Metastable Ion Study of Organosilicon Compounds Part IV. 1,1,1,3,3,3-Hexamethyldisilazane and 1,1,3,3-Tetramethyldisilazane

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The unimolecular fragmentations of 1,1,1,3,3,3-hexamethyldisilazane (**1**), and 1,1,3,3-tetramethyldisilazane (**2**) were investigated by mass-analyzed ion kinetic energy (MIKE) spectra. D-Labeling studies and high resolution data were also included. One of the characteristic fragmentations of these compounds was the loss of CH₄ after the expulsion of CH₃ or H from the molecular ions.

In the case of **1**, D-labeling study indicated that the hydrogen atom bonded to nitrogen atom concerned this CH₄ loss. Almost complete scrambling of CH₃ groups occurs prior to loss of CH₄. An unusual NH₃ elimination was found in the MIKE spectra of the [M-CH₃-CH₄]⁺ ion for **1** and of the [M-CH₃]⁺ ion for **2**.

The fragmentations of **2** were compared with those of its carbon analogue, diisopropylamine, **3**.

1. Introduction

Organosilicon compounds are very important intermediates in synthetic organic chemistry. Trimethylsilyl derivatives are also important to analyze involatile compounds by mass spectrometer. An excellent review on mass spectra of organosilicon compounds has been published.¹⁾ The silicon-containing organic ions undergo a number of interesting rearrangements during decomposition.¹⁻⁵⁾ However, very little has been reported on the fragmentation mechanisms of these compounds by using the mass analyzed ion kinetic energy (MIKE) spectra.^{3, 4)}

In previous paper, we have reported the fragmentation mechanisms of hexamethyldisiloxane, ((CH₃)₃SiOSi(CH₃)₃).^{4b)} This is one of the typical compounds of

siloxanes, which have fundamental bond unit (Si-O-Si) of silicone. An almost complete scrambling of CH₃ groups prior to losses of CH₄ and (CH₃)₂SiO from [M-CH₃]⁺, was found by the analysis of the MIKE spectra.

The purpose of this report is to investigate the fragmentation mechanisms of 1,1,1,3,3,3-hexamethyldisilazane, **1** and 1,1,3,3-tetramethyldisilazane, **2** by the combined use of the MIKE spectra, D-labeling studies and high resolution data. Both compounds have the same bond unit (Si-NH-Si), instead of (Si-O-Si) of hexamethylsiloxane. The fragmentation mechanism of **1** has been already reported, but not in detail, by Tamas and Miklos⁶⁾ by D-labeling studies and high resolution data. In this paper, however, more detailed fragmentation mechanisms

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of **1** are presented by using MIKE spectra. Further, the fragmentation of **2** is compared with that of its carbon analogue, diisopropylamine, **3**.

The compounds studied here are as follows: $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ (**1**), $(\text{CH}_3)_2\text{HSiNHSiH}(\text{CH}_3)_2$ (**2**), $(\text{CH}_3)_3\text{SiNHSi}(\text{CD}_3)_3$ (**1-d₉**), $(\text{CD}_3)_3\text{SiNHSi}(\text{CD}_3)_3$ (**1-d₁₈**) and $(\text{CH}_3)_2\text{CHNHCH}(\text{CH}_3)_2$ (**3**).

2. Experimental

The mass spectra and high resolution data were obtained with a Hitachi M-80 A double-focusing mass spectrometer. The unimolecular MIKE spectra were measured on a modified Hitachi RMU-7M reversed geometry mass spectrometer. The detail was described previously.⁷⁾ Samples were introduced *via* a heated inlet system at 150°C. The ion source temperature was 180°C. Electron accelerating voltage was 70 V, total emission current was 100 μA . Ion accelerating voltages were 3.2 kV for a Hitachi M-80A, and 4.8 kV for a Hitachi RMU-7M, respectively.

The amount of kinetic energy release (KER) was estimated from the metastable peak width at half-height in the MIKE spectrum, after correction for the width of the main beam of the stable ions.^{8, 9)}

The deuterium labelling compounds (**1-d₉** and **1-d₁₈**) were synthesized as follows and were purified by means of gas chromatography.

Since all attempts to separate **1-d₉** from **1-d₁₈** were unsuccessful, the crude mixture of these compounds was measured by the MIKE spectra. The compounds **1** and **2** were G. R. Grade products from Shin-Etsu

Chemical Co., Ltd., and were used without further purification. The compound **3** was G. R. Grade product from Tokyo Kasei Co., Ltd.

