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Unimolecular decomposition of ethyl lactate, $CH_3CH(OH)COOC_2H_5$, upon electron impact

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Abstract

The spontaneous unimolecular fragmentation of metastable ions of ethyl lactate, $CH_3CH(OH)COOC_2H_5$, **1**, (MW:118) by electron ionization has been investigated by using mass-analyzed ion kinetic energy (MIKE) spectrometry and D labeling. The fragmentation of **1** is compared with those of methyl lactate, $CH_3CH(OH)COOCH_3$,**2**, (MW:104), and ethyl glycolate, $CH_2(OH)COOC_2H_5$, **3**, (MW:104), which are lower homologues of **1**. The metastable ions of $\mathbf{1}^{+\cdot}$ decompose to give the three fragment ions *m*/*z* 89 ($\dot{C}_2H_5$ loss), 75 ($CH_3\dot{C}O$ loss) and 45 ($\dot{C}OOC_2H_5$ loss). The first fragmentation is accompanied with a large kinetic energy release (KER) in analogy with that for the case of $\dot{C}H_3$ loss from $\mathbf{2}^{+\cdot}$. Double hydrogen atom migration occurs in the second reaction in a similar manner as those in **2** and **3**. The last fragment ion is CH_3CH^+OH and this is also generated by the other two processes. These fragmentations of $\mathbf{1}^{+\cdot}$ are similar to those of $\mathbf{2}^{+\cdot}$, except for CO loss observed in $\mathbf{2}^{+\cdot}$, however, are different from those of $\mathbf{3}^{+\cdot}$. (Int J Mass Spectrom 181 (1998) 89–98) © 1998 Elsevier Science B.V.

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1. Introduction

Information about the mechanism with double hydrogen atom migration during the fragmentation of ions plays an important role in the interpretation of the mass spectra of certain kinds of organic compounds. Double hydrogen atom migration, which produces the so-called $[\text{McLafferty} + 1]^+$ ion, is observed in the mass spectra of propyl and higher alkyl esters [1–14]. This migration is also observed during the fragmentations of the ionized alkyl α-hydroxyacetate, such as methyl glycolate, $CH_2(OH)COOCH_3$ [15–20] and ethyl glycolate, $CH_2(OH)COOC_2H_5$, **3**, (MW:104) [15,21], isobutanol [22–25], 1, 2-ethanediol [26–35], and hydroxyacetone [36–43].

In a previous paper, we reported that the consecutive double hydrogen atom migrations were observed in the fragmentations of the molecular ion of methyl lactate, $CH_3CH(OH)COOCH_3$, **2**, (MW:104) by using mass-analyzed ion kinetic energy (MIKE) spectrometry and D labeling [44]. In this work, we investigate the fragmentation pathways of ethyl lactate, $CH_3CH(OH)COOC_2H_5$, **1**, (MW:118), which is a higher homologue of **2** and **3**, with attention to double hydrogen atom migration by using MIKE spectrom-

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etry and D-labeling because, to the authors' knowledge, the fragmentation of **1** upon electron ionization has not been reported yet. The results are compared with those of **2** and **3**.

2. Experimental

The mass and MIKE spectra were obtained with a JEOL JMS-HX100, EBE type triple focusing mass spectrometer. Samples were introduced via a heated (100°C) indirect inlet system. The ion-source temperature was 180°C. The electron energy was 70 eV, and the ion accelerating voltage was 5.0 kV. The kinetic energy release (KER) was estimated from the width of the metastable peaks at half-height [45].

The sample **1**, obtained from Tokyo Kasei, Co. Ltd., was reagent grade and was used without further purification. The D-labeled isopomer, $CH_3CH(OH)COOCD_2CD_3$, **1**-d_5, (MW:123) was prepared by esterifying $CH_3CH(OH)COOH$ with CD_3CD_2OH. The degree of labeling of **1**-d_5, estimated from the peak heights in the normal mass spectrum, was better than 98%. The other D-labeled one, $CH_3CH(OD)COOC_2H_5$, **1**-O-d_1, (MW:119) was obtained by repeated exchange of **1** with D_2O. The deuterium contents of this isotopomer is not so good (about 70%).

3. Results and discussion

3.1. Fragmentation of the molecular ion of 1

The molecular ion peak of **1** at m/z 118 is very weak (<1%), similar to those of **2** [44] and **3** [21]. The MIKE spectra of $\mathbf{1}^{+\cdot}$, **1**-O-$d_1^{+\cdot}$, and **1**-$d_5^{+\cdot}$ are shown in Fig. 1.

