Metastable ion study of organosilicon compounds. Part IX. [1] $CH_3COOSi(CH_3)_3$ and $CF_3COOSi(CH_3)_3$

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Abstract

The unimolecular metastable dissociation of trimethylsilyl acetate, $CH_3COOSi(CH_3)_3$, (1), and its fluorine analogue, trimethylsilyl trifluoroacetate, $CF_3COOSi(CH_3)_3$ (2), upon electron impact have been investigated by means of a B/E linked scan, high resolution data, and D-labeling. The results are compared with those of the carbon analogue, *tert*-butyl acetate, $CH_3COOC(CH_3)_3$ (3). No molecular ion of any of these compounds can be observed, but loss of CH_3 occurs exclusively from the trimethylsilyl or *tert*-butyl groups. The fragmentation of $1^{+\cdot}$ is slightly different from that of $3^{+\cdot}$, and quite different from that of $2^{+\cdot}$. In the case of $3^{+\cdot}$, $(CH_3)_2C=O$ is eliminated from $[3-CH_3]^+$, giving rise to the peak at m/z 43, but the loss of $(CH_3)_2Si=O$ does not occur from $[1-CH_3]^+$. In the case of $2^{+\cdot}$, an interesting fluorine atom (F) migration is observed.
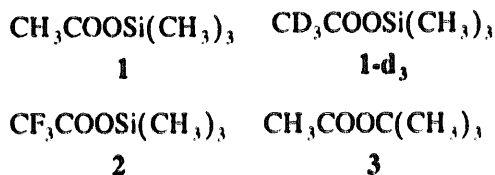
Keywords: Silicon; Si-compound; F-compound; Mass spectrometry; B/E linked scan; D-labeling

1. Introduction

Unimolecular fragmentation processes of gaseous organosilicon ions produced by electron impact have been studied extensively [2]. By using metastable ion spectrometry/high resolution data/D-labeling, we have investigated the fragmentations of some ions of organosilicon compounds and compared the results with those of the corresponding carbon analogues [3]. In the compounds studied, the fragmentation processes of the former were different from those of the latter.

To the authors' knowledge, little is known concerning the unimolecular fragmentation of the compounds which contain both silicon (Si) and fluorine (F) atoms [4–6]. In this paper we report the results of the B/E linked scan spectrometry/high resolution data/D-labeling investigation into the detailed fragmentation pathways of trimethylsilyl acetate, $CH_3COOSi(CH_3)_3$ (1), and its fluorine analogue, trimethylsilyl trifluoroacetate, $CF_3COOSi(CH_3)_3$ (2). The dissociation characteristics of the ions from these compounds are compared with those of the carbon analogue, *tert*-butyl acetate, $CH_3COOC(CH_3)_3$ (3). The compounds studied are shown below.

$$CH_3COOSi(CH_3)_3 \qquad CD_3COOSi(CH_3)_3$$
$$\textbf{1} \qquad\qquad\qquad \textbf{1-d}_3$$

$$CF_3COOSi(CH_3)_3 \qquad CH_3COOC(CH_3)_3$$
$$\textbf{2} \qquad\qquad\qquad \textbf{3}$$

2. Experimental

The mass and B/E linked scan spectra were recorded on a Hitachi M-80B double focusing mass spectrometer. Samples were introduced via a heated indirect inlet system. The ion-source temperature was 180°C, the electron accelerating voltage 70 V, and the total emis-

sion current 100 μA. The ion accelerating voltage was
3.0 kV.

