International Journal of Mass Spectrometry 207 (2001) 217–222

Formation and decomposition of the *m/z* 75 fragment ions from the molecular ion of ethyl lactate, $CH_3CH(OH)COOCH_2CH_3$

Susumu Tajima[a,]*, Daisuke Watanabe[a], Satoshi Nakajima[a], Osamu Sekiguchi[a], Nico M.M. Nibbering[b]

[a]*Chemistry and Materials Science, Gunma National College of Technology, Maebashi, Gunma, Japan*
[b]*Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

Received 2 November 2000; accepted 22 January 2001

Abstract

The *m/z* 75 fragment ions are formed by the loss of a neutral species with 43 Da from the molecular ions of ethyl lactate [$CH_3CH(OH)COOCH_2CH_3$]. In contrast to the previously reported results, it is shown that the population of these ions consists of at least three different ionic species, which are $CH^+(OH)OCH_2CH_3$ (protonated ethyl formate), $CH_3CH(OH)O^+{=}CH_2$, and $CH^+(OH)COOH$ (protonated glyoxylic acid). The protonated ethyl formate species decomposes into the *m/z* 47 ion (protonated formic acid) by the loss of ethylene, the second ion decomposes into the *m/z* 45 ion (protonated acetaldehyde) by the loss of formaldehyde and the protonated glyoxylic acid eliminates two molecules of carbon monoxide to generate the *m/z* 19 ion (protonated water). (Int J Mass Spectrom 207 (2001) 217–222) © 2001 Elsevier Science B.V.

Keywords: MIKE spectrometry; *m/z* 75 ion; Protonated ethyl formate; Protonated glyoxylic acid; Ethyl lactate

---

1. Introduction

Some of us have reported on the electron ionization induced decomposition of ionized ethyl lactate [$CH_3CH(OH)COOCH_2CH_3$, **1**, MW 118] as studied by use of mass-analyzed ion kinetic energy (MIKE) spectrometry and deuterium labeling [1]. The peak at *m/z* 75 in the MIKE spectrum of $\mathbf{1}^{+\cdot}$ shifted to *m/z* 80 in the MIKE spectrum of the d_5-isotopomer of $\mathbf{1}^{+\cdot}$ [$CH_3CH(OH)COOCD_2CD_3$, **1**-d_5, MW 123]. The conclusion was therefore drawn that the *m/z* 75 ion was generated by the loss of CH_3CO by way of a double hydrogen atom migration in a similar way as that loss from the lower homologue of **1** [2], that is ionized methyl lactate [$CH_3CH(OH)COOCH_3$]. Further, it was concluded that the *m/z* 75 ions are protonated ethyl formate [$CH^+(OH)OCH_2CH_3$] and that the source-generated *m/z* 75 ions decompose into the ions *m/z* 47 (C_2H_4 loss) and *m/z* 45 (CH_2O loss). The fragmentation of the *m/z* 75 ions into the *m/z* 19 ions has not been discussed in the previous article, because the relative abundance of the *m/z* 19 ions is low in the MIKE spectrum of the *m/z* 75 ion [1].

Recently, however, we have noticed that the source-generated $CH^+(OH)OCH_2CH_3$ ions, corresponding to protonated ethyl formate, decompose in the metastable time window only into the ions *m/z* 47 due to the loss of C_2H_4 by means of a proton-bridged intermediate [3–6], but not into the ions *m/z* 45. These

---

* Corresponding author. E-mail: tajima@chem.gunma-ct.ac.jp

PII S1387-3806(01)00372-4

protonated ethyl formate m/z 75 ions were generated both by the losses of $H^{\cdot}$ and C_2H_4 from diethoxymethane [$CH_2(OCH_2CH_3)_2$, **2**, MW 104] [6], and by the loss of $CF_3^{\cdot}$ from the molecular ion of trifluoroacetaldehyde ethyl hemiacetal [$CF_3CH(OH)OCH_2CH_3$, **3**, MW 144]. The m/z 75 ions ($C_3H_7O_2^+$) generated by chemical ionization (CI) of ethyl formate [$HCOOCH_2CH_3$, **4**, MW 74] also decomposed only into the ions m/z 47. This prompted us to reinvestigate the formation and decomposition of the m/z 75 ions generated by the loss of 43 Da from $\mathbf{1}^{+\cdot}$.

2. Experimental

The standard mass and unimolecular MIKE spectra were obtained using a JEOL JMS-HX100 tandem mass spectrometer. The CI spectrum was obtained using a JEOL JMS-DX303 tandem mass spectrometer equipped with a CI source (reagent gas:isobutane).