Fig. 1(a) shows two narrow peaks at m/z 75 and 45 in addition to the relatively broad peak at m/z 89. The KER associated with the last reaction is 325 meV. This value is too large to regard as this reaction is a simple cleavage one [46]. This is similar to the case of the loss of $\dot{C}H_3$ from $\mathbf{2}^{+\cdot}$ giving the ion at m/z 89 [44].

The peaks at m/z 89, 75 and 45 in Fig. 1(a) shift to m/z 90, 76 and 46 in Fig. 1(b), respectively. However, in Fig. 1(c), only the peak at m/z 75 in Fig. 1(a) shifts to m/z 80, and the other ones at m/z 89 and 45 remain at the same masses. These results indicate that the ions at m/z 89, 75 and 45 from the unlabeled precursor, $\mathbf{1}^{+\cdot}$, are generated by the losses of $\dot{C}_2H_5$, $CH_3\dot{C}O$ and $\dot{C}OOC_2H_5$, respectively.

Taking into account the results of the fragmentation of $\mathbf{2}^{+\cdot}$ [44], we can estimate that the m/z 75 ion from $\mathbf{1}^{+\cdot}$ would be generated by the loss of $CH_3\dot{C}O$ with double hydrogen atom migration. Further, this ion at m/z 75 would be a protonated ethyl formate $[CH(OH)OC_2H_5]^+$ [44]. Support for the proposed reaction would be obtained from comparison of the MIKE spectrum of $\mathbf{1}^{+\cdot}$ with that of **1**-O-$d_1^{+\cdot}$ [see Figs. 1(a) and 1(b)]. These spectra show that the relative abundance of the ion because of loss of acetyl radical is lower for **1**-O-$d_1^{+\cdot}$ than for $\mathbf{1}^{+\cdot}$. This observation indicates that an isotope effect [47] operates in this reaction. That is, the hydroxy hydrogen atom participates in this reaction. From the ion abundance ratios $([m/z\ 75]/[m/z\ 45])_1/([m/z\ 76]/[m/z\ 46])_{1\text{-O-}d_1}$, the intermolecular primary isotope effect is estimated to be 2.9, neglecting the secondary isotope effect for the formation of m/z 46 ion. This is in good agreement with the known isotope effect [47]. The mechanism of the double hydrogen atom migration is depicted in Scheme 1.

In the case of **3**, $H\dot{C}O$ loss, instead of $CH_3\dot{C}O$ loss in the case of **1**, was eliminated with double hydrogen atom migration. The process, however, was minor (about 4% of the total metastable ion fragmentation) [21].

As described above, the KER associated with the fragmentation of $\mathbf{1}^{+\cdot}$ to the ion at m/z 89 is too large to regard as this reaction is a simple cleavage one [46]. Further, the intermolecular isotope effect 1.3 is also observed for the cases of $\mathbf{1}^{+\cdot}$ and **1**-O-$d_1^{+\cdot}$ (this value is estimated by the ion abundance ratio $([m/z\ 89]/[m/z\ 45])_1/([m/z\ 89]/[m/z\ 46])_{1\text{-O-}d_1}$) [see Figs. 1(a) and 1(b)]. These experimental results suggest that the hydroxyl hydrogen atom also participates in the formation of the ion at m/z 89. From these experimental results, we propose the plausible mechanism of $\dot{C}_2H_5$ loss as shown in Scheme 2, that is, the hydroxyl hydrogen atom migration to ether oxygen