3. Results and Discussion

1, 1, 1, 3, 3, 3-Hexamethyldisilazane (**1**)

The mass spectrum of **1** is shown in Fig. 1 with those of **2** and **3**. The molecular ion peak at m/z 161 of **1** is not abundant. The unimolecular MIKE spectrum of this ion, however, clearly shows that this ion fragments only to the ion at m/z 146 in the metastable time frame, as shown in Fig. 2 (a). This means that the ion at m/z 146 ($\text{C}_5\text{H}_{16}\text{NSi}_2^+$) is generated by loss of one of the CH_3 groups, in a similar manner to the cases of hexamethyldisiloxane.^{4b)} The elemental compositions of all ions indicated in this paper, were confirmed by the high resolution data.

The unimolecular MIKE spectrum of the ion at m/z 146 $[\text{M}-\text{CH}_3]^+$ is also shown in Fig. 2(b). A large portion of these ions fragments to the ion at m/z 130 by loss of CH_4 . This fragmentation is different from that of the case of hexamethylsiloxane,^{4b)} since the daughter ion at m/z 73 can not be observed in the case of **1**. The predominant fragmentations of $[\text{M}-\text{CH}_3]^+$ generated from hexamethylsiloxane were competitive losses of CH_4 , C_2H_4 and $(\text{CH}_3)_2\text{Si}=\text{O}$.^{4b)} The loss of CH_4 is undoubtedly preceded by the transfer of a hydrogen atom to CH_3 group. As shown in Fig. 2(b), a dish-topped metastable peak was observed for this metastable fragmentation. The KER value ($T_{50\%}$) estimated from this peak width was about 940 meV. This extremely large KER value implies that this ion at m/z 130 is of great stability, as was suggested by Tamas and Miklos.⁶⁾

In order to reveal these fragmentations,

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Fig. 1. EI mass spectra of (a) 1, (b) 2, and (c) 3 at 70 eV.

Fig. 2. Unimolecular MIKE spectra of the ions at (a) m/z 161, (b) m/z 146, and (c) m/z 130 from **1**.

the unimolecular MIKE spectra of D-labelling analogues (**1-d₉** and **1-d₁₈**) were measured. The loss of methyl radical (CD_3) from **1-d₁₈** gives rise to the ion at m/z 161. Fig. 3 shows the partial unimolecular MIKE spectrum of the ion at m/z 161 from **1-d₁₈**. Only the ion at m/z 142, corresponding to the loss of CD_3H , was observed. This metastable peak shape is not a dish-topped one, but a simple gaussian-shaped one, in contrast to the case of **1**. The KER value estimated from this peak width was about 280 meV. This isotope effect in the KER value is very strange, because, when the reverse activa-

Fig. 3. Partial unimolecular MIKE spectrum of the ion at m/z 161 from **1-d₁₈**.

Fig. 4. Partial unimolecular MIKE spectra of the ions at (a) m/z 155 and (b) m/z 152 from **1-d₉**.

tion energy can not be negligible as the case of this CH_4 loss, the KER value of D-labelling compound is generally larger than that of unlabelling one.^{10, 11)} Further, this difference is too large to regard as the secondary isotope effect.^{2, 10)} Unfortunately, we could not rationalize this strange

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Scheme 1.

isotope effect in this study. We can conclude unambiguously, however, that the hydrogen atom bonded to nitrogen atom concerned the CH_4 loss in the 2nd field-free region from the $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_2^+$ ion. This conclusion in the metastable time frame, is in agreement with that obtained from the fragmentation of the ions having higher internal energy.⁶⁾

Fig. 4 shows the partial unimolecular MIKE spectra of the ions at m/z 155 and m/z 152 from **1-d₉**. These ions correspond to the loss of CH_3 and CD_3 from the molecular ion of **1-d₉**, respectively. In both MIKE spectra, the peak due to the loss of methane molecule, splits to the two peaks. One of them is due to the loss of CH_4 , and

the other is due to the loss of CD_3H . Two different mechanisms may be proposed to explain this result. [1] One of the methyl groups in both $(\text{CH}_3)_3\text{Si}$ and $(\text{CH}_3)_2\text{Si}$ groups concern this methane loss reaction, that is, two mechanisms are involved in the reaction. [2] The fragmentation mechanism is only one, and almost complete scrambling of five methyl groups occurs prior to this reaction, in analogy to the case of hexamethyldisiloxane.^{4b)}