Compounds **1–4** and 2,2,2-trifluorolactic acid [$CF_3CH(OH)COOH$, **5**, MW 144], used as source of the reference ion of protonated glyoxylic acid, were research grade products from Tokyo Kasei Co. Ltd, and were used without further purification. Compound **1**-d_5 was prepared by esterification of $CH_3CH(OH)COOH$ with CD_3CD_2OD [1].

3. Results and discussion

The mass spectrum of **1** is shown in Fig. 1(a). The relative abundance of the molecular ion is very low. Also the abundances of the fragment ions generated by the losses of 15 and 43 Da are low, but the corresponding peaks are clearly observed at m/z 103 and 75, respectively. The peak of the former ion shifts in the mass spectrum of **1**-d_5 [Fig. 1(b)] to m/z 108, suggesting that this ion is generated by the loss of a methyl group from the 2-position of $\mathbf{1}^{+\cdot}$ and not from the ethyl group. The peak at m/z 75 in Fig. 1(a) shifts to m/z 76 and 77 in Fig. 1(b). Although the relative abundance of the ion at m/z 80 in Fig. 1(b) is very low, a part of the peak at m/z 75 may also shift to m/z 80. Because the peak at m/z 75 in the MIKE spectrum of $\mathbf{1}^{+\cdot}$ shifted to m/z 80 in the MIKE spectrum of the d_5-isotopomer of $\mathbf{1}^{+\cdot}$ [1].

As shown in Fig. 2, the source-generated m/z 75 ions from $\mathbf{1}^{+\cdot}$ decompose into the ions m/z 47, 45, and 19. As mentioned in the introduction, the decomposition of these m/z 75 ions into the ions m/z 47 and 45 has been suggested to occur from protonated ethyl formate [$CH^+(OH)OCH_2CH_3$] [1].

Table 1 shows the MIKE spectra of the ions m/z 75 in the protonated ethyl formate structure [$CH^+(OH)OCH_2CH_3$] as generated by (a) the losses of $H^{\cdot}$ and C_2H_4 from $\mathbf{2}^{+\cdot}$, (b) loss of $CF_3^{\cdot}$ from $\mathbf{3}^{+\cdot}$, and (c) CI of **4**. These clearly indicate that the m/z 75 ions that have the structure of protonated ethyl formate decompose only into the ions m/z 47 by eliminating a 28 Da neutral species and not into the ions m/z 45 and 19. According to deuterium labeling, this neutral species is an ethylene molecule lost by way of a proton-bridged intermediate [3–6], and not CO, whereas the resulting ion is $C^+H(OH)_2$ [6]. Taking these results together, it must be concluded that the source-generated ions m/z 75 from $\mathbf{1}^{+\cdot}$ cannot be only protonated ethyl formate (see Scheme 1 for the proposed mechanism of its formation and decomposition from $\mathbf{1}^{+\cdot}$), but must also be present in other isomeric structures.

The MIKE spectra of the source-generated ions m/z 80, 77, and 76 from $\mathbf{1}\text{-}d_5^{+\cdot}$ are shown in Table 2. The m/z 80 ions decompose only into the ions m/z 48 by loss of C_2D_4 [1], the ions m/z 77 decompose only into the ions m/z 45 by elimination of a neutral 32 Da species (CD_2O), and the ions m/z 76 decompose to give the fragment ions m/z 20 (H_2DO^+). These observations suggest that the source-generated ions m/z 75 from $\mathbf{1}^{+\cdot}$ occur in at least three different structures, one of them being protonated ethyl formate. If this is true, the fragment ion peaks at m/z 47, 45, and 19 in Fig. 2 may be considered and rationalized as being due to a superposition of the fragment ions generated from these three different precursor ions m/z 75. This is substantiated by the following experimental observations.

The MIKE spectra of the m/z 103 ions from $\mathbf{1}^{+\cdot}$ and the m/z 108 ions from $\mathbf{1}\text{-}d_5^{+\cdot}$ presented in Fig. 3(a) and (b) show that the peak at m/z 75 in the former