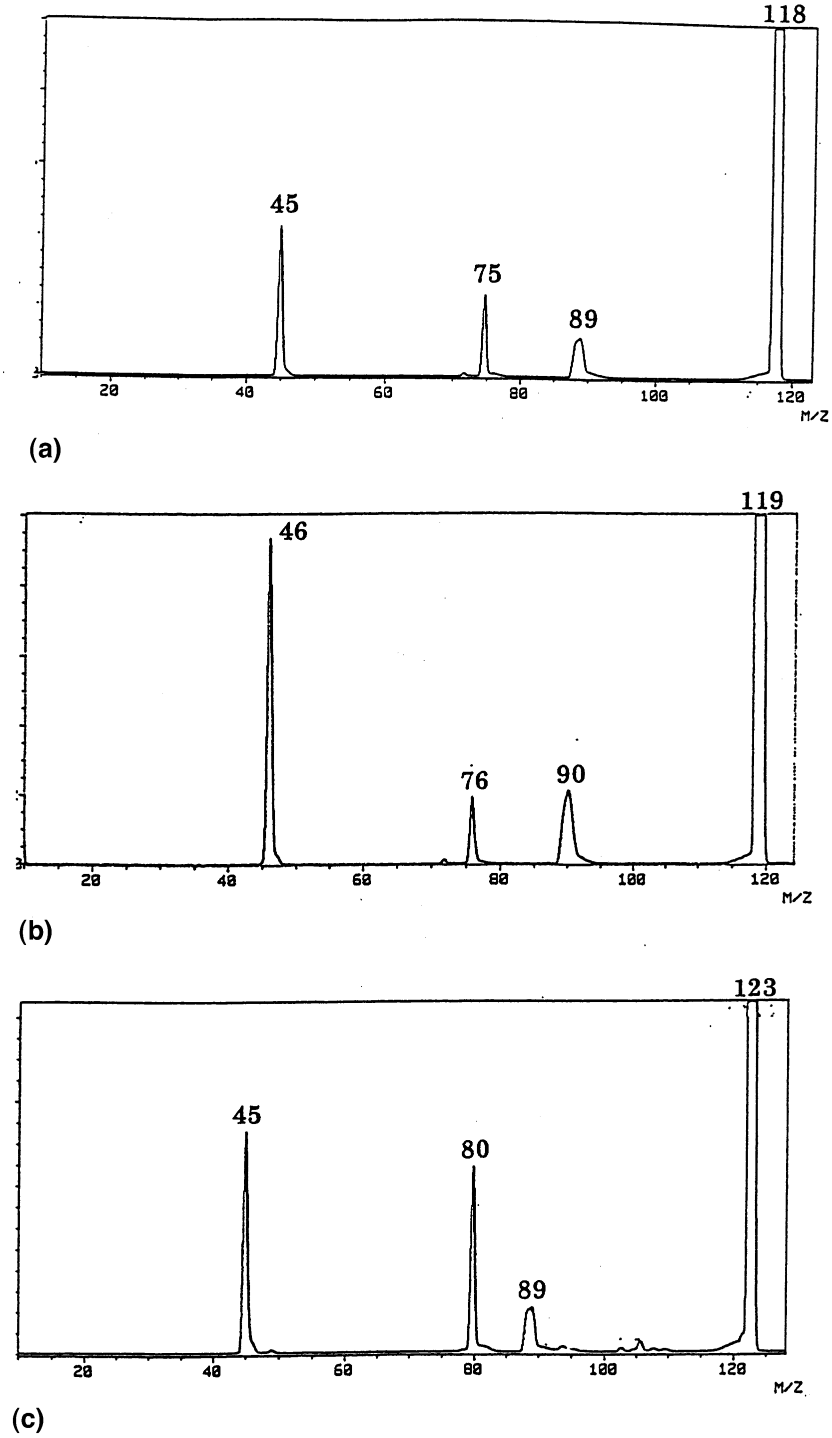
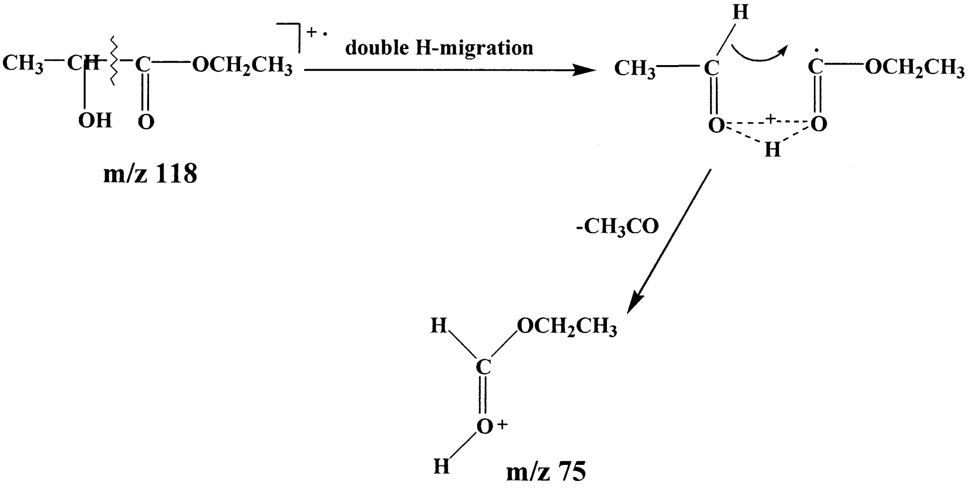


Fig. 1. MIKE spectra of the molecular ions of (a) ethyl lactate, **1**, (b) **1**-O-d_1 and (c) **1**-d_5, generated by 70 eV electron ionization.



