals, CPDS-$(H_2O)_n^+$ and CPDS-$(CH_3OH)_n^+$ ($n \geq 1$) and found remarkable microscopic solvation effects depending on the cluster-size.



CPDS

CPDS vapor seeded in He gas was supersonically expanded into a vacuum chamber through a pulsed nozzle with an orifice of 0.8 mm in diameter. A little amount of contaminated H_2O vapor in the sample handling was enough to observe CPDS-H_2O complexes in our experimental condition. On the other hand, CPDS-CH_3OH complexes were prepared in a free jet with a gaseous mixture of CPDS vapor, CH_3OH, and He. These complexes were selectively ionized by the REMPI method through its S_1 state with the second harmonics of the tuned output of an excimer or a YAG pumped dye laser. The resulting ionic species were mass-analyzed by a Q-pole mass filter of ±1 amu mass resolution, and detected by an electron multiplier.

Figure 1 shows the REMPI spectrum of the S_1–S_0 transition obtained by monitoring the total ion current without mass selection. The spectral pattern is identical to the LIF excitation spectra reported previously.[5] In addition to the peaks due to the CPDS monomer, several peaks appear in the low frequency side, which are assigned as those due to the CPDS-$(H_2O)_n$ clusters (n = 1 and 2), by a mass spectrometric analysis described below. The electronic band origins of the spectra of CPDS-$(H_2O)_n$ clusters are found to be red-shifted from that of the monomer (35520 cm^{-1}) by 62 and 122 cm^{-1} for n = 1 and 2, respectively. Progressions of about 25 cm^{-1} spacing observed for the monomer and its clusters may be assigned to the torsional motion around a C_{Ph}–Si bond. A similar vibrational mode is found in phenylpentamethyldisilane.[6]

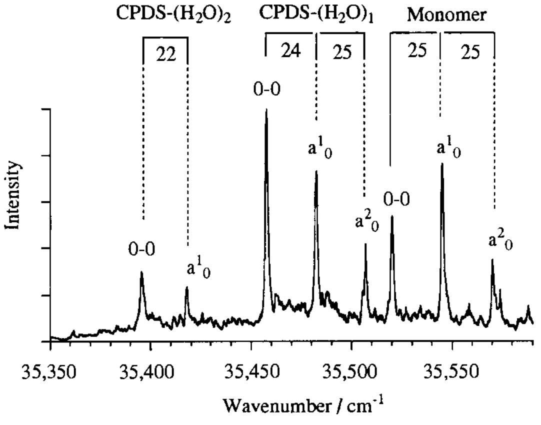


Figure 1. REMPI spectrum of the S_1 - S_0 transition of jet-cooled CPDS monomer and CPDS-$(H_2O)_n$ cluster (n = 1 and 2) obtained by monitoring the total ion.

The mass spectra obtained by the REMPI of CPDS monomer and its water complexes are shown in Figure 2. As shown in Figure 2(a), only an intense peak at *M* = 233 amu appears in a mass spectrum of the CPDS monomer. This mass pattern of the CPDS monomer cation radical ($CPDS^+$) is quite simple compared with that observed by the EI method.[7] Since the parent $CPDS^+$ is prepared with a large amount of excess energy in the ionization and since collisions of $CPDS^+$ with the carrier He gas after the ionization cannot be avoided in the present experimental condition, fragmentation to give Me_3Si^+ (*M* = 73 amu) or *p*-$CNC_6H_4SiMe_2^+$ (*M* = 160 amu) may occur in $CPDS^+$. When the laser intensity is increased, a small peak due to Me_3Si^+ is observed in addition to $CPDS^+$.

In a mass spectrum of CPDS-$(H_2O)_1$ (Figure 2(b)), again a predominant peak due to $CPDS^+$ at *M* = 233 amu is observed together with a weak peak due to CPDS-$(H_2O)_1$ ion at *M* = 251 amu. The results indicate that the major reaction of the CPDS-$(H_2O)_1$ ion is simple detachment of H_2O molecule. Weak peaks due to *p*-CN-C_6H_4-$SiMe_2^+$ and Me_3Si^+ will be produced via detachment of a water followed by a spontaneous Si-Si cleavage.

In contrast, the cracking pattern of CPDS-$(H_2O)_2$ is rather complicated as shown in Figure 2(c). Two characteristic peaks at *M* = 178 and 196 amu are observed in addition to intense peaks at *M* = 233 and 251 amu, which are easily assigned to be ions produced by the consecutive detachment of water molecules from CPDS-$(H_2O)_2^+$. The mass numbers of 178 and 196 amu correspond to [*p*-CN-$C_6H_4SiMe_2$ + $H_2O]^+$ and [*p*-CN-