Samples 1 and 3 were GR grade products, from

Shin-Etsu Chemical Co. Ltd. and Tokyo Kasei Co. Ltd.
respectively. The D-labeled isotopomer 1-d₃ and sam-
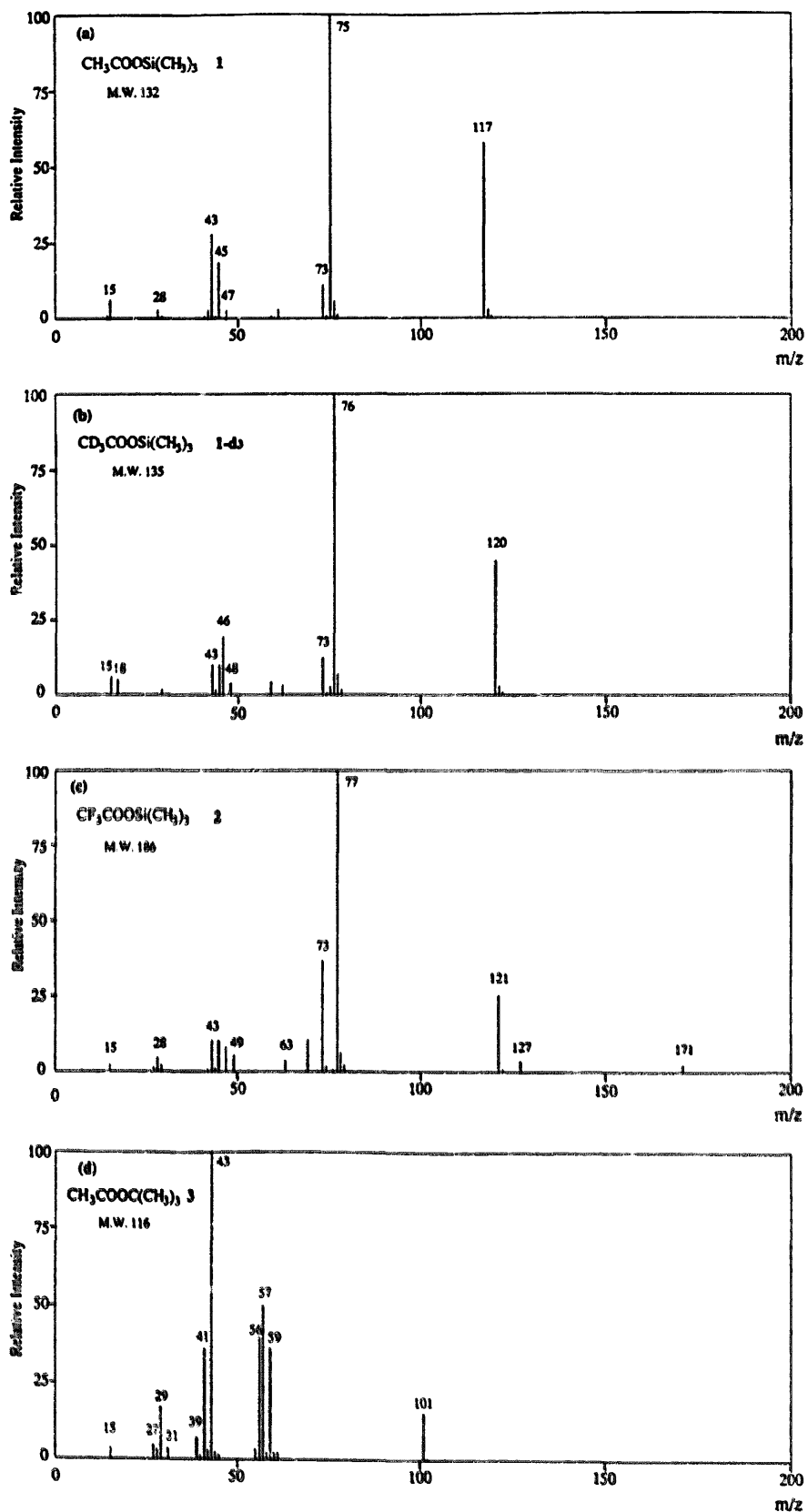ple 2 were prepared by the esterification of the corre-

Fig. 1. Mass spectra of (a) 1, (b) 1-d₃, (c) 2 and (d) 3 at 70 eV.

sponding acid and trimethylsilanol, and were purified by means of distillation.

