Decomposition of metastable methyl trifluoroacetate and ethyl trifluoroacetate upon electron impact

Osamu Sekiguchi*, Sou Tajima, Risei Koitabashi, Susumu Tajima

Gunma National College of Technology, 580 Toriba-machi, Maebashi, Gunma 371, Japan

Abstract

Fragmentation mechanism of metastable ions generated from methyl trifluoroacetate, CF_3COOCH_3 (1), and ethyl trifluoroacetate, $CF_3COOCH_2CH_3$ (2), upon electron impact was investigated by means of mass analyzed ion kinetic energy (MIKE) spectra and ab initio molecular orbital (MO) calculations. The metastable $[1–H]^+$ ion decomposes to the m/z 99 ion by losing CO. This fragmentation proceeds with CF_3 migration via an ion-neutral complex. The metastable $[1–F]^+$ ion decomposes to m/z 81 ion by losing CO, too. In this case, however, the fragmentation proceeds with CH_3O migration to CF_2 group via a conventional three-membered ring transition state. The kinetic energy release (KER) values for these CO loss reactions are very different from each other, and are rationalized based on the different fragmentation mechanisms. The fragmentation pathways of $2^{+\cdot}$ are similar to those of $1^{+\cdot}$. However, the loss of F_2CO from $[2–H]^+$ accompanies a very large KER value compared with that from $[1–H]^+$. (Int J Mass Spectrom 177 (1998) 23–30) © 1998 Elsevier Science B.V.

Keywords: Organofluorine compounds; Metastable ion; MIKE; Ion-neutral complexes

1. Introduction

Fluorine-containing organic compounds are important raw materials for industrial products, because of their characteristic properties. Recently, the physiological activity of some organofluorine compounds has received considerable attention [1]. Mass spectrometric investigations have been performed on the wide range of organofluorine compounds by many groups [2–11]. These compounds show fragmentation pathways distinct from those in fluorine-free analogs. The migration of a fluorine atom or a fluorine-containing group, such as a trifluoromethyl group, CF_3, is sometimes observed [2–7,9–11].

Trifluoroacetic acid is one of the most familiar organofluorine compounds. Mass spectra of aryl esters of trifluoroacetic acid were reported nearly three decades ago [2]. Hsu et al. [4,5] have reported fragmentation processes of some alkyl esters of trifluoroacetic acid studied by the collision-induced dissociation (CID) mass spectra with a particular regard to the distribution of labeled isotopes. However, the detailed mechanism of the metastable fragmentation was not mentioned in these reports. Moreover, to the authors' knowledge, fragmentation processes of more simple esters of trifluoroacetic acid, e.g., methyl or ethyl ester, have not been studied in detail. In this report, metastable fragmentation mechanism of methyl trifluoroacetate, CF_3COOCH_3 (1), and ethyl trifluoroacetate, $CF_3COOCH_2CH_3$ (2), upon

---

* Corresponding author.

electron impact was investigated on the basis of mass analyzed ion kinetic energy (MIKE) spectra and molecular orbital (MO) calculations.

2. Experimental

The electron impact (EI) mass and the CID spectra were recorded on a Jeol JMS HX-100 tandem mass spectrometer and a Hitachi M80-B double focusing mass spectrometer, respectively. The conditions of the measurement of CID spectra were as follows: ion accelerating voltage, 3200 V; the main beam intensity was reduced to ca. 30% with He collision gas. The MIKE spectra were obtained with a modified HITA-CHI RMU-7M double focusing mass spectrometer of reversed geometry.

The kinetic energy release (KER) value is estimated from the width at half-height of the metastable peak.

Methyl trifluoroacetate, CF_3COOCH_3 (M 128, 1) and ethyl trifluoroacetate, $CF_3COOC_2H_5$ (M 142, 2) were obtained from Tokyo Kasei Kogyo Co., Ltd., and were used without further purification. Ethyl-d_5 trifluoroacetate (M 147, 2-d_5) was synthesized by the esterification of CF_3COOH with C_2D_5OD.

3. Theoretical method

Ab initio MO calculations were performed with the Gaussian 94 suite of programs [12]. The results shown in Figs. 3 and 4 are those obtained at MP2/6-31G(d)//MP2/6-31G(d) level of calculations, while those in Figs. 5 and 7 are at HF/6-31G(d)//HF/6-31G(d) level of calculations. Vibrational analysis for the transition states concerned showed that there is only one vibration with an imaginary frequency. The energies mentioned are those without zero point correction.