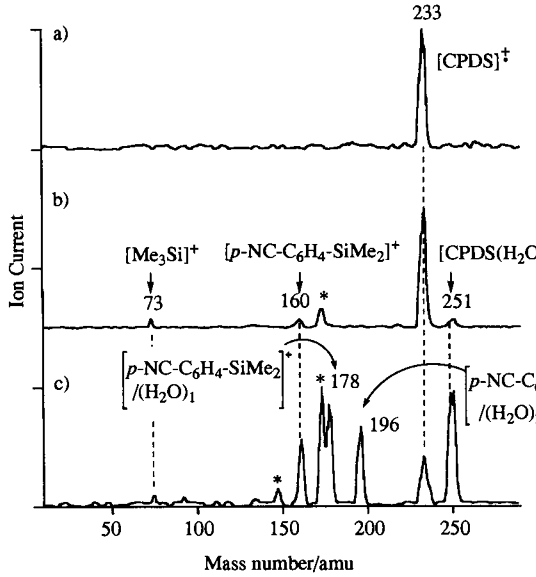
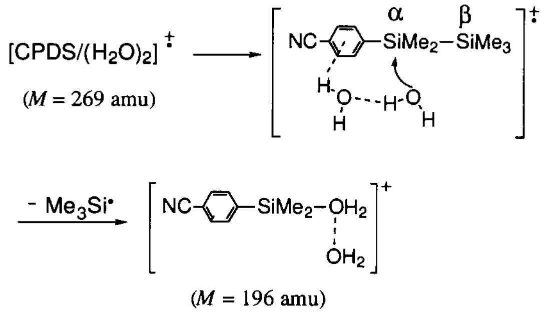


Figure 2. Low resolution mass spectra obtained by the two-photon ionization of the jet-cooled CPDS-$(H_2O)_n$ clusters via the excitation of their 0-0 bands; (a) n = 0 (CPDS monomer), (b) n = 1, and (c) n = 2. Asterisks indicates unidentified ions.

$C_6H_4SiMe_2 + 2(H_2O)]^+$, respectively. The appearance of these ions indicates that the facile Si–Si bond cleavage from CPDS-$(H_2O)_2{}^+$ cluster occurs in competition with the detachment of solvent molecule(s). Although the parent ion (*M* = 269 amu) is not detected in this condition, the appearance of [p-CN-$C_6H_4SiMe_2 + 2(H_2O)]^+$ suggests that the parent ion is [CPDS–$(H_2O)_2]^+$. In general, a simple detachment of the solvent molecules occurs before a breaking of the intramolecular bond in the ionization of the solvated clusters, since the binding energy between the solute and solvent molecules is much weaker than the intramolecular bond dissociation energy. For instance, the Si–Si bond dissociation energy for a disilane cation radical is roughly estimated to be ca. 40 kcal/mol, which is a half of the dissociation energy in a neutral disilane.[8] This value is much larger than the energy for an intermolecular binding such as a hydrogen bond. Thus, the mechanism of the formation of the [p-CN-$C_6H_4SiMe_2 + H_2O]^+$ and [p-CN-$C_6H_4SiMe_2 + 2(H_2O)]^+$ ions would be ascribed to a solvent assisted Si–Si bond cleavage rather than the spontaneous cleavage of the Si–Si bond from the cluster. That is, the facile Si–Si bond cleavage is assisted by a nucleophilic attack of H_2O to the α-silicon atom in the cluster ions, as shown in Scheme 1.[9] On the other hand, the formation of Me_3Si^+ and p-CN-$C_6H_4SiMe_2{}^+$ in the ionization of CPDS-$(H_2O)_2$, is considered to occur via a spontaneous Si–Si bond cleavage of CPDS after the detachment of H_2O molecules. Whereas the solvent assisted Si–Si bond cleavage of disilane cation radicals is often suggested to occur in solution,[2f,g] the present results exhibits the first direct evidence for the nucleophilic Si-Si bond cleavage in a cluster cation in the gas phase. The reason why the solvent assisted Si–Si bond cleavage occurs exclusively in the CPDS-$(H_2O)_2$ cation may be attributed to higher nucleophilicity of an oxygen in the H_2O dimer than that of the monomeric H_2O. Similar solvent-size dependence in the intracluster nucleophilic substitution reaction has been observed in the fluorobenzene-methanol system.[4]



Scheme 1.

The electronic band origins of the REMPI spectra of CPDS-$(CH_3OH)_n$ clusters are red-shifted from that of CPDS monomer by 70 and 147 cm^{-1} for n = 1 and 2, respectively. The exact cluster size for the latter has not yet been determined. Intracluster Si–Si bond cleavage reactions are observed not only in CPDS-$(CH_3OH)_n$ ($n \geq 2$) but also in CPDS-CH_3OH cluster cations. In the CPDS-$(CH_3OH)_n$ cation, an ion due to $[Me_3Si + CH_3OH]^+$ (*M* = 105 amu) appears together with ions due to [p-CN-$C_6H_4SiMe_2 + CH_3OH]^+$ (*M* = 192 amu) and [p-CN-$C_6H_4SiMe_2 + 2(CH_3OH)]^+$ (*M* = 224 amu). The appearance of the $[Me_3Si + CH_3OH]^+$ ion suggests that the nucleophilic substitution occurs not only at the α-silicon but also at the β-silicon of CPDS.

References and Notes

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9 By means of size-selected infrared spectroscopy and theoretical calculations, it is suggested that in the neutral benzonitrile-$(H_2O)_2$ cluster, a terminal hydrogen in a water dimer is bonded with a CN group and a basic oxygen interacts with an ortho-hydrogen of the aromatic ring. Whereas a similar structure is suggested for the neutral CPDS–$(H_2O)_2$, the corresponding cation radical may have a significantly different structure.