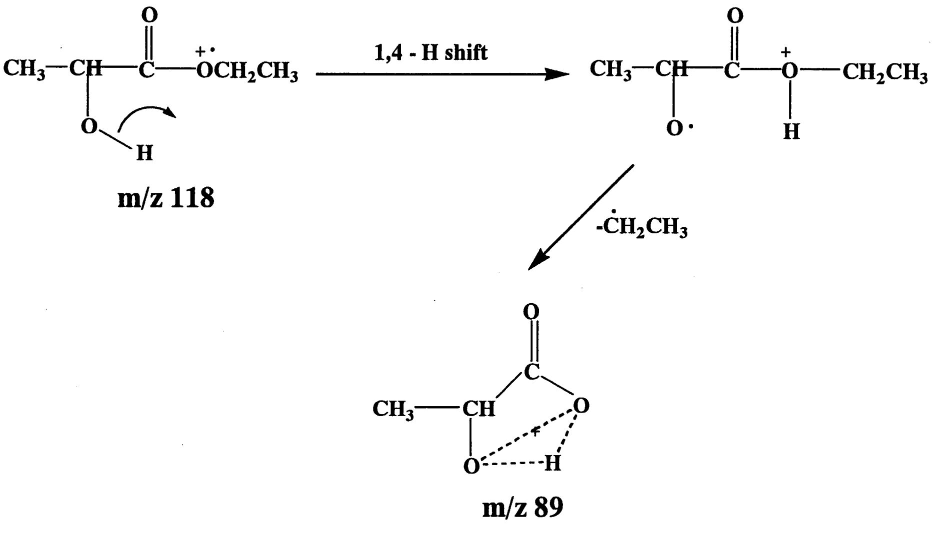
Scheme 1. Mechanism of the double hydrogen atom migration for the loss of $CH_3\dot{C}O$ from $1^{+\cdot}$.

occur to expel the ethyl radical. This rearrangement is a so-called "hidden" hydrogen atom migration [48].

The ion at m/z 45 generated by the loss of $\dot{C}OOC_2H_5$ from $\mathbf{1}^{+\cdot}$ would have the same structure as that of the m/z 45 ion generated by the loss of $\dot{C}OOCH_3$ from $\mathbf{2}^{+\cdot}$ [44], because these two m/z 45 ions decompose into the ions at m/z 29, 27 and 19 by losses of CH_4, H_2O and C_2H_2, respectively.

In the MIKE spectrum of $\mathbf{2}^{+\cdot}$, four fragment peaks were observed at m/z 89, 76, 61 and 45 corresponding to the losses of $\dot{C}H_3$, CO, $CH_3\dot{C}O$ and $\dot{C}OOCH_3$ [44]. Thus, the fragmentation pathways of metastable $\mathbf{1}^{+\cdot}$ are similar to those of $\mathbf{2}^{+\cdot}$, except for the loss of CO.

On the other hand, the fragmentation pathways of $\mathbf{1}^{+\cdot}$ are different from those of $\mathbf{3}^{+\cdot}$, because the latter ions decompose mainly to give the fragment ions m/z 76 by losing C_2H_4, and there was no fragment ion at m/z 45 [21].



Scheme 2. Proposed mechanism of the "hidden" hydrogen atom migration for the loss of $\dot{C}_2H_5$ from $\mathbf{1}^{+\cdot}$.