4. Results and discussion

4.1. Methyl trifluoroacetate (1)

The mass spectra of 1 and 2 are listed in Table 1. These spectra are not so different from the NIST data

Table 1
Mass spectra of CF_3COOCH_3 and $CF_3COOC_2H_5$

| | Relative intensity | |
| | CF_3COOCH_3 | $CF_3COOC_2H_5$ |
m/z	1	2
15	46.7	2.6
27		25.3
28		13.4
29	10.2	100.0
50	10.7	3.2
51		3.2
59	100.0	
69	66.5	48.9
73		3.7
78	2.9	
97	3.6	2.9
99	8.5	16.1
109	4.1	
113		1.4
127	1.0	6.5
141		1.6

(http://webbook.nist.gov/), except for the peak at m/z 15 in the spectrum of 1. The abundance of the molecular ion $1^{+\cdot}$ in the ion source is rather low, but the MIKE spectrum of the molecular ion can be measured with sufficient intensity.

Figure 1 shows the MIKE spectra of the molecular ion and some fragment ions of 1. The molecular ion of 1 (m/z 128) decomposes into m/z 127 and m/z 59 by losing H˙ and ĊF$_3$, respectively [Fig. 1(a)]. It is seen from Fig. 1(b) that the m/z 127 ion ([CF_3COOCH_2]$^+$) decomposes to m/z 99 by losing a neutral with 28 atomic mass unit (u). The only possible neutral with 28 u lost from [CF_3COOCH_2]$^+$ (m/z 127) is CO. The loss of CO is a very familiar reaction in the organic mass spectrometry [3,9,10,13–16]. However, this reaction is not observed in the fragmentation of the fluorine-free analog of 1, i.e., methyl acetate [17–19]. Stach et al. also reported that the molecular ion of phenyl trifluoroacetate metastably loses CO to produce the molecular ion of α,α,α-trifluoroanisole [10]. However, they did not discuss the detailed mechanism of this reaction.

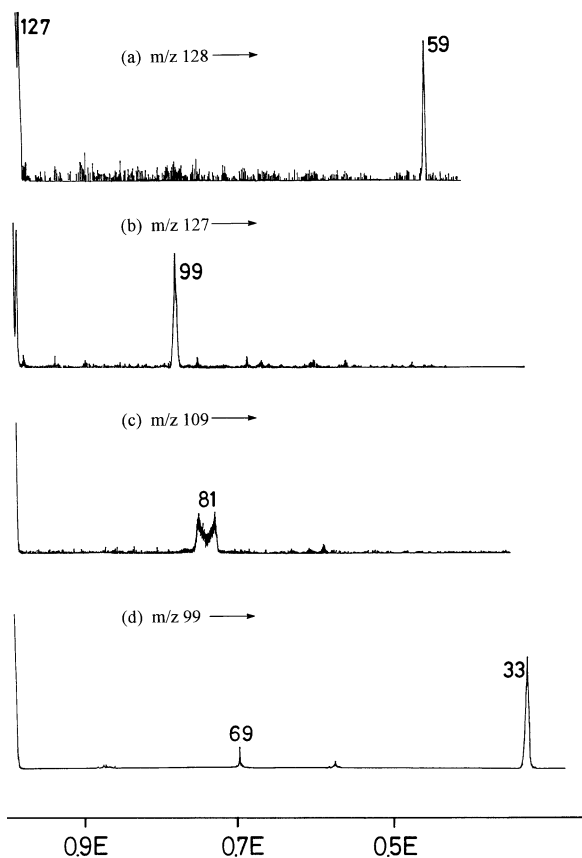For the loss of CO from [CF_3COOCH_2]$^+$ (m/z

Fig. 1. MIKE spectra of (a) the molecular ion, (b) [M–H]$^+$, (c) [M–F]$^+$, and (d) [M–H–CO]$^+$ from methyl trifluoroacetate.

127), two plausible mechanisms, as shown in Scheme I, can be considered. In mechanism (1), the loss of CO occurs with the migration of CF_3 from the carbonyl carbon to the ether oxygen, and the structure of the resulting m/z 99 ion is $[CF_3OCH_2]^+$. In mechanism
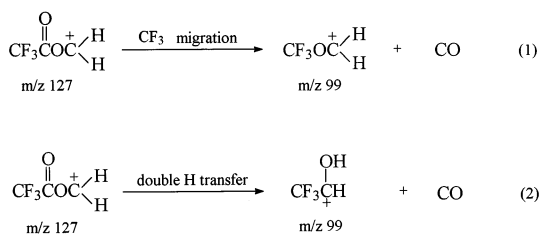
Scheme 1.

(2), the reaction follows double hydrogen transfer from the methylene group to the carbonyl group, and the structure of the m/z 99 ion in this case is $[CF_3CHOH]^+$. The m/z 99 ion with a structure of $[CF_3CHOH]^+$ is produced from 1,1,1,3,3,3-hexafluoro-2-propanol, $(CF_3)_2CHOH$, upon electron impact by losing $\dot{C}F_3$ [6]. The MIKE spectrum of $[CF_3CHOH]^+$ shows only a composite peak at m/z 79 due to the loss of HF [6–8]. Fig. 1(d) shows the MIKE spectrum of the m/z 99 ion from 1. A prominent peak appears at m/z 33, and a weak peak at m/z 69 is observed, but there is no peak at m/z 79. The MIKE spectrum of the m/z 99 ion from 1 is completely different from that of the m/z 99 ion from $(CF_3)_2CHOH$. Hence, the structure of the m/z 99 ion from 1 is not $[CF_3CHOH]^+$, and we consider that to be $[CF_3OCH_2]^+$, which is produced through the loss of CO from $[CF_3COOCH_2]^+$ with a CF_3 migration [mechanism (1) in Scheme 1]. A more detailed mechanism of this reaction will be discussed later.