If the mechanism [1] is valid, it is expected that the MIKE spectrum of the processes, m/z 161 $\rightarrow$ m/z 142 for **1-d₁₈**, is a composite one.¹²⁾ However, the metastable peak shape is a simple gaussian-shaped one, as shown in Fig. 3. Therefore, to

Fig. 5. Unimolecular MIKE spectra of the fragment ions at (a) m/z 132, (b) m/z 116, and (c) m/z 118 from 2.

explain the results shown in Fig. 4, it is assumed that almost complete scrambling of methyl groups occurs prior this decomposition. The statistical intensity ratio for the losses of CH_4 and CD_3H calculated by assuming no isotope effect is 2 : 3 in the MIKE spectrum of the ion at m/z 155. On the other hand, the ratio is 3 : 2 in the MIKE spectrum of the ion at m/z 152. However, these ratios estimated from the area of the metastable ion peak in Fig. 4 were 2 : 1.82 and 3 : 1.07, respectively. These differences imply that a considerable isotope effect is operative for these reactions. The isotope effects ($k_{\text{H}}/$

k_{D}) can be estimated to be 1.65 and 1.87, respectively. The average isotope effect $k_{\text{H}}/k_{\text{D}}=1.76$ obtained by assuming a complete scrambling, may be too large to regard as the secondary isotope effect.¹⁰⁾ However, this is in agreement with that of the secondary isotope effect $k_{\text{H}}/k_{\text{D}}=1.43$ for loss of $\text{C}_2\text{H}_5/\text{C}_2\text{D}_5$ from M^+ of D-labelling hexamethyldisiloxane.²⁾ It is difficult to consider a partial degree of scrambling, because if it is so, this consideration makes it necessary to assume more large isotope effect in order to rationalize the results in Fig. 4(a).

The unimolecular MIKE spectrum of the ion at m/z 130 for 1 is also shown in Fig. 2(c). This spectrum contains many metastable peaks, which can be assigned to loss of NH_3 , C_2H_4 , $\text{CH}_3\text{CH}=\text{NH}$, and CH_3SiN , leading to m/z 113, m/z 102, m/z 87 and m/z 73 ($(\text{CH}_3)_3\text{Si}^+$), respectively. All of these fragmentation are due to the competitive metastable fragmentations, because the internal energy of the ion at m/z 130 is too low to undergo consecutive decomposition in the same field-free region.¹³⁾ An unusual NH_3 elimination which should involve considerable rearrangement, gives rise to the most abundant peak at m/z 113 in metastable time frame. The losses of NH_3 and $\text{CH}_3\text{CH}=\text{NH}$ correspond to those of H_2O and $\text{C}_2\text{H}_4\text{O}$ in the case of hexamethyldisiloxane.^{4b)} The peaks of all ions in Fig. 4b are gaussian-shape. In spite of a rearrangement reaction, the KER value accompanying with the NH_3 loss is small ($T_{50\%}=56$ meV), compared with that of CH_4 loss from $[\text{M}-\text{CH}_3]^+$ ion.

Tamas and Miklos have proposed a simple structure, $(\text{CH}_3)_2\text{Si}^+\text{N}=\text{Si}(\text{CH}_3)_2$, for the ion at m/z 130, and suggested that NH_3 loss from this ion involves extensive rearrangement.⁶⁾

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Scheme 2.

To rationalize these complex metastable decompositions, one of the plausible structures for m/z 130 ion is shown in Scheme 1 by reference to the case of hexamethyldisiloxane.^{4b)}

1,1,3,3-Tetramethyldisilazane (2)

The mass spectrum of 2 is also shown in Fig. 1(b). The loss of CH_3 from the molecular ion gives rise to the most abundant peak at m/z 118 ($C_3H_{12}NSi_2^+$), as well as in the cases of 1 (Fig. 1(a)) and of diisopropylamine, 3, which is the carbon analogue of 2 (Fig. 1(c)). In addition, this molecular ion also decomposes to the ions at

m/z 132 ($C_4H_{14}NSi_2^+$) by loss of H. This is in contrast to the case of 1 and 3, because the elimination of H is a minor process in the mass spectra of these compounds.

