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Metastable ion study of organosilicon compounds VIII ☆. Dimethoxydiphenylsilane

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Abstract

The spontaneous unimolecular dissociation reaction of the molecular ion of dimethoxydiphenylsilane (1) has been investigated by mass-analyzed ion kinetic energy spectroscopy, collision-induced dissociation, a D-labeling study and high resolution data. The results are compared with those of the corresponding carbon analogue, dimethoxydiphenylmethane (2). The fragmentation of the metastable $1^{\cdot+}$ is more complex than that of $2^{\cdot+}$. The latter eliminates the methoxy radical only, whereas the former eliminates methanol and benzene molecules, and C_7H_7 radical in addition to the formation of the molecular ion of biphenyl (3).

The intensity of the $[M-C_6H_5]^+$ ion at $m/z = 167$ is much larger than that of $[M-OCH_3]^+$ ion at $m/z = 213$ in the normal mass spectrum of 1. On the contrary, in the case of 2, the intensity of $[M-C_6H_5]^+$ ions is smaller than that of $[M-OCH_3]^+$ ions.

1. Introduction

Organosilicon compounds are finding increasing use as raw materials for industrial products. Knowledge of their fundamental properties is therefore of considerable importance. Many workers have investigated the fragmentation characteristics of some organosilicon compounds ionized by electron impact, by comparison with those of the corresponding carbon analogues [1-8].

An excellent review on the mass spectra of organosilicon compounds has been published by Schwarz [9].

It is known that a fairly intense peak is observed at $m/z = 154$ in the normal mass spectra of silicon compounds, which have two aromatic rings [10,11]. This ion has the same elemental composition as the molecular ion of biphenyl ($C_{12}H_{10}$) (3) (molecular weight, 154).

However, little is known concerning the detailed fragmentation of these compounds.

In this work, the mass-analyzed ion kinetic energy (MIKE) spectrometry, collision-induced dissociation (CID) spectrometry, D-labeling study and high resolution data were used to investigate the fragmentations of dimethoxydiphenylsilane $((C_6H_5)_2Si(OCH_3)_2)$ (1) (molecular weight, 244), which is one of the organosilicon compounds containing two aromatic rings. The results were also compared with those of the corresponding carbon analogue, dimethoxydiphenylmethane $((C_6H_5)_2C(OCH_3)_2)$ (2) (molecular weight, 228).

2. Experimental details

A Hitachi M-80A double-focusing mass spectrometer was used to obtain the 70 eV electron impact mass spectra, whereas the MIKE and CID mass spectra were obtained with a modified Hitachi RMU-7M and JEOL

JMS HX 100 instruments respectively. The MIKE spectrum of 2-d_6 was measured with a Hitachi M-80B (EBE type).

Compounds 1 and 3, obtained from Shin-Etsu Chemical and Tokyo Kasei Kogyo respectively, were of reagent grade and were used without further purification. Compound 1-d_6 was prepared from CD_3OD and dichlorodiphenylsilane and was purified by means of gas chromatography. They were introduced via a heated (150°C) inlet system to the ion sources which were maintained at 180°C.

Compound 2 and the D-labeled isotopomer 2-d_6 were prepared by the dropwise addition of dichlorodiphenyl-

Table 1
The values of dissociation energy

Bond	DE (kJ mol^{-1})
Si–C_6H_5	415
Si–OCH_3	481
C–C_6H_5	397
C–OCH_3	345

methane to CH_3ONa and CD_3ONa respectively. These were purified by means of recrystallization and were introduced via a direct inlet system. The degree of labeling obtained was better than 94%.

3. Results and discussion

3.1. Mass spectra

Fig. 1 shows the mass spectra of 1, 1-d_6, 2 and 2-d_6. Major ions in the mass spectrum of 1 shift to the appropriate mass in that of 1-d_6, i.e. $m/z = 244 \rightarrow 250$, $m/z = 213 \rightarrow 216$, $m/z = 167 \rightarrow 173$, $m/z = 137 \rightarrow 141$, $m/z = 107 \rightarrow 109$ and $m/z = 91 \rightarrow 93$. In contrast, the ion at $m/z = 154$ stays at the same m/z value. In the mass spectra of 2 and 2-d_6, the ions at $m/z = 228$, 197 and 151 shift to the ions at $m/z = 234$, 200 and 157 respectively. The ions at $m/z = 182$, 105 and 77, however, stay at the same m/z values.

The molecular ion of 1 at $m/z = 244$ is fairly intense (about 9% of the total ion intensity), but that of 2 ($m/z = 228$) is very weak (about 1%). This means that the molecular ion of the organosilicon compound is more stable than that of the corresponding carbon analogue, in the same manner as in the other cases [10–12].

In the mass spectrum of 1 (Fig. 1(a)), the intensity of [M–C_6H_5]$^+$ ion ($m/z = 167$) is much higher than that of [M–OCH_3]$^+$ ion ($m/z = 213$). Contrary to this, in the case of 2 the intensity of [M–C_6H_5]$^+$ ion ($m/z = 151$) is lower than that of [M–OCH_3]$^+$ ion ($m/z = 197$).

Fig. 1. Mass spectra of (a) 1, (b) 1-d_6, (c) 2 and (d) 2-d_6 at 70 eV.