In the mass spectrum of 1, a peak at m/z 109 due to the loss of $F\cdot$ from $1^{+\cdot}$ is observed. The MIKE spectrum of the ion at m/z 109 is shown in Fig. 1(c). A broad peak at m/z 81 is observed, which is owing to the loss of a neutral with 28 u. The only possible neutral fragment with 28 u in this case is again CO. The loss of CO from $[CF_2COOCH_3]^+$ (m/z 109) would proceed with the migration of the CH_3O group from the carbonyl carbon to the positively charged carbon atom of the CF_2 group. It is obvious from Figs. 1(b) and 1(c) that the KER accompanying the loss of CO from $[CF_2COOCH_3]^+$ (900 meV) is much larger than that from $[CF_3COOCH_2]^+$ (74 meV). Very recently, Kralj et al. reported the loss of CO from $[CF_2COOCH_3]^+$ produced under chemical ionization of CF_3COOH with CH_3OH [11].

Figure 2 shows the CID spectra of $[CF_3COOCH_2]^+$ (m/z 127) and $[CF_2COOCH_3]^+$ (m/z 109). The most prominent peak in the former spectrum is that due to the loss of CO. In the latter spectrum, the peak due to CF_2 loss (m/z 59) is most prominent, and that due to CO loss at m/z 81 is weak. These results indicate that a considerable amount of the m/z 127 ions would not have retained the original structure of $[CF_3COOCH_2]^+$, while the m/z 109 ions
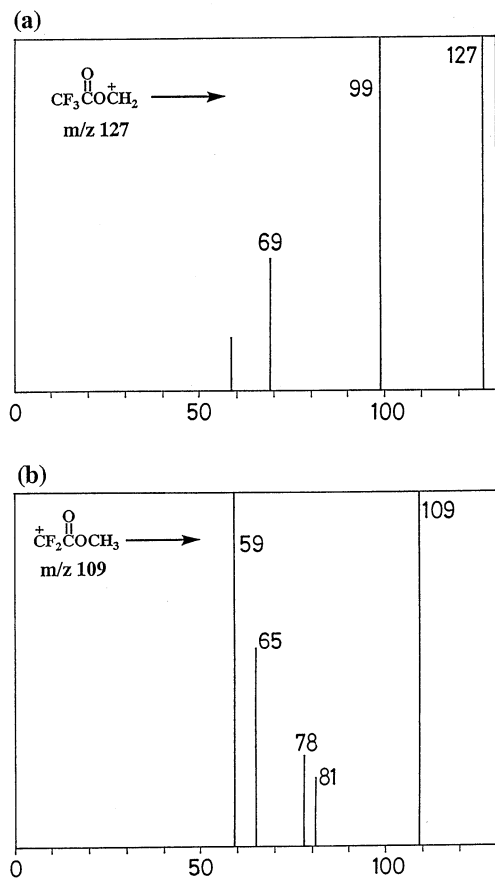
(a)

(b)

Fig. 2. CID spectra of (a) $[M-H]^+$ and (b) $[M-F]^+$ from methyl trifluoroacetate.

Fig. 3. Calculated [MP2/6-31G(d)] energy diagram for the loss of CO from $[CF_2COOCH_3]^+$.

would have retained the original structure ($[CF_2COOCH_3]^+$) [20].