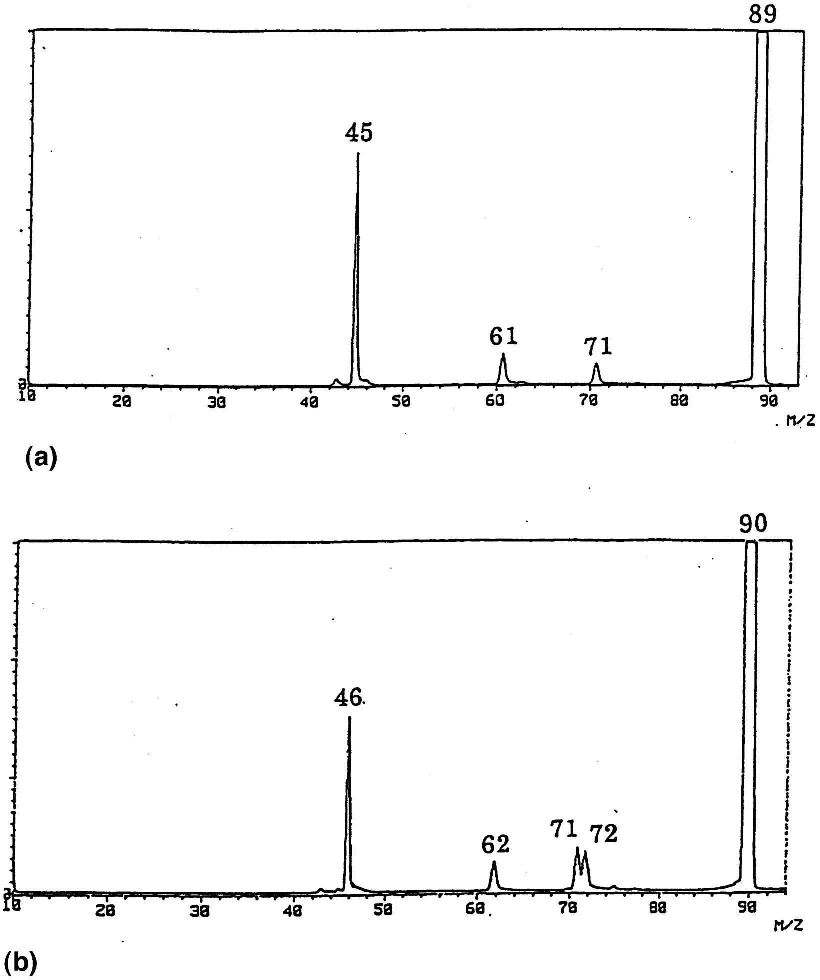


Fig. 2. MIKE spectra of (a) the m/z 89 ions from $1^{+\cdot}$ and (b) the m/z 90 ions from 1-O-$d_1^{+\cdot}$, generated by 70 eV electron ionization.

3.2. Fragmentation of the ion at m/z 89 from $1^{+\cdot}$

The MIKE spectra of the source-generated ions at m/z 89 from $1^{+\cdot}$ and m/z 90 from 1-O-$d_1^{+\cdot}$ are given in Fig. 2. The MIKE spectrum of the m/z 89 ion from 1-$d_5^{+\cdot}$ was nearly the same as that of $1^{+\cdot}$. The m/z 89 ions decompose into three ions at m/z 71, 61 and 45, which correspond to the losses of the species with 18, 28 and 44 Da, respectively.

As shown in Fig. 2(b), the peak at m/z 71 in Fig. 2(a) splits into two peaks at m/z 72 and 71, corresponding to the losses of 18 and 19 Da, respectively. This means that hydrogen atom scrambling may occur prior to the loss of water molecule or two distinct fragmentation pathways exist. However, we can not decide from this experiment which mechanism is favored, because the ion abundance of the m/z 71 in the normal mass spectrum of **1** is too weak to clarify the mechanism ($<1\%$).

The second and third peaks at m/z 61 and 45 in Fig. 2(a) shift to m/z 62 and 46 in Fig. 2(b), respectively. These results indicate that those peaks correspond to the losses of CO and CO_2, respectively. From the latter process, CH_3CH^+OH ion at m/z 45 is also produced from the intermediate ion at m/z 89.