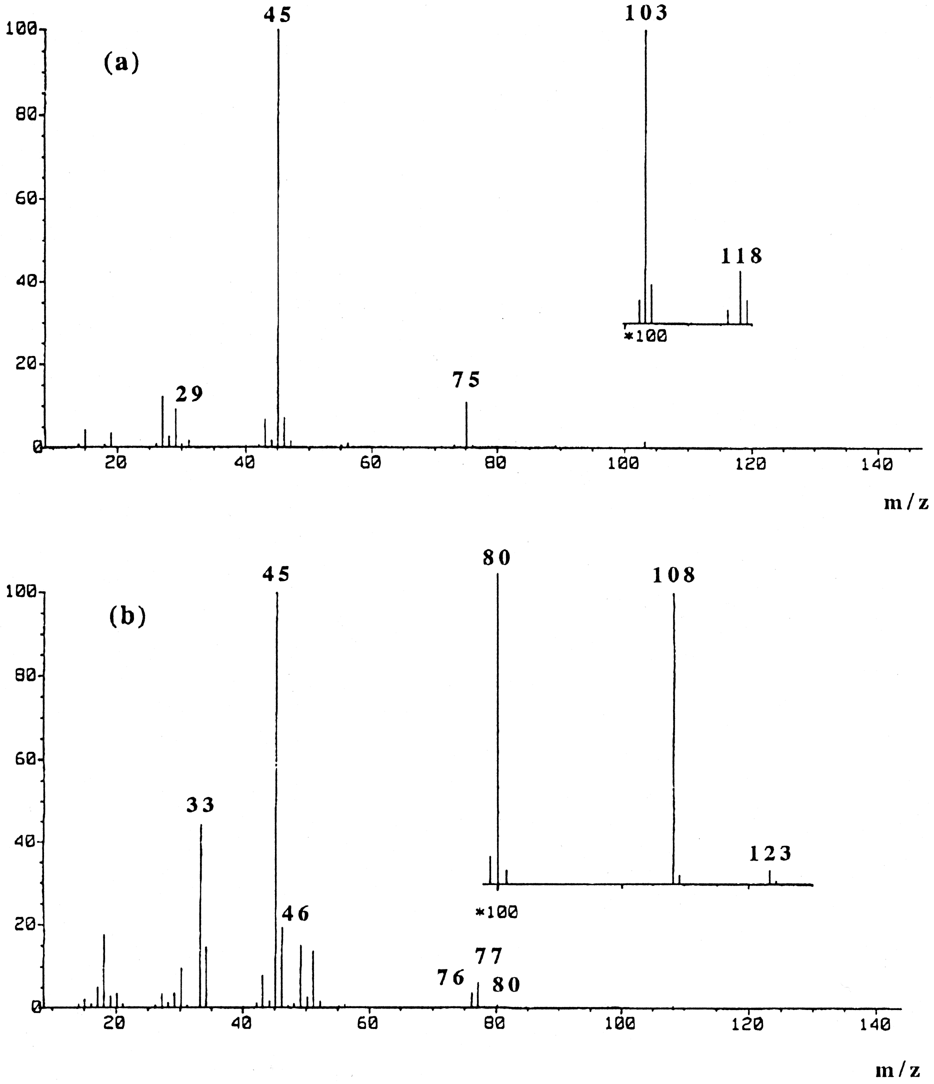


Fig. 1. Standard mass spectra of (a) **1**, ethyl lactate, and (b) **1**-d_5, pentadeuteroethyl lactate.

spectrum shifts to *m/z* 76 in the latter spectrum. This means that the neutral 28 Da species lost from the ion *m/z* 103 from $\mathbf{1}^{+\cdot}$ is ethylene and not CO. The fragmentation of the *m/z* 103 ion, $CH^+(OH)COOCH_2CH_3$, to give the *m/z* 75 ion could well occur by means of a proton-bridged intermediate [3–6], which is in agreement with the D-labeling results and which would yield the protonated glyoxylic acid species $CH^+(OH)COOH$ at *m/z* 75. This suggestion is further supported by the following observation.

The ions *m/z* 75 [$CH^+(OH)COOH$] generated by the loss of $CF_3^{\cdot}$ from $\mathbf{5}^{+\cdot}$ decompose in the metastable time window only into the ions *m/z* 19 (H_3O^+). This fragmentation is very similar, if not identical, to that of the d_1-labeled *m/z* 76 ion from $\mathbf{1}\text{-}d_5^{+\cdot}$ (see Table 2). In mechanistic terms the formation of the *m/z* 75 ions in the protonated glyoxylic acid structure from $\mathbf{1}^{+\cdot}$ and their decomposition to *m/z* 19 ions have been rationalized in Scheme 2. Rapid decomposition of ethylenedione, O=C=C=O, into two CO molecules has been reported by Schwarz and co-workers [7,8].