The mechanism of the CO loss from $[CF_2COOCH_3]^+$ (m/z 109) ion was investigated on the basis of ab initio molecular orbital calculations of MP2/6-31G(d)//MP2/6-31G(d) level, and the result is summarized in an energy diagram shown in Fig. 3. First, the CH_3O group approaches the positively charged carbon atom of CF_2 to form a three-membered ring transition state TS1, which gives rise to an intermediate IM1. Optimized structures of TS1 and IM1 are shown in Scheme 2. The intermediate IM1 expels CO without discernible energy barrier. The reverse activation energy for this reaction is 149.5 kJ/mol. As mentioned above, the KER value of this
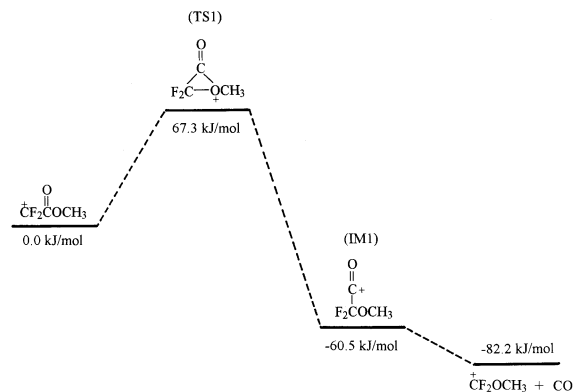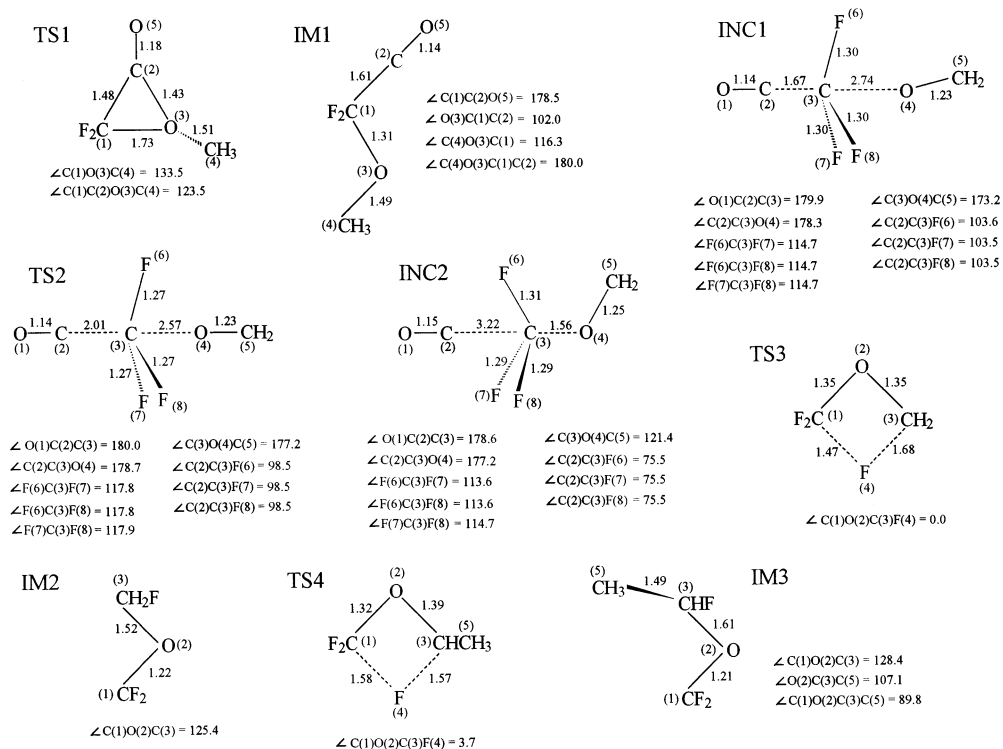
reaction is ca. 900 meV, i.e. about 60% of the reverse activation energy is released as kinetic energy [21]. The mechanism of CO loss proposed is akin to those in some carboxylic acid derivatives proposed by Grützmacher et al. [14–16].

In the case of the loss of CO from $[CF_3COOCH_2]^+$ (m/z 127), on putting the CF_3 group close to the ether oxygen, the energy of the system becomes very high, and the attempt to locate a transition state similar to TS1 proved abortive. We consider the mechanism of this reaction to be one in which ion-neutral complexes [22–24] play an important role. An energy diagram for the proposed mechanism obtained with MP2/6-31G(d)//MP2/6-31G(d) level of calculations is shown in Fig. 4.

The MO calculation shows that, in $[CF_3COOCH_2]^+$ (m/z 127), the C–O bond linking CF_3CO moiety and OCH_2 moiety is rather weak, and is easily elongated. Indeed, the optimized structure of $[CF_3COOCH_2]^+$ has a C–O bond length of 1.72 Å, which is distinctly longer than the ordinary value. (The C–O bond length in CF_3COOCH_3, estimated computationally of the same level of theory, is 1.34 Å.) Hence, an ion-neutral complex composed of $[CF_3CO]^+$ and OCH_2 would be formed easily. The moieties composing the ion-neutral complex can rotate with respect to each other before fragmentation [22–24]. Thus, it would be possible that the CF_3CO moiety rotates and the CF_3 group faces the oxygen atom in the OCH_2 moiety. For such an orientation of

TS1

O (5)
|1.18
C (2)
1.48 / \ 1.43
F₂C —— O (3)
(1) 1.73 \ 1.51
CH₃
(4)

∠C(1)O(3)C(4) = 133.5
∠C(1)C(2)O(3)C(4) = 123.5

IM1

O (5)
(2) C ⫽ 1.14
1.61
F₂C (1)
|1.31
(3) O
|1.49
(4) CH₃

∠C(1)C(2)O(5) = 178.5
∠O(3)C(1)C(2) = 102.0
∠C(4)O(3)C(1) = 116.3
∠C(4)O(3)C(1)C(2) = 180.0

INC1

F (6)
|1.30
O —1.14— C —1.67— C ⋯2.74⋯ O ⋯ CH₂ (5)
(1) (2) (3) (4) 1.23
|1.30
(7)F F (8)
1.30

∠O(1)C(2)C(3) = 179.9   ∠C(3)O(4)C(5) = 173.2
∠C(2)C(3)O(4) = 178.3   ∠C(2)C(3)F(6) = 103.6
∠F(6)C(3)F(7) = 114.7   ∠C(2)C(3)F(7) = 103.5
∠F(6)C(3)F(8) = 114.7   ∠C(2)C(3)F(8) = 103.5
∠F(7)C(3)F(8) = 114.7