3. Results and discussion

3.1. Trimethylsilyl acetate (1)

Fig. 1 shows the mass spectra of 1 (MW 132), 1-d$_3$ (MW 135), and 2 (MW 186). For comparison, the mass spectrum of 3 (MW 116) is also shown in Fig. 1(d). No molecular ion can be detected in these spectra. Although the peak at m/z 171 in 2 is fairly weak, peaks are clearly found at the m/z value corresponding to the loss of 15 atomic mass unit (amu) from the molecular ions in these spectra (m/z 117, 120, 171, and 101 respectively). In the case of 1, the CH$_3$ group comes from the trimethylsilyl group, because the m/z 117 ion of 1 shifts to m/z 120 in the mass spectrum of 1-d$_3$ (Fig. 1(b)). Therefore, the major fragmentation pro-
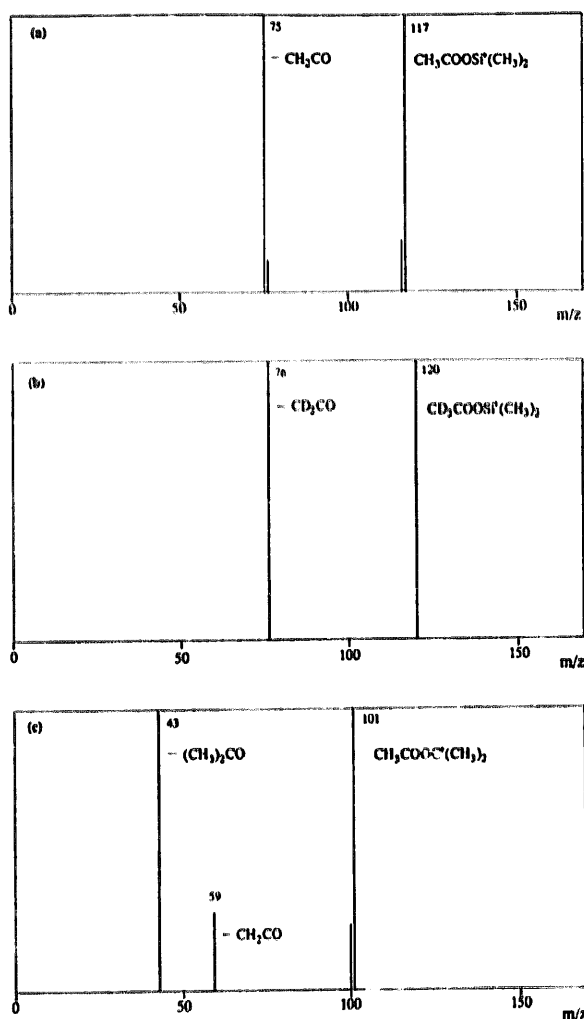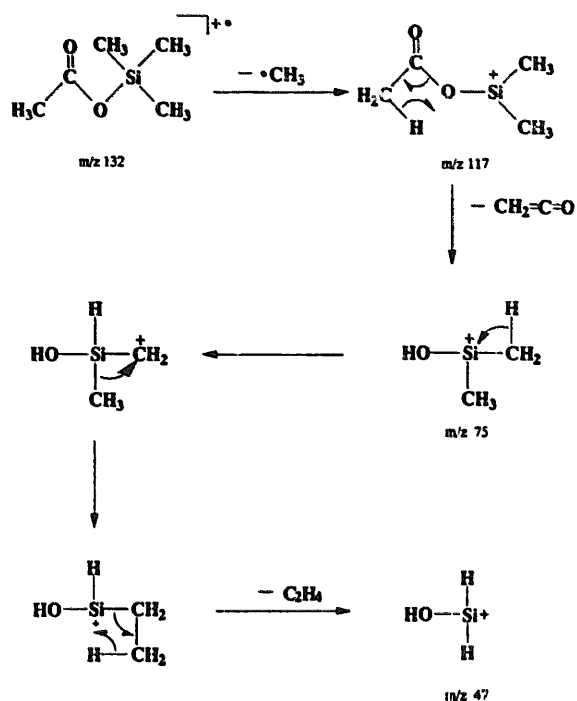

Scheme 1. Fragmentation pathways of 1$^{+\cdot}$.

Fig. 2. B/E linked scan spectra of the ions at (a) m/z 117 from 1$^{+\cdot}$, (b) m/z 120 from 1-d$_3^{+\cdot}$, and (c) m/z 101 from 3$^{+\cdot}$.

cesses will begin with methyl radical loss from the trimethylsilyl (TMS) group, although this is not confirmed in 2. These results are similar to those for 3, as shown in Fig. 1(d); the [M–CH$_3$]$^+$ ion is fairly abundant, with CH$_3$ coming from the tert-butyl group, and the molecular ion cannot be observed at m/z 116 [7–9].

The B/E linked scan spectra of the ions at m/z 117 from 1$^{+\cdot}$ and at m/z 120 from 1-d$_3^{+\cdot}$ are shown in Fig. 2. A very intense peak at m/z 75, corresponding to the loss of 42 amu, characterizes the B/E linked scan spectrum of the m/z 117 ion (Fig. 2(a)). In Fig. 2(b), this ion shifts to m/z 76, which corresponds to the loss of 44 amu. These findings mean that the loss of CH$_2$CO (ketene) occurs following transfer of one of the hydrogen atoms in the acetyl group to the ether oxygen via a four-membered transition state. As shown in Fig. 2(c), CH$_2$CO loss is also observed in the B/E linked scan spectrum of the ion at m/z 101 ([M–CH$_3$]$^+$) from 3$^{+\cdot}$. A ketene elimination has been observed in the mass spectra of the other organic compounds which contain an acetyl group [10–13].