Fig. 5 shows the unimolecular MIKE spectra of the ions at m/z 132, 116 and 118. The first one fragments only to the ion at m/z 116 by loss of CH_4 . As shown in Fig. 5(b), this fragment ion at m/z 116 further decomposes to the ions at m/z 100 ($C_2H_6NSi_2^+$) and at m/z 73 ($(CH_3)_3Si^+$) by losses of CH_4 and $HNSi$, respectively. The transfer of, at least, one methyl group to the other Si-atom is essential for the generation of the ion at m/z 73. This fact may

Fig. 6. Unimolecular MIKE spectra of the fragment ions at (a) m/z 100 and (b) m/z 86 from **3**.

substantiate the scrambling of CH_3 groups in **1** described above. The ion corresponding to the loss of NH_3 could not be observed at m/z 99 in this MIKE spectrum. The last one fragments to the ions at m/z 102, 101 and 73. These fragmentations are different from the case of **3** (*vide infra*). Although the fragmentation of $[\text{M}-\text{H}]^+$ ion has not been confirmed by D-labelling study, the hydrogen atom bonded to nitrogen atom may concern this CH_4 loss, taking the fragmentation mechanism of the m/z 146 ion for **1** into account. As shown in Fig. 5(a), dish-topped metastable peak is also observed for the reaction, m/z 132 $\rightarrow$ m/z 116 ($T=870$ meV). This means that the m/z 116 ion is of great stability, too.

The ions at m/z 102 and 101 shown in Fig. 5(c) are assigned to $(\text{C}_2\text{H}_8\text{NSi}_2)^+$ and $(\text{C}_3\text{H}_9\text{Si}_2)^+$, respectively. So, these are due to losses of CH_4 and NH_3 . An unusual NH_3 elimination is also observed in the fragmentation of this ion. This means that

the m/z 118 ion undergoes to a number of rearrangements prior to decomposition in analogy with the m/z 130 ion from **1** (see before).

The KER value accompanying with the CH_4 loss from the ion at m/z 118 was also very large ($T=700$ meV). This value was estimated from two times of half-width of the left side in the peak, because this is interfering in the peak corresponding to NH_3 loss as shown in Fig. 5(c). This large KER value indicates that the $[\text{M}-\text{CH}_3-\text{CH}_4]^+$ ion is very stable.

The KER value accompanying with the NH_3 loss from the m/z 118 ion could not be estimated, because this metastable peak was interfering in the peak corresponding to the CH_4 loss, as mentioned above. However, it is obvious from Figs. 2(c) and 5(c) that this KER value is considerably larger than that of the loss of NH_3 from the m/z 130 ion for **1**. The ion at m/z 73 further fragments to the $\text{CH}_3\text{SiH}_2^+$ ion (m/z 45) by loss of C_2H_4 . The detailed fragmentation mechanisms of this ion at m/z 45 have been already reported elsewhere.¹⁴⁾ A possible fragmentation mechanism of **2** is shown in Scheme 2.

Diisopropylamine (**3**)

The fragmentation mechanism of secondary amines has been already reported by using D-labelling studies,^{15,16)} but not by MIKE spectra. It was revealed that an ion generated by the initial cleavage of β -bond was followed by α -bond cleavage with β -hydrogen atom transfer to the nitrogen atom.^{15,16)}

In order to compare the fragmentation mechanism of **2** with that of its carbon analogue (**3**), the decomposition of **3**, $((\text{CH}_3)_2\text{CHNHCH}(\text{CH}_3)_2)$, was investigated by using MIKE spectra.

The mass spectrum of **3** is shown in Fig. 1(c). The ion at m/z 100 ($C_6H_{14}N^+$) and 86 ($C_5H_{12}N^+$) were generated by expulsions of H and CH_3 , respectively, in a similar manner as its silicon analogue, **2**.

The MIKE spectra of the ions at m/z 100 and 86 were shown in Fig. 6. These two ions fragment to the ions at m/z 58 and 44, respectively, by loss of propene molecule ($CH_3CH=CH_2$). These metastable decomposition processes are in agreement with those suggested by the data of the normal mass spectra.^{15, 16)} In spite of rearrangement reactions, the KER values accompanying with propene loss were small (21.5 and 28.1 meV).

Although the primary fragmentations of the molecular ion of **3** are the same with those of its silicon analogue, **2**, as described above, the secondary fragmentations are completely different from each other. This is probably due to the difference of thermochemical stabilities between organosilicon compounds and their carbon analogues.¹⁾

Acknowledgments

The authors thank Mr. Naoto Sekiguchi for assistance in making some of the measurements.

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Keywords

Metastable ion study
Mass-analyzed ion kinetic energy spectra
1,1,1,3,3,3-Hexamethyldisilazane
1,1,3,3-Tetramethyldisilazane