TS2

F (6)
|1.27
O —1.14— C ⋯2.01⋯ C ⋯2.57⋯ O —1.23— CH₂ (5)
(1) (2) (3) (4)
1.27 / \ 1.27
(7)F F (8)

∠O(1)C(2)C(3) = 180.0   ∠C(3)O(4)C(5) = 177.2
∠C(2)C(3)O(4) = 178.7   ∠C(2)C(3)F(6) = 98.5
∠F(6)C(3)F(7) = 117.8   ∠C(2)C(3)F(7) = 98.5
∠F(6)C(3)F(8) = 117.8   ∠C(2)C(3)F(8) = 98.5
∠F(7)C(3)F(8) = 117.9

INC2

F (6)   CH₂ (5)
|1.31   /1.25
O —1.15— C ⋯3.22⋯ C —1.56— O (4)
(1) (2) (3)
1.29 / \ 1.29
(7)F F (8)

∠O(1)C(2)C(3) = 178.6   ∠C(3)O(4)C(5) = 121.4
∠C(2)C(3)O(4) = 177.2   ∠C(2)C(3)F(6) = 75.5
∠F(6)C(3)F(7) = 113.6   ∠C(2)C(3)F(7) = 75.5
∠F(6)C(3)F(8) = 113.6   ∠C(2)C(3)F(8) = 75.5
∠F(7)C(3)F(8) = 114.7

TS3

O (2)
1.35 / \ 1.35
F₂C (1)   (3) CH₂
1.47 \ / 1.68
F
(4)

∠C(1)O(2)C(3)F(4) = 0.0

IM2

CH₂F (3)
|1.52
O (2)
|1.22
(1) CF₂

∠C(1)O(2)C(3) = 125.4

TS4

O (2)
1.32 / \ 1.39
F₂C (1)   (3) CHCH₃ (5)
1.58 \ / 1.57
F
(4)

∠C(1)O(2)C(3)F(4) = 3.7

IM3

CH₃ (5) —1.49— CHF (3)
|1.61
O (2)
|1.21
(1) CF₂

∠C(1)O(2)C(3) = 128.4
∠O(2)C(3)C(5) = 107.1
∠C(1)O(2)C(3)C(5) = 89.8

Scheme 2.

[OCCF₃]⁺ and OCH₂, an ion-neutral complex (INC1) as shown in Scheme II locates a minimum on the MP2 potential energy surface. In INC1, C(2)–C(3) distance is 1.67 Å, whereas C(3)–O(4) distance is 2.74 Å

(Scheme 2). This complex is expressed as [H₂CO/CF₃CO]⁺. By making the C(3)–O(4) distance shorter, the system reaches a transition state TS2, that combines INC1 and INC2 (Scheme 2). In INC2, C(2)–

CF₃C̊O + H₂CO
138.7 kJ/mol

87.6 kJ/mol

TS2
94.8 kJ/mol

[H₂CO ⫽ CF₃CO]⁺
(INC1)