Table 2
Heats of formation ΔH_f of neutral species used in this study

Species	ΔH_f (kJ mol^{-1})
C_6H_5–Si$(CH_3)_3$	–89
CH_3O–Si$(CH_3)_3$	–468
C_6H_5–C$(CH_3)_3$	–22
CH_3O–C$(CH_3)_3$	–283
C_6H_5	329
OCH_3	16
Si$(CH_3)_3$	–3
C$(CH_3)_3$	46

One of the reasons why this reverse result occurs in the primary fragmentation of the molecular ion studied here, may be the difference in the bond dissociation energies (DE) [12b].

The values of DE in Table 1 were estimated from the following equation:

$$DE(R-X) = \Delta H_f(R) + \Delta H_f(X) - \Delta H_f(RX) \qquad (1)$$

As the thermochemical data for 1 and 2 were not available, we used those of the species listed in Table 2 [13]. The estimated value of $DE(Si-C_6H_5)$ is less than that of $DE(Si-OCH_3)$, while the value of $DE(C-C_6H_5)$ is larger than that of $DE(C-OCH_3)$. The above experimental results are in accordance with the difference in the values of DE given in Table 1.

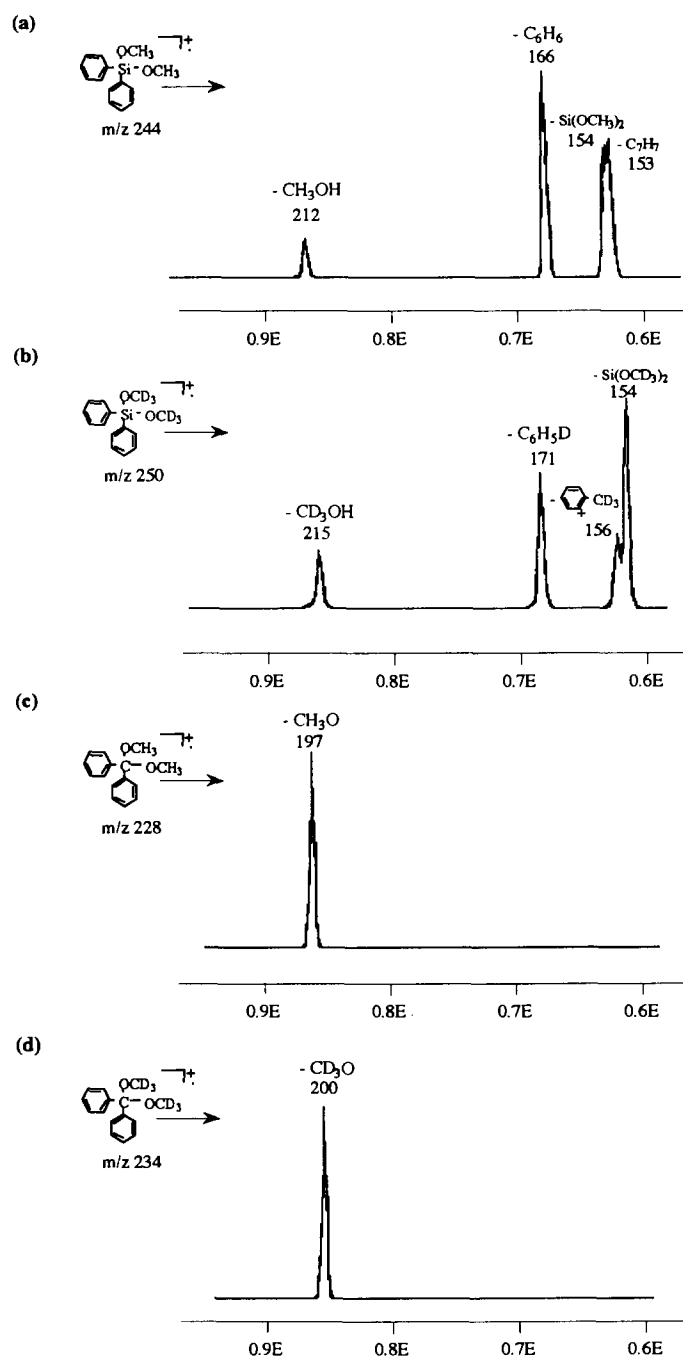In Figs. 1(a) and 1(b), a fairly intense peak is ob-

Fig. 2. MIKE spectra of the molecular ions of (a) $\mathbf{1}^{\cdot+}$ at $m/z = 244$, (b) $\mathbf{1}\text{-}d_6^{\cdot+}$ at $m/z = 250$, (c) $\mathbf{2}^{\cdot+}$ at $m/z = 228$ and (d) $\mathbf{2}\text{-}d_6^{\cdot+}$ at $m/z = 234$.

served at $m/z = 154$. The elemental composition of this ion is the same as that of the molecular ion of **3**. This was confirmed by high resolution data ($C_{12}H_{10}$; observed, 154.0790, 0.8 ppm).

3.2. Fragmentation of the molecular ions of 1 and 2

The MIKE spectra of the $1^{·+}$, 1-$d_6^{·+}$, $2^{·+}$ and 2-$d_6^{·+}$ are shown in Fig. 2. As shown in Fig. 2(c), a single peak at $m/z = 197$ corresponding to the loss of $·OCH_3$ characterizes the MIKE spectrum of ions $2^{·+}$, and this ion shifts to the $m/z = 200$ in Fig. 2(d).