In the case of 3, in addition to the loss of CH$_2$CO, the 58 amu is eliminated from the metastable ion at m/z 101 to give rise to the peak at m/z 43 (Fig. 2(c)). This corresponds to the loss of an acetone molecule, (CH$_3$)$_2$CO [9]. As shown in Fig. 2(a), in the case of 1 no ion which corresponds to the loss of (CH$_3$)$_2$Si=O is observed at m/z 43. This may be because the Si atom, in contrast to the C atom, rarely makes a double bond with an O atom in neutral species [14], although the loss

of $(CH_3)_2Si=O$ has been proposed in the mass spectra of the TMS derivatives of several organic compounds [15,16].

The m/z 75 ion from $1^{+\cdot}$ and the m/z 76 ion from $1\text{-}d_3^{+\cdot}$ further decompose into m/z 47 and 48 respectively by the loss of 28 amu (not shown). No deuterium atoms take part in this reaction. Specifically, this fragmentation is due to the loss of C_2H_4. Taking into account the recently accepted fragmentation intermediate, i.e. the ion-neutral complex [17,18], this C_2H_4 loss consists of a stepwise 1,2-hydrogen/1,2-methyl migration [19,20].

This C_2H_4 loss in 1 is also similar to the case of 3 [9]. Consequently, it may be said that the fragmentation processes of $1^{+\cdot}$ are similar to those of the carbon

analogue $3^{+\cdot}$, except for the loss of $(CH_3)_2CO$ from $[M-CH_3]^{+\cdot}$.

The fragmentation processes of $1^{+\cdot}$ are shown in Scheme 1, taking into account those of $3^{+\cdot}$ [7-9] and the concept of the ion-neutral complex [17,18]. Even though the CH_3 loss from $3^{+\cdot}$ has been explained by the α-cleavage reaction initiated by the ether oxygen atom [21], a radical cation in $1^{+\cdot}$ is not depicted on any atom.

3.2. Trimethylsilyl trifluoroacetate (2)

As shown in Fig. 3, the ions at m/z 171 spontaneously decompose into the ions at m/z 127 and 121 by loss of CO_2 and difluorocarbene, CF_2, respectively.
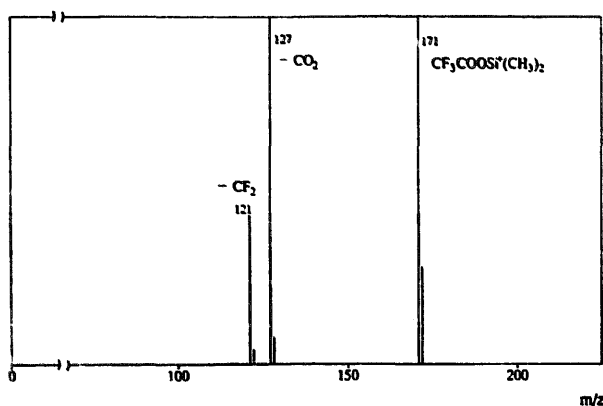

Scheme 2. Fragmentation pathways of $2^{+\cdot}$.
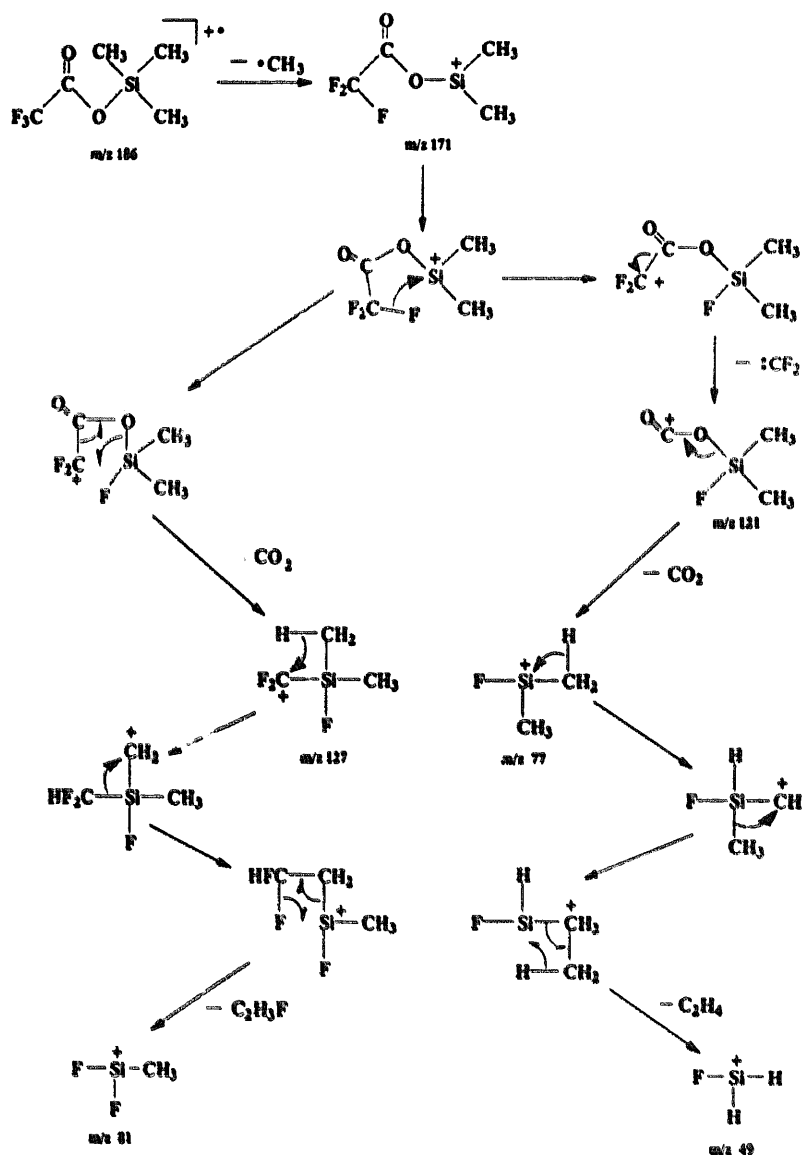
Fig. 3. B/E linked scan spectrum of the ions at m/z 171 from 2⁺·.