CF₃CŌCH₂ + CO
17.0 kJ/mol

CF₃COOCH₂⁺
0.0 kJ/mol

-4.2 kJ/mol

[CH₂OCF₃ ⫽ CO]⁺
(INC2)
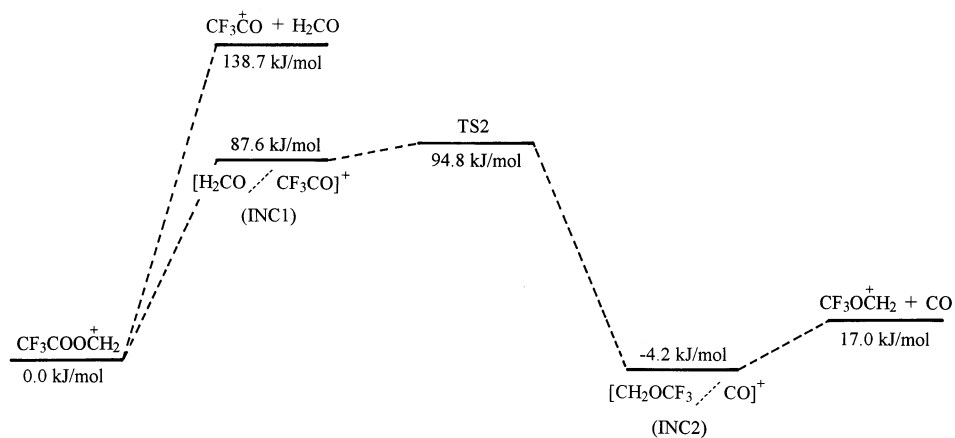
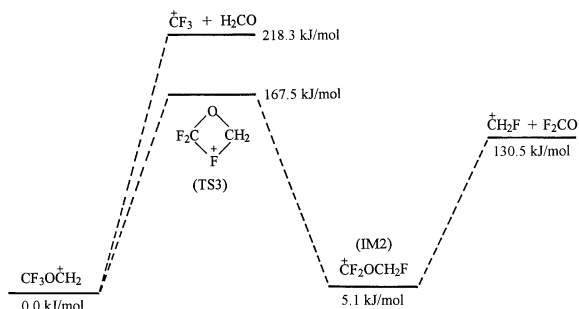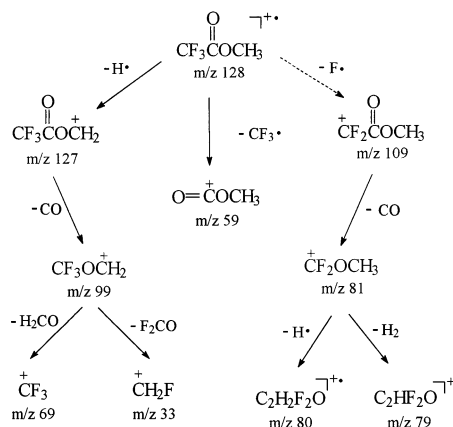Fig. 4. Calculated [MP2/6-31G(d)] energy diagram for the loss of CO from [CF₃COOCH₂]⁺.

Fig. 5. Calculated [HF/6-31G(d)] energy diagram for the decomposition of $[CF_3OCH_2]^+$.

Scheme 3.

C(3) distance is 3.22 Å, whereas C(3)–O(4) distance is 1.56 Å, and this complex is expressed as $[H_2COCF_3/CO]^+$. The energy needed to expel CO from INC2 is quite small (21.2 kJ/mol). The reverse activation energy of this reaction is 77.8 kJ/mol, and the KER value is 74 meV (vide ante), which is about 10% of the reverse activation energy. This fairly small KER value is in agreement with the proposed mechanism of CO loss in which ion-neutral complexes play an important role [22].

As mentioned above, the m/z 99 ion from 1, $[CF_3OCH_2]^+$, decomposes metastably to m/z 69 (30 u loss) and m/z 33 (66 u loss) ions, with the latter being far more probable than the former. The m/z 69 ion is $[CF_3]^+$, and is produced through H_2CO loss by the simple bond cleavage. On the other hand, the m/z 33 ion is $[CH_2F]^+$, and is produced through F_2CO loss with the migration of an F atom from the trifluoromethyl group to the methylene group. Fig. 5 shows a calculated (HF/6-31G(d)//HF/6-31G(d)) energy diagram for the decomposition of $[CF_3OCH_2]^+$ (m/z 99). When the bond linking the CF_3 group and the OCH_2 moiety is elongated, the energy increases monotonously until a complete cleavage of the bond is achieved, i.e., the formation of $[CF_3]^+$ and H_2CO. In the case of the formation of $[CH_2F]^+$ (m/z 33), a four-membered ring transition state (TS3) for the migration of an F atom is formed, then the F_2CO is expelled via an intermediate IM2 (Scheme II). The threshold energy to form $[CF_3]^+$ and H_2CO is 218.3 kJ/mol, whereas that to form $[CH_2F]^+$ and F_2CO is 167.5 kJ/mol. The formation of the $[CH_2F]^+$ (m/z 33)

and F_2CO is energetically much more favorable, and hence the peak at m/z 33 is much more intense than that at m/z 69, as shown in Fig. 1(d).

The m/z 81 ($[CH_3OCF_2]^+$) ion produced through the loss of CO from $[CF_2COOCH_3]^+$ (m/z 109) decomposes metastably to m/z 80 and m/z 79 by losing H and H_2, respectively. In this case, the loss of F_2CO or H_2CO was not observed.

Scheme 3 summarizes the metastable decomposition pathways of $[CF_3COOCH_3]^+$ concerned here. In this scheme, solid arrows represent the decomposition pathways observed in the MIKE spectra, whereas dashed arrows represent those not observed in the MIKE spectra, but which are observed in the normal mass spectrum.

4.2. Ethyl trifluoroacetate (2)

The MIKE spectrum of 2 is listed in Table 1. The abundance of the molecular ion in the ion source is very low, and a reliable MIKE spectrum of the molecular ion cannot be obtained.