The former ion is also the base peak in the normal mass spectrum (Fig. 1(c)). In contrast, the base peak at $m/z = 167$ in Fig. 1(a) is not observed in the MIKE spectrum of $1^{·+}$ (Fig. 2(a)). However, the metastable ion $1^{·+}$ decomposes in a variety of ways; four peaks are observed, at $m/z = 212, 166, 154$ and 153 which correspond to the competitive losses of CH_3OH, C_6H_6, $Si(OCH_3)_2$ (biphenyl ion formation) and C_7H_7 respectively. The first two and the last peaks shift to $m/z =$

215, 171 and 156 and the remaining ion at $m/z = 154$ stays at the same m/z value as shown in Fig. 2(b).

From the above experimental results, the following fragmentation mechanisms of metastable $1^{·+}$ are estimated.

(1) The first reaction is accompanied by hydrogen transfer from the phenyl ring to the methoxy oxygen.

(2) The second occurs with the hydrogen transfer from the methyl group to the phenyl ring.

(3) The third generates the molecular ion of **3** by the migration of one of the two phenyl groups to another.

(4) The last occurs by the transfer of one of the methyl groups on the silicon atom to the phenyl ring.

These are shown in Scheme 1.

3.3. Formation of the molecular ion of biphenyl

Fig. 3 shows the CID spectrum of the $m/z = 154$ ion generated from $1^{·+}$. The CID spectra of the molecular ions of **3** and acenaphthene, which have the same elemental composition as that of the $m/z = 154$ ion

Scheme 1.
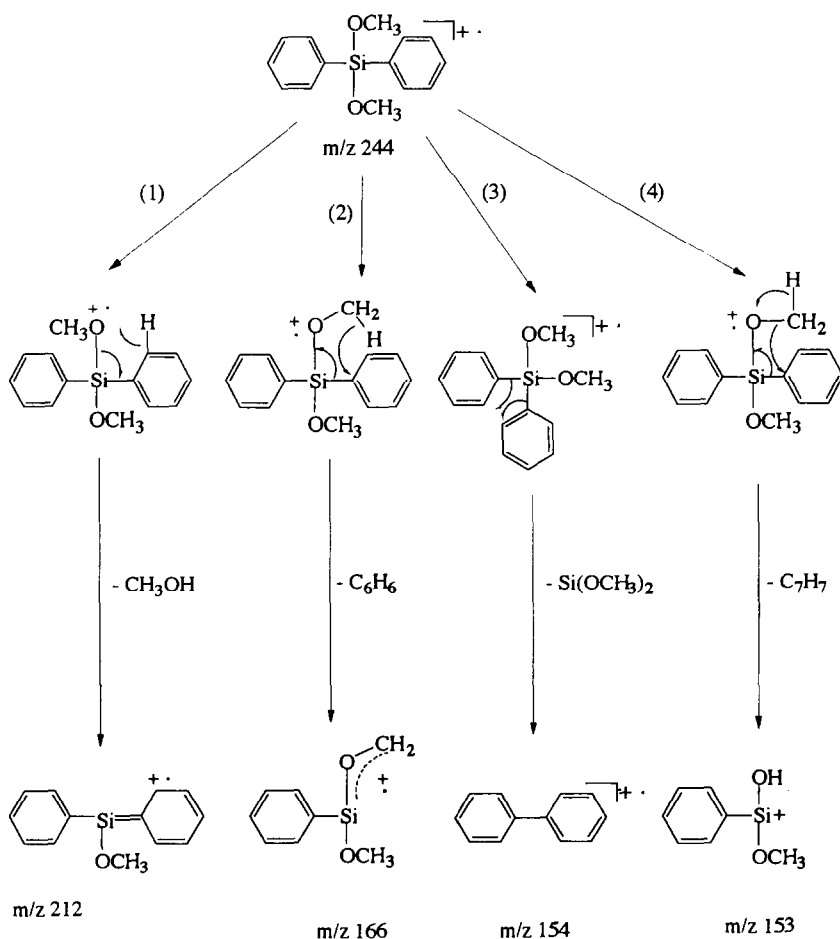
from $\mathbf{1}^{\cdot+}$, are also shown in Fig. 3. The CID spectrum of the $m/z = 154$ ion from $\mathbf{1}^{\cdot+}$ is nearly the same as that of $\mathbf{3}^{\cdot+}$. This means that $\mathbf{3}^{\cdot+}$ is produced from the fragmentation of the energetic $\mathbf{1}^{\cdot+}$.

3.4. Fragmentation of the [M–OCH₃]⁺ ion

Fig. 4 shows the MIKE spectra of the ions generated by the loss of OCH_3 from $\mathbf{1}^{\cdot+}$, $\mathbf{1}\text{-}d_6^{\cdot+}$, $\mathbf{2}^{\cdot+}$ and $\mathbf{2}\text{-}d_6^{\cdot+}$. As shown in Figs. 4(a) and 4(b), the ion at $m/z = 183$ shifts to $m/z = 184$. This means that this $m/z = 183$ ion was generated by the elimination of CH_2O from $[\mathbf{1}\text{-}OCH_3]^+$. The CH_2O loss is specific in the mass spectra of organosilicon compounds containing the Si–

OCH_3 group [13]. In contrast, the ions at $m/z = 182$ and 105 in Fig. 4(c) remain at the same m/z value in Fig. 4(d). That is, these ions are generated by the losses of CH_3 and C_7H_8 respectively. The former is assignable to a molecular ion of benzophenone and the latter corresponds to a benzoyl ion. These were also confirmed by means of the MIKE spectra (not shown).