This was confirmed by the high resolution data ($C_3H_6SiF_3$, 127.0200, 0.9 ppm; $C_3H_6O_2SiF$, 121.0110, −1.0 ppm). The latter fragmentation is specific in the mass spectra of organopolyfluorocompounds [22–25], because this type of reaction rarely occurs in the carbon analogues.

One reason why the loss of CF_2 is pronounced may be that the CF_2 radical is very stable compared with CH_2 ($\Delta H_f(CF_2)$ = −205 kJ mol⁻¹; $\Delta H_f(CH_2)$ = 390 kJ mol⁻¹ [26]).

The ion at m/z 121 from 2⁺· further decomposes into the ion at m/z 77 (C_2H_6SiF, 77.0161, −6.0 ppm) and this m/z 77 ion further decomposes into the m/z 49 ion. This corresponds to the consecutive loss of CO_2 and C_2H_4 respectively. The latter is similar to the cases of 1 and 3, but the former is different.

The formation of the ion at m/z 127 (Fig. 3) involves CO_2 loss after the migration of the CF_3 group to the remaining ion species. Loss of CO_2 was also observed in the mass spectra of TMS derivatives of hydroxy dicarboxylic acids [27]. Although the ion at m/z 81 is rarely observable in the normal mass spectrum (see Fig. 1(c)), the metastable ion at m/z 127 further

Table 1
PM3-calculated relative energies for various structures of $[C_3H_6-SiF_3]^+$

	Structure	Relative energies (kJ mol⁻¹)
(a)	CH₃ F‑C–Si–CH₃ / F	−15
(b)	F / F–C–Si–CH₃ / CH₃	119
(c)	H F‑C–Si–CH₃ / CH₂F	262

decomposes into the ion at m/z 81 by loss of C_2H_3F. This experimental result suggests that the formation of the m/z 127 should involve considerable rearrangement during the fragmentation, because the fragmentation of the m/z 127 ion to the m/z 81 ion can never be rationalized by simple rearrangement processes alone.

The heats of formation of the several $[C_3H_6SiF_3]^+$ ions were estimated by the PM3 method (Table 1). The structure of the m/z 127 ion may be assumed to be $C^+F_2Si(CH_3)_2F$ (a), because this ion has the lowest heat of formation among its isomers. From this ion structure, the loss of C_2H_3F with F migration can be reasonably rationalized.

Plausible fragmentation processes of 2⁺· deduced from the above experimental results are shown in Scheme 2.

4. Conclusions

1. The unimolecular fragmentation of trimethylsilyl acetate 1 upon electron impact is similar to that of tert-butyl acetate 3, except for the loss of an acetone molecule from $[3-CH_3]^+$ (m/z 101). This is due to the fact that Si atoms rarely make a double bond with an O atom in neutral species [14].

2. The fragmentation of the fluorine analogue of 1⁺·, trimethylsilyl trifluoroacetate 2⁺·, is different from those of 1⁺· and 3⁺· except for a methyl loss from the molecular ions. In the case of 2⁺·, some considerably complex F atom migrations occur during the fragmentations.

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