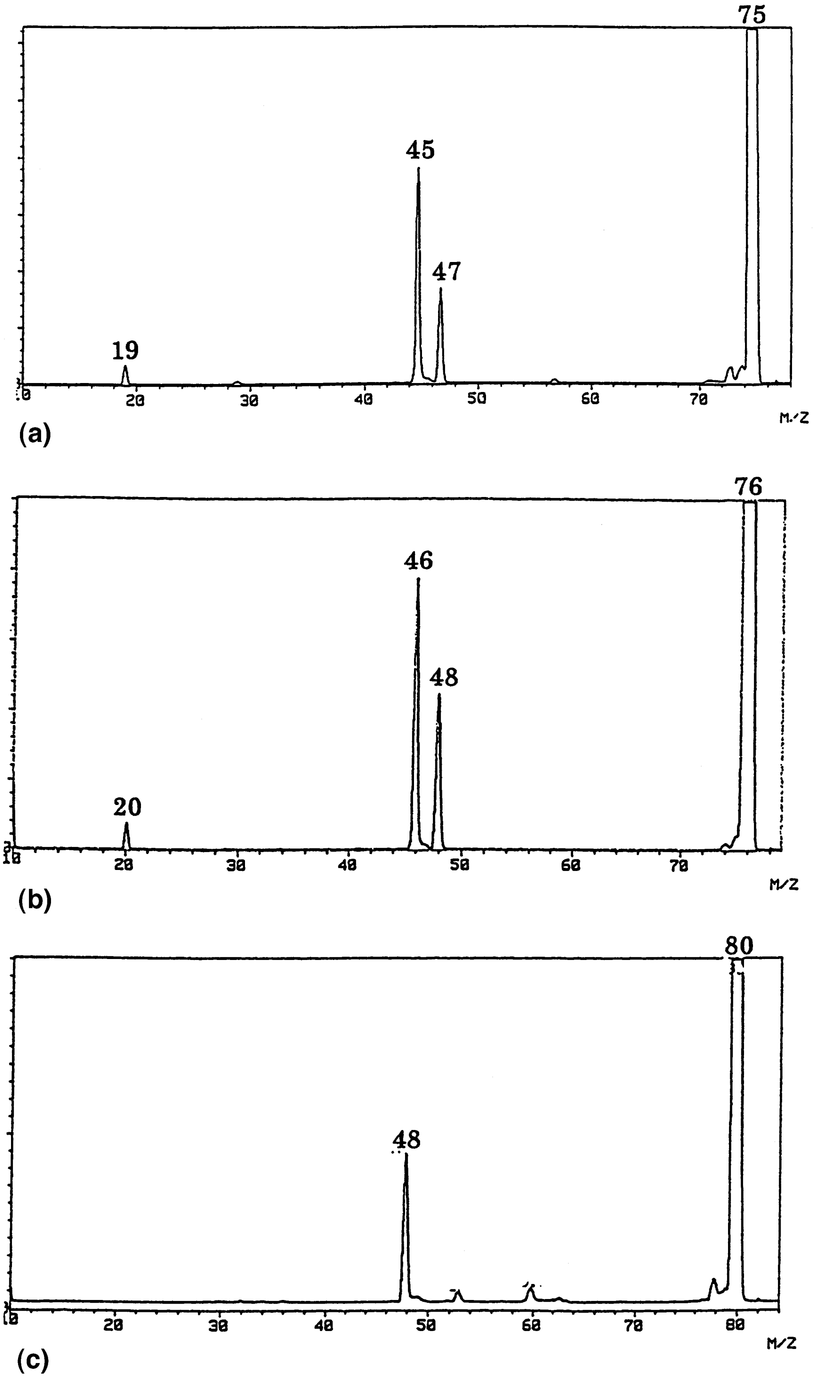
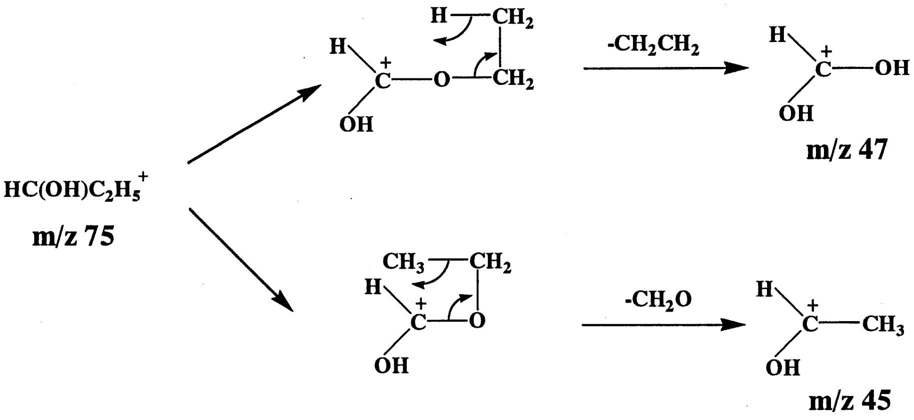


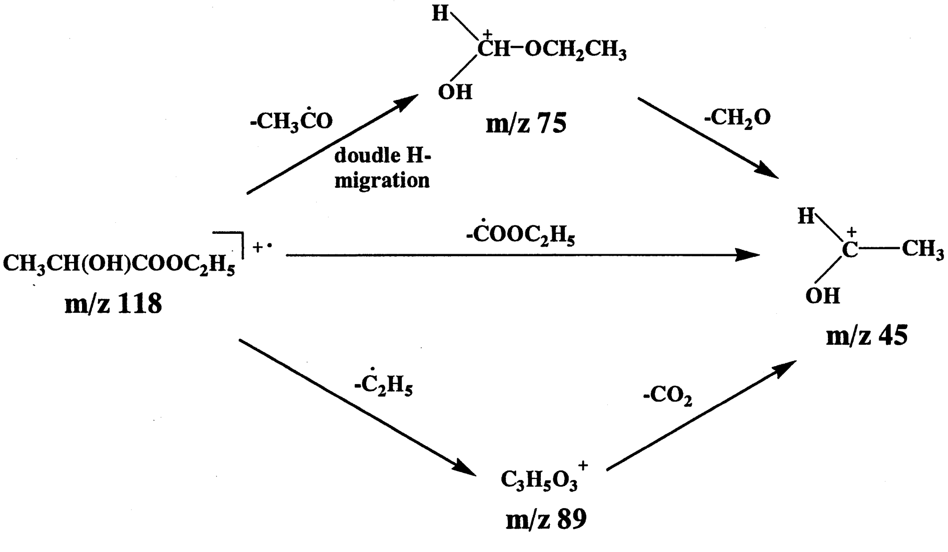
Fig. 3. MIKE spectra of (a) the *m*/*z* 75 ions from $\mathbf{1}^{+\cdot}$, (b) the m/z 76 ions from $\mathbf{1}$-O-$d_1^{+\cdot}$ and (c) the *m*/*z* 80 ions from $\mathbf{1}$-$d_5^{+\cdot}$, generated by 70 eV electron ionization.