3.5. Fragmentation of the [M–C₆H₅]⁺ ion

The MIKE spectra of the ions generated by the loss of C_6H_5 from $\mathbf{1}^{\cdot+}$, $\mathbf{1}\text{-}d_6^{\cdot+}$, $\mathbf{2}^{\cdot+}$ and $\mathbf{2}\text{-}d_6^{\cdot+}$ are shown in Fig. 5.
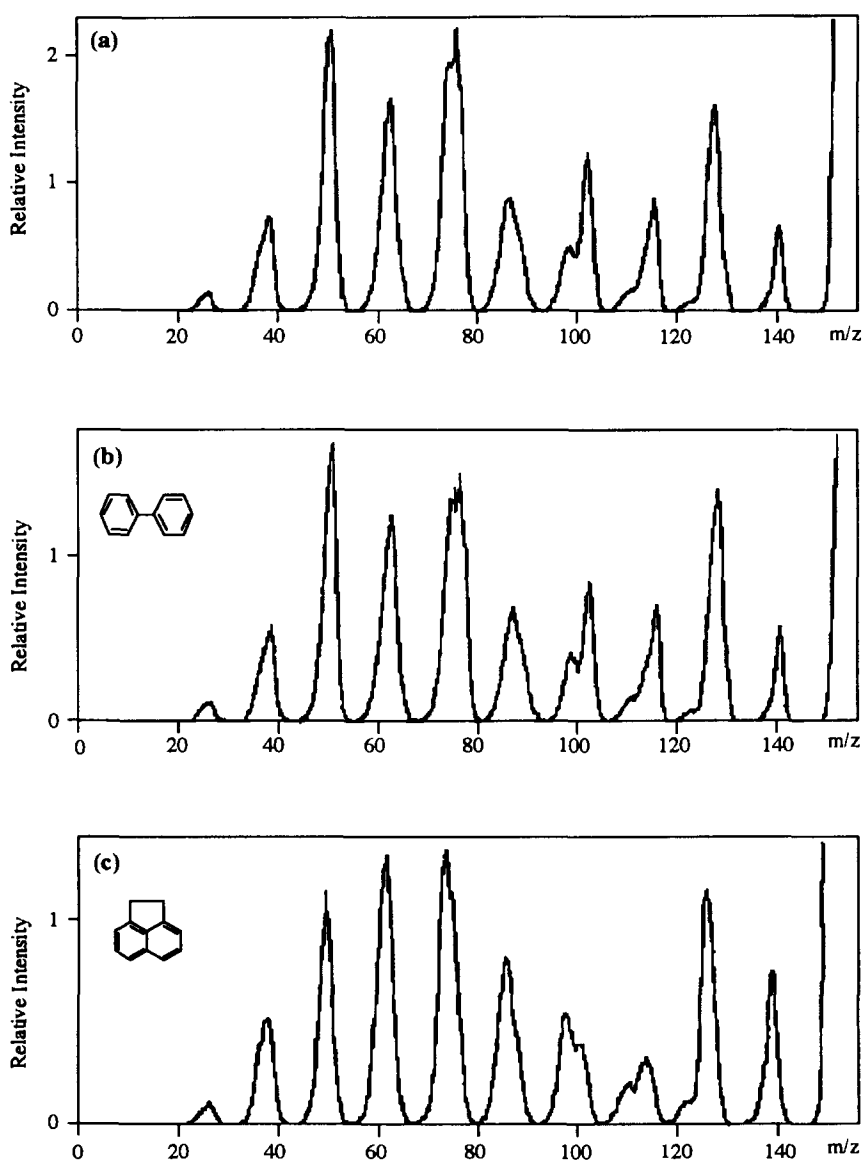

Fig. 3. CID spectra of (a) the ion at $m/z = 154$ from $\mathbf{1}^{\cdot+}$, (b) the molecular ion of $\mathbf{3}$ at $m/z = 154$ and (c) the molecular ion of acenaphthene at $m/z = 154$.