Fig. 6 shows the MIKE spectra of some fragment ions of ethyl trifluoroacetate 2. In the MIKE spectrum of m/z 141 ion ($[2–H]^+$), the peaks at m/z 113 (28 u loss) are observed. The hydrogen atom lost from $2^{+\cdot}$ to produce the m/z 141 ion would be mostly a methylene hydrogen, because the relative energy of $[CF_3COOCHCH_3]^+$ estimated from an MO calcula-
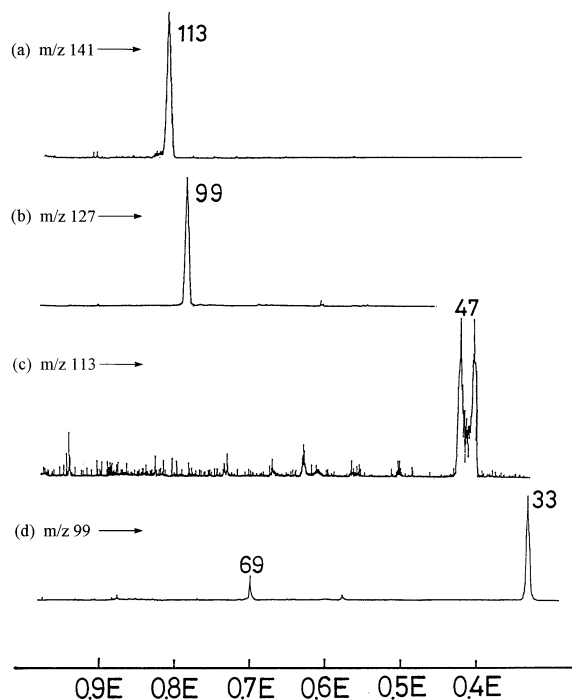
Fig. 6. MIKE spectra of (a) [M–H]$^+$, (b) [M–CH$_3$]$^+$, (c) [M–H– CO]$^+$, and (d) [M–CH$_3$–CO]$^+$ from ethyl trifluoroacetate.

Fig. 7. Calculated (HF/6-31G(d)) energy diagram for the decomposition of [CF$_3$OCHCH$_3$]$^+$.

tion at HF/6-31G(d,p) level is lower than that of [CF$_3$COOCH$_2$CH$_2$]$^+$ by 121 kJ/mol. In order to identify the neutral species with 28 u lost from [CF$_3$COOCHCH$_3$]$^+$ in the formation of the m/z 113 ion, we measured the MIKE spectrum of the deuterated species. In the MIKE spectrum of m/z 145 ion ([CF$_3$COOCDCD$_3$]$^+$), the peak at m/z 117 (28 u loss) is still observed. Hence, the neutral species lost from [CF$_3$COOCHCH$_3$]$^+$ is CO.

For the m/z 141 ion ([CF$_3$COOCHCH$_3$]$^+$), MO calculations of HF/6-31G(d) level show that the C–O bond linking CF$_3$CO and OCHCH$_3$ moieties is easy to cleave. The CID spectrum of the m/z 141 ion shows prominent peaks at m/z 113 (CO loss) and m/z 69 ([CF$_3$]$^+$). These situations are very similar to the case of [CF$_3$COOCH$_2$]$^+$ in 1. Thus, the mechanism of the loss of CO from the m/z 141 ion will be the same, in principle, as that from [CF$_3$COOCH$_2$]$^+$ (m/z 127) in 1, i.e. one in which an intermediate ion-neutral complex plays an important role. The resulting m/z 113 ion would be [CF$_3$OCHCH$_3$]$^+$.
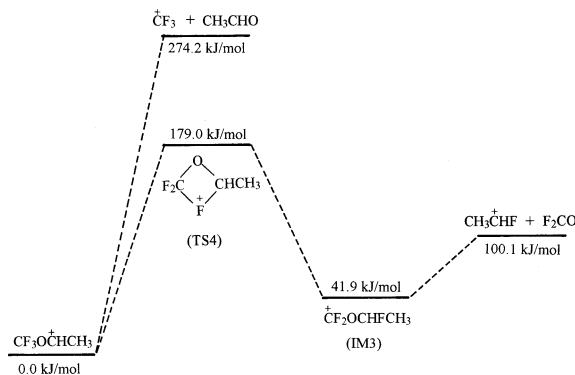
In the MIKE spectrum of the m/z 113 ion ([CF$_3$OCHCH$_3$]$^+$), a single dish-topped peak at m/z 47 (66 u loss) is observed [Fig. 6(c)]. The KER value estimated is ~550 meV. On deuteration, this peak shifts to a single dish-topped peak at m/z 51 (66 u loss) in the MIKE spectrum of the m/z 117 ion ([CF$_3$OCDCD$_3$]$^+$). This means that the neutral fragment lost contains no hydrogen atoms. Hence, this fragmentation is the loss of F$_2$CO accompanying an F atom migration. The mechanism of this reaction would be akin to that from [CF$_3$OCH$_2$]$^+$ (m/z 99) in the methyl ester, although the KER value in the ethyl ester is much larger than that in the methyl ester. The energy diagram for this fragmentation calculated at HF/6-31G(d)//HF/6-31G(d) level is shown in Fig. 7. Comparing Figs. 5 and 7, it is obvious that the reverse activation energy for the F$_2$CO loss from [CF$_3$OCHCH$_3$]$^+$ (78.9 kJ/mol) is larger than that from [CF$_3$OCH$_2$]$^+$ (37.0 kJ/mol). This would be one of the reasons why the KER value for the former is much larger than that for the latter.