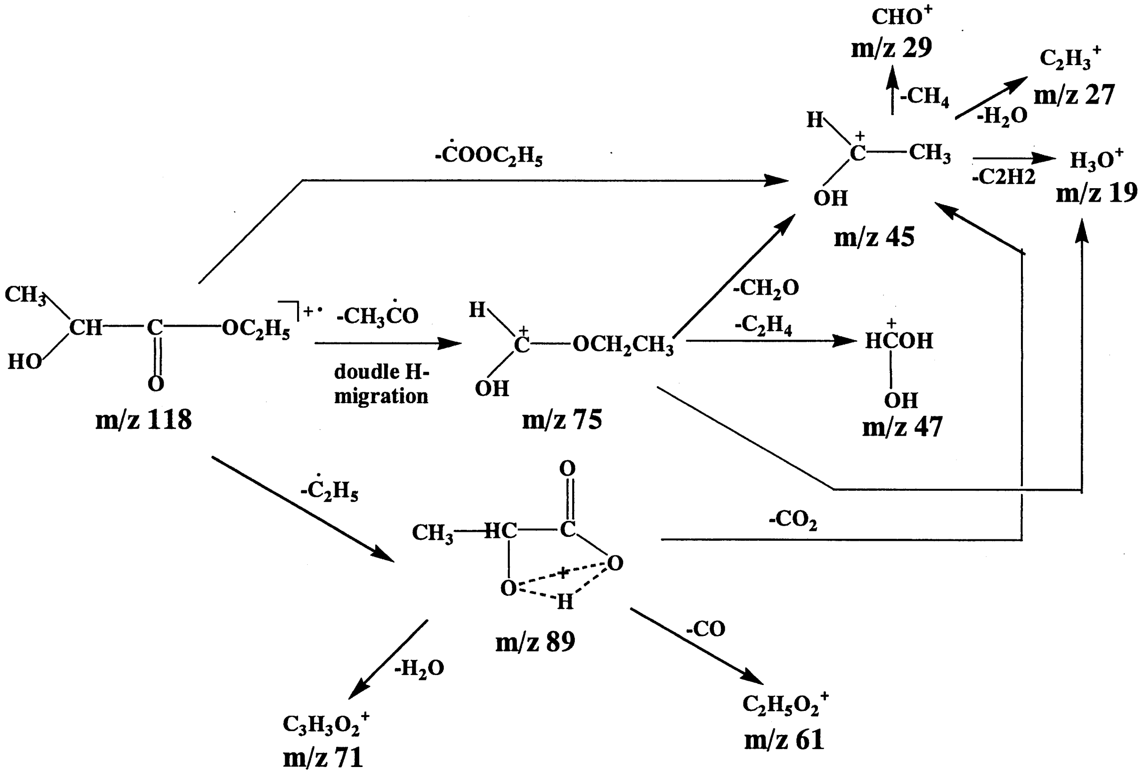
Scheme 3. Proposed mechanisms for the fragmentation of the m/z 75 ions into the *m/z* 47 and 45 ions for **1**.

3.3. Fragmentation of the ion at m/z 75 from $1^{+\cdot}$

Fig. 3 shows the MIKE spectra of the ions at *m/z* 75 from $\mathbf{1}^{+\cdot}$, 76 from $\mathbf{1}$-O-$d_1^{+\cdot}$ and 80 from $\mathbf{1}$-$d_5^{+\cdot}$. The MIKE spectrum of the ions at *m/z* 75 [Fig. 3(a)] is slightly different from that of the *m/z* 75 ion from $\mathbf{3}^{+\cdot}$. This is because the fact that the latter *m/z* 75 ions consist of the two isobaric ions generated by losing $\dot{C}_2H_5$ or $\dot{C}HO$. The ions at *m/z* 75, $HOCH^+OC_2H_5$, from $\mathbf{1}^{+\cdot}$ mainly decompose into ions at *m/z* 47 and 45. These shift to *m/z* 48 and 46 in Fig. 3(b). However, in the MIKE spectrum of the *m/z* 80 ion from $\mathbf{1}$-$d_5^{+\cdot}$ [Fig. 3(c)], these shift exclusively to *m/z* 48. These results mean that the *m/z* 47 ion from $\mathbf{1}^{+\cdot}$ is not generated by the loss of CO, but by the loss of C_2H_4 from the original ethyl group. In contrast, loss of CO would give rise to a peak at *m/z* 52. This fragmentation contrasts with those of the *m/z* 61 ions generated by the loss of $CH_3\dot{C}O$ with double hydrogen atom migration from $\mathbf{2}^{+\cdot}$ and by the loss of $H\dot{C}O$ from methyl glycolate because the large amounts of these *m/z* 61 ions decomposed to the *m/z* 33 ion by losing CO with double hydrogen atom migration [44].