The ions at $m/z = 137$ and 91 in Fig. 5(a) shift to $m/z = 141$ and 93, showing that the latter corresponds to the loss of CH_4O_2Si and not of C_6H_4, and the former is due to the loss of CH_2O. The ion at $m/z = 105$ in Fig. 5(c) again stays at the same m/z value in Fig. 5(d). This means that these ions at $m/z = 105$ are generated by the loss of dimethyl ether molecule (CH_3OCH_3).
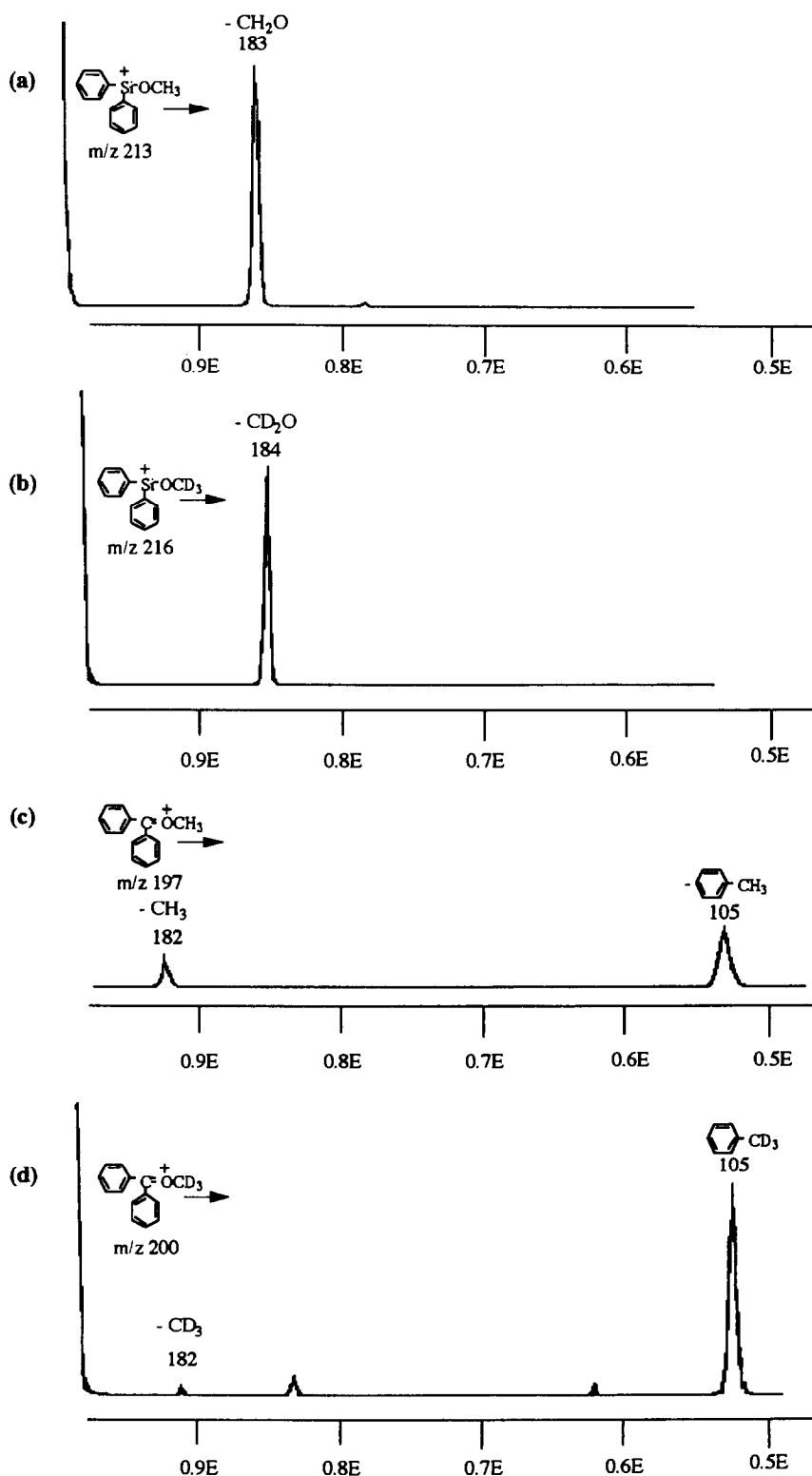

Fig. 4. MIKE spectra of the ions of methoxy loss from (a) $1^{\cdot +}$ at $m/z = 213$, (b) $1\text{-}d_6^+$ at $m/z = 216$, (c) $2^{\cdot +}$ at $m/z = 197$ and (d) $2\text{-}d_6^+$ at $m/z = 200$.

Fig. 6 shows the MIKE spectra of the ions at $m/z = 137$ from $1^{\cdot +}$ and $m/z = 141$ from $1\text{-}d_6^{\cdot +}$. The ions at $m/z = 107$ and 91 in Fig. 6(a) shift to $m/z = 109$ and 93 in Fig. 6(b). The latter is assigned to the loss of H_2SiO, and the former is due to the loss of CH_2O.