In the mass spectrum of 2, ions at m/z 127 and m/z 99 are observed. The former would be produced from the molecular ion of 2 by losing $\dot{C}$H$_3$, and the latter by losing $\dot{C}$H$_3$ and CO from 2$^{+\cdot}$. Thus, the m/z 127 ion is [CF$_3$COOCH$_2$]$^+$ and the m/z 99 ion is [CF$_3$OCH$_2$]$^+$, both of which are also observed in the case of methyl ester. The MIKE spectrum of the m/z 127 ion and the m/z 99 ion in the ethyl ester, Figs. 6(b) and 6(d), are
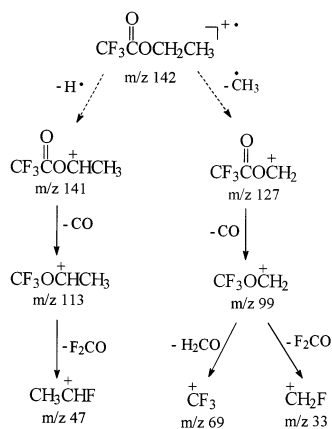
Scheme 4.

identical to those in the methyl ester. Hence, the assignment mentioned above is reasonable. The metastable decomposition pathways of $[CF_3COOCH_2CH_3]^{+\cdot}$ involved are summarized in Scheme 4.

References

[1] J.T. Welch, S. Eswarakrishnan, Fluorine in Bioorganic Chemistry, Wiley, New York, 1991.
[2] M.J. Saxby, Org. Mass Spectrom. 4 (1970) 133.
[3] T. Yanagisawa, S. Tajima, M. Iizuka, S. Tobita, M. Mitani, H. Sawada, T. Matsumoto, Int. J. Mass Spectrom. Ion Processes 125 (1993) 55.
[4] C.S. Hsu and D. Farcasiu, Org. Mass Spectrom., 24 (1989) 737.
[5] D. Farcasiu, G. Miller, C.S. Hsu, Org. Mass Spectrom. 25 (1990) 409.
[6] S. Tajima, T. Shirai, S. Tobita, N.M.M. Nibbering, Org. Mass Spectrom. 28 (1993) 473.
[7] M. Carbini, L. Conte, G. Gambaretto, S. Catinella, P. Traldi, Org. Mass Spectrom. 27 (1992) 1248.
[8] P. Varnai, L. Nyulaszi, T. Veszpremi, K. Vekey, Chem. Phys. Lett. 233 (1995) 340.
[9] S. Tajima, S. Tobita, M. Mitani, K. Akuzawa, H. Sawada, M. Nakayama, Org. Mass Spectrom. 26 (1991) 1023.
[10] J. Stach, D. Zimmer, M. Moder, R. Herzschuh, Org. Mass Spectrom. 24 (1989) 946.
[11] B. Kralj, D. Zigon, R. Susic, Rapid Commun. Mass Spectrom. 12 (1998) 87.
[12] Gaussian 94, Revision D.1, M.J. Frisch, G. W. Trucks, H. B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Charllacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
[13] D.G.I. Kingston, B.W. Hobrock, M.M. Bursey, J.T. Bursey, Chem. Rev. 75 (1975) 693.
[14] R. Wolf, A.-M. Dommrose, H.-F. Grützmacher, Org. Mass Spectrom. 23 (1988) 26.
[15] R. Wolf, H.-F. Grützmacher, Org. Mass Spectrom., 24 (1989) 398.
[16] R. Wolf, H.-F. Grützmacher, J. Phys. Org. Chem. 3 (1990) 301.
[17] J.K. Terlouw, J.L. Holmes, P.C. Burgers, Int. J. Mass Spectrom. Ion Processes 66 (1985) 239.
[18] J.L. Holmes, C.E.C.A. Hop, J.K. Terlouw, Org. Mass Spectrom. 21 (1986) 776.
[19] N. Heinrich, J. Schmidt, H. Schwarz, Y. Apeloig, J. Am. Chem. Soc. 109 (1987) 1317.
[20] M.C. Bissonnette, M. George, J.L. Holmes, Int. J. Mass Spectrom. Ion Processes 101 (1990) 309.
[21] K. Levsen, Fundamental Aspects of Organic Mass Spectrometry, Verlag Chemie, Weinheim, 1978.
[22] D.J. McAdoo, Mass Spectrom. Rev. 7 (1988) 363.
[23] P. Longevialle, R. Botter, Org. Mass Spectrom. 18 (1983) 1.
[24] T.H. Morton, Org. Mass Spectrom. 27 (1992) 353.