Scheme 4. Three formation routes of the *m/z* 45 ions for **1**.



Scheme 5. Total fragmentation pathways of $\mathbf{1}^{+\cdot}$.

Further, we can conclude that in the case of **1**, the *m/z* 45 ion from the *m/z* 75 ion does not contain the methylene group in the original ethyl one, i.e. this ion may be generated by the loss of OCH_2 in the ethoxy group, with methy migration in the original ethyl group. The plausible mechanisms of the fragmentation of the *m/z* 75 ion to the *m/z* 47 and 45 ions for **1** are depicted in Scheme 3. The fragmentation of the *m/z* 75 ion, $HOCH^+OC_2H_5$, generated by the loss of $\dot{C}HO$ from $\mathbf{3}^{+\cdot}$ with double hydrogen atom migration has not been reported [15,21]. However, it can be concluded that this fragmentation is identical with that of the *m/z* 75 ion from $\mathbf{1}^{+\cdot}$, as shown above. On the other hand, the fragmentation of the *m/z* 75 ion, $C_2H_3O_3^+$, generated by the loss of $\dot{C}_2H_5$ radical from $\mathbf{3}^{+\cdot}$ is different from that of the *m/z* 75 ion from $\mathbf{1}^{+\cdot}$, as described above.

The sums of the heats of formation of possible product ions and neutral fragments for the following reactions were estimated by the PM3 (Parametric Method 3) method

$$HCOH^+OC_2H_5(m/z\ 75) \rightarrow CH(OH^+)OH(m/z\ 47) + C_2H_4\ (1)\ 467\ \mathrm{kJ\ mol}^{-1}$$

$$\rightarrow H_2O^+C_2H_5(m/z\ 47) + CO\ (2)\ 550\ \mathrm{kJ\ mol}^{-1}$$

$$\rightarrow CH_3CH^+OH(m/z\ 45) + CH_2O\ (3)\ 471\ \mathrm{kJ\ mol}^{-1}$$

The value of the sums of the heats of formation of the products in reaction (1) is lower than that of the reaction (2). This may be one of the reasons why the *m/z* 47 ion is not generated by the loss of CO with double hydrogen atom migration, but by the loss of C_2H_4 from the ethyl group [49]. Similar ion intensities at *m/z* 47 and 45 in Fig. 3(a) can be rationalized by comparing the value of the reactions (1) and (3).

A small peak at m/z 19 in Fig. 3(a) shifts to m/z 20 in Fig. 3(b). This shows that this ion is a H_3O^+, and the hydroxy hydrogen is fully retained in this ion.

3.4. Fragmentation of the ion at m/z 45 from $1^{+\cdot}$

As described above, the m/z 45 ions are generated by the three separated routes (Scheme 4). The MIKE spectrum of the source-generated m/z 45 ion for **1** was identical to those of the ions at m/z 45 from **2** and isopropanol [44]. That is, it showed the three peaks at m/z 29, 27 and 19, corresponding to the losses of CH_4, H_2O and C_2H_2, respectively. Therefore, we can conclude that the structure of the m/z 45 ion from $\mathbf{1}^{+\cdot}$ is CH_3CH^+OH. The total fragmentation pathways of $\mathbf{1}^{+\cdot}$ are shown in Scheme 5.

4. Conclusion

The molecular ion of ethyl lactate, **1**, decomposes into ions at m/z 89, 75, and 45 by the losses of $\dot{C}_2H_5$, $CH_3\dot{C}O$, and $\dot{C}OOC_2H_5$, respectively. These fragmentations are similar to those of methyl lactate, **2**, which is one of the lower homologues, but considerably different from those of ethyl glycolate, **3**, which is another lower homologue.

The first fragmentation occurs with "hidden" hydrogen atom migration. The second fragment ion decomposes into m/z 47 and 45 ions. The latter is generated by the loss of CH_2O in the ethoxy group with methyl migration in original ethyl group. The former is generated by the loss of C_2H_4, not by the loss of CO. These are rationalized by the energetic consideration. These two fragmentation pathways contrast to the case of **2**. The ion at m/z 45 is produced by the three different fragmentation routes, and decomposes into the three ions at m/z 29, 27 and 19 by losses of CH_4, H_2O and C_2H_2, respectively.

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