From Fig. 5(a) and Fig. 6(a), the ions at $m/z = 91$ are generated by two separate routes. These ions have the same elemental composition $C_7H_7^+$ because, as described below, if the elemental composition of the one of the $m/z = 91$ ions is $C_2H_7O_2Si^+$, the $m/z = 91$
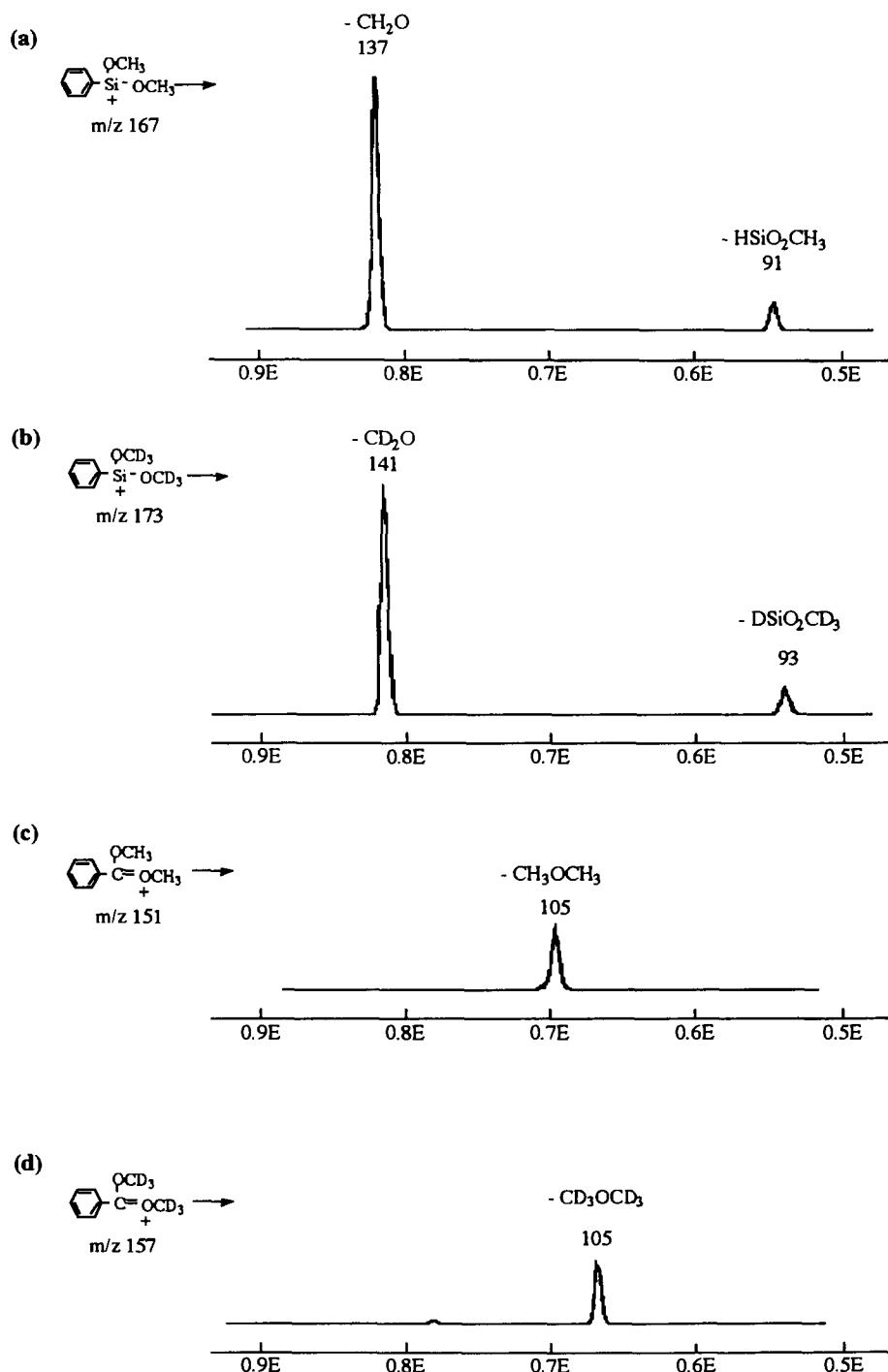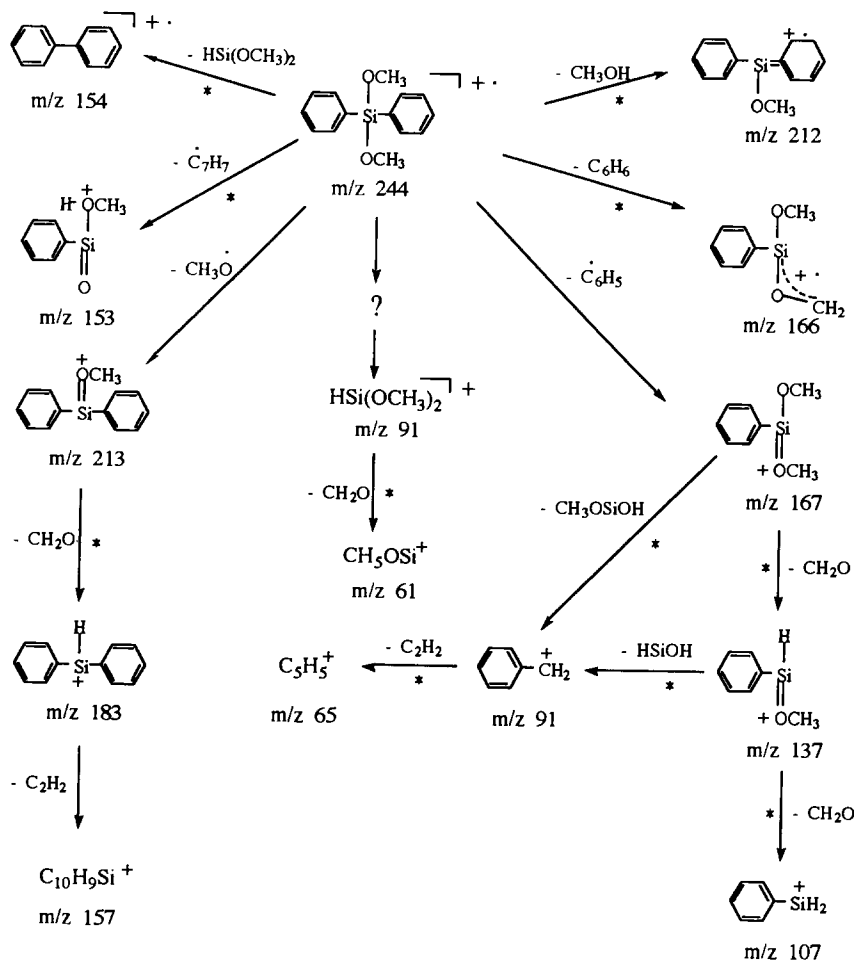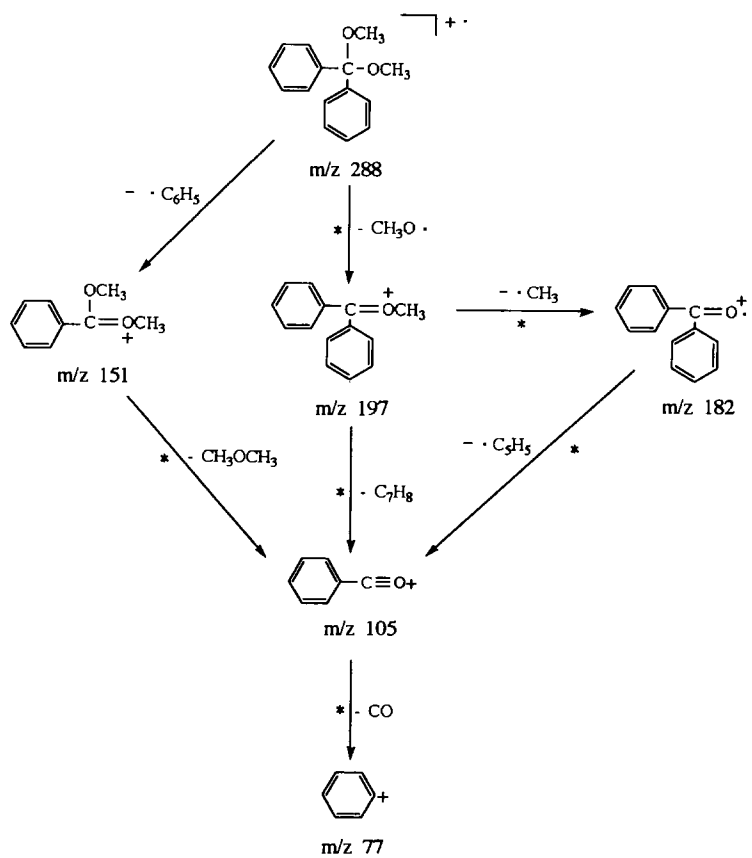

Fig. 5. MIKE spectra of the ions of phenyl loss from (a) $1^{\cdot +}$ at $m/z = 167$, (b) $1\text{-}d_6^{\cdot +}$ at $m/z = 173$, (c) $2^{\cdot +}$ at $m/z = 151$ and (d) $2\text{-}d_6^{\cdot +}$ at $m/z = 157$.

Scheme 2

m/z 154

\- HSi(OCH$_3$)$_2$

OCH$_3$ / OCH$_3$]$^{+\cdot}$

m/z 244

\- CH$_3$OH

m/z 212

\- C$_7$H$_7$

m/z 153

\- CH$_3$O

\- C$_6$H$_6$

\- C$_6$H$_5$

m/z 166

m/z 213

?

HSi(OCH$_3$)$_2$]$^+$

m/z 91

m/z 167

\- CH$_2$O   *

CH$_5$OSi$^+$

m/z 61

\- CH$_3$OSiOH

\- CH$_2$O

\- CH$_2$O   *

m/z 183

C$_5$H$_5^+$

m/z 65

\- C$_2$H$_2$

m/z 91

\- HSiOH

m/z 137

\- C$_2$H$_2$

\- CH$_2$O

C$_{10}$H$_9$Si$^+$

m/z 157

SiH$_2$

m/z 107

Scheme 2.

Scheme 3

OCH$_3$ / C-OCH$_3$]$^{+\cdot}$

m/z 288

\- ·C$_6$H$_5$

\- CH$_3$O ·

m/z 151

C=OCH$_3$

m/z 197

\- ·CH$_3$

C=O$^{+\cdot}$

m/z 182

\- CH$_3$OCH$_3$

\- C$_7$H$_8$

\- ·C$_5$H$_5$

C≡O+

m/z 105

\- CO

m/z 77

Scheme 3.

ion must split to $m/z = 97$ and 93 in Fig. 5(b). The high resolution data of the ions at $m/z = 91$ show that these ions may consist of two components (C_7H_7; observed, 91.0569, 2.2 ppm) ($C_2H_7O_2Si$; observed, 91.0208, -0.7 ppm). In order to confirm these results, the MIKE spectrum of the ion at $m/z = 91$ from 1 was measured (Fig. 7(a)).

The MIKE spectrum of the benzyl ion ($C_7H_7^+$) generated by the loss of Br from benzyl bromide and that of $HSi(OCH_3)_2^+$ generated by the loss of OCH_3 from trimethoxysilane ($HSi(OCH_3)_3$) are also shown in Fig. 7. It is obvious that the ion of $m/z = 91$ from 1 consists of $[C_7H_7]^+$ and $[HSi(OCH_3)_2]^+$.

Although the origin of the latter ion could not be rationalized in this metastable ion study, from considering the fragmentation pattern trimethoxyphenylsilane [14], this ion may be generated by the loss of C_6H_4 from the $[M-C_6H_5]^+$ ion.

As described above, the ions at $m/z = 105$ from 2 are also conceivably generated by two separate routes. However, both ions at $m/z = 105$ should be benzoyl ion, because these ions decompose into the ion at $m/z = 77$ by loss of CO (not shown) [15,16].

3.6. Fragmentation of the $[M-C_6H_6]^{\cdot+}$ ion

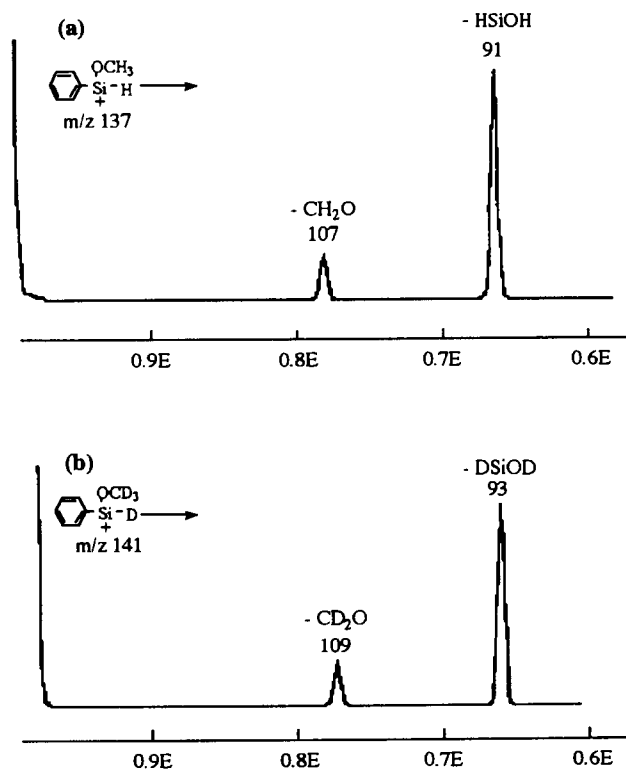The ions at $m/z = 166$ eliminate CH_3, H_2O, CH_2O and CH_5OSi to produce product ions at 151, 148, 136
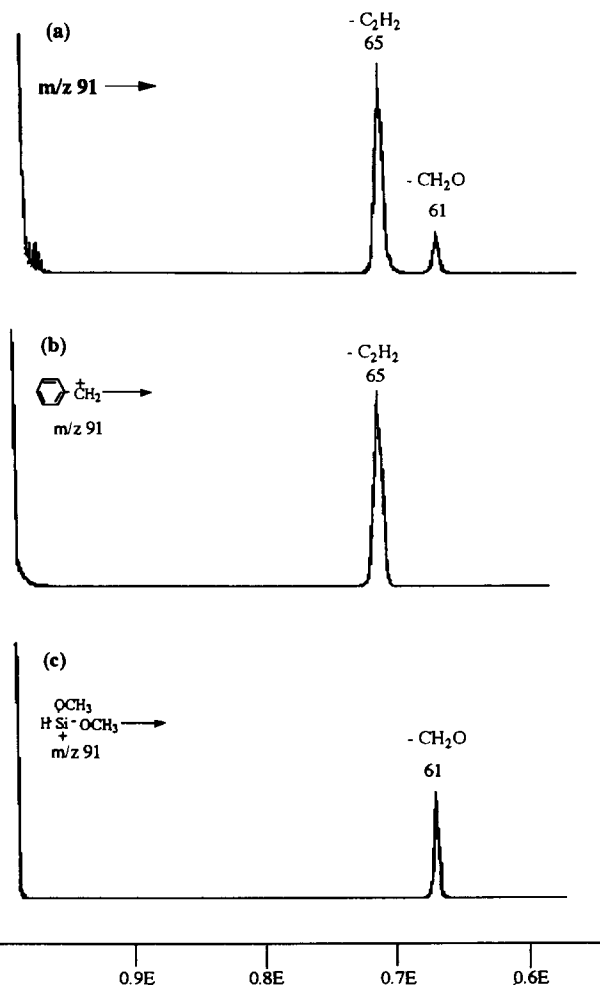

Fig. 7. MIKE spectra of (a) the ions at $m/z = 91$ from $1^{\cdot+}$, (b) $C_7H_7^+$ at $m/z = 91$ from benzylbromide and (c) $HSi(OCH_3)_2^+$ at $m/z = 91$ from trimethoxysilane.

Fig. 6. MIKE spectra of the ions at (a) $m/z = 137$ from $1^{\cdot+}$ and (b) $m/z = 141$ from $1\text{-}d_6^{\cdot+}$.

and 105 respectively. These are confirmed by the MIKE spectra (not shown).

Taking account of the above experimental results, possible fragmentation mechanisms of $1^{\cdot+}$ and $2^{\cdot+}$ are shown in Schemes 2 and 3 respectively.

4. Conclusion

In the normal mass spectrum of dimethoxydiphenylsilane (1), the intensity of the $[M-C_6H_5]^+$ ion is much larger than that of the $[M-OCH_3]^+$ ion. On the contrary, in the case of the corresponding carbon analogue, dimethoxydiphenylmethane (2), the peak due to $[M-OCH_3]^+$ is more intense than that due to $[M-C_6H_5]^+$. This result was explained by the thermochemical data.

The fragmentation of the metastable $1^{\cdot+}$ is more complex than that of $2^{\cdot+}$. Metastable molecular ions of 1 decompose into the ions at $m/z = 212$, 166, 154 and 153 by the losses of CH_3OH, C_6H_6, $Si(OCH_3)_2$ and

C_7H_7 respectively. In contrast, metastable **2**$^{\cdot+}$ decomposes into only one ion at $m/z = 197$ by loss of OCH_3.

The $m/z = 154$ ion generated from **1**$^{\cdot+}$ is the molecular ion of biphenyl.

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