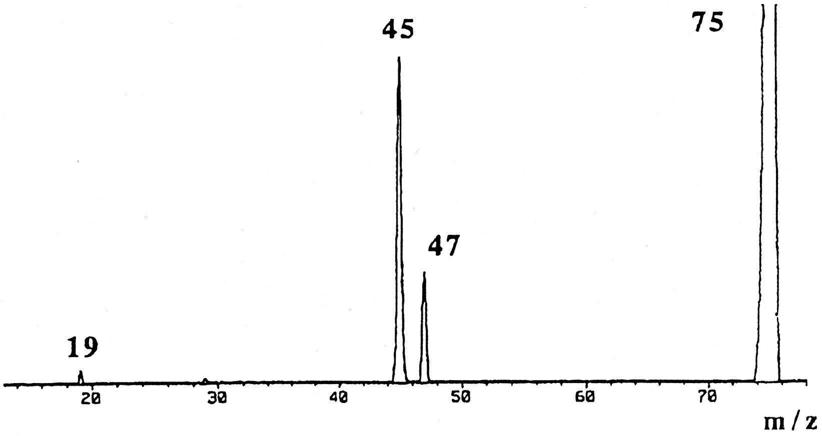
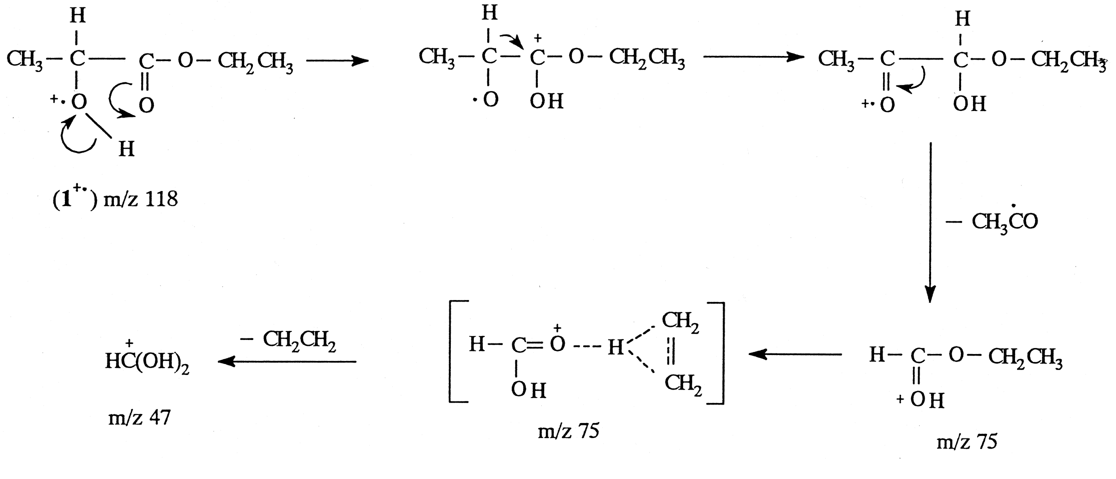


Fig. 2. MIKE spectrum of the ion *m/z* 75 from $\mathbf{1}^{+\cdot}$.

Information on the third isomeric ion *m/z* 75 is provided by the MIKE spectrum of the *m/z* 77 ions which are generated by the successive elimination of $CD_3^{\cdot}$ and CO from $\mathbf{1}$-$d_5^{+\cdot}$ and which contain two D atoms. This spectrum, shown in Table 2, indicates that the *m/z* 77 ions eliminate the neutral 32 Da species CD_2O to give the ions *m/z* 45. According to the D-labeling results, the unlabeled analogous *m/z* 75 ions should thus have the $CH_3CH(OH)O^+{=}CH_2$ structure and their fragment *m/z* 45 ions the protonated acetaldehyde structure. The latter is confirmed by the MIKE spectra of the *m/z* 45 ions from $\mathbf{1}^{+\cdot}$ and the $CH_3CH^+(OH)$ ions generated by the loss of $CH_3^{\cdot}$ from the molecular ions of 2-propanol [$(CH_3)_2CHOH$, MW

Table 1
MIKE spectra of the ions *m/z* 75 generated by (a) the losses of $H^{\cdot}$ and C_2H_4 from $\mathbf{2}^{+\cdot}$, (b) the loss of $CF_3^{\cdot}$ from $\mathbf{3}^{+\cdot}$, and (c) CI of **4**

	Fragment ion abundance at *m/z*		
Precursor ion	19	45	47
(a) $CH^+(OH)COOH$	0%	0%	100%
(b) $CH^+(OH)COOH$	0%	0%	100%
(c) $CH^+(OH)COOH$	0%	0%	100%



Scheme 1. Proposed mechanism for the formation and decomposition of the ions *m/z* 75 in the protonated ethyl formate structure generated from $\mathbf{1}^{+\cdot}$.

Table 2
MIKE spectra of the ions *m/z* 80, 77, and 76 from **1**-$d_5^{+\cdot}$

m/z of precursor ion	Fragment ion abundance at *m/z*		
	20	45	48
(a) 80	0%	0%	100%
(b) 77	0%	100%	0%
(c) 76	100%	0%	0%

60] [2] which show similar peak patterns (and peak intensity ratios) at *m/z* 29, 27, and 19.

The proposed mechanism for the formation and decomposition of these last-discussed ions *m/z* 75 from **1**$^{+\cdot}$ is rationalized and depicted in Scheme 3.

4. Conclusion

The conclusion in the previous article, that the *m/z* 75 ions from **1**$^{+\cdot}$ are only protonated ethyl formate, is not correct. The population of *m/z* 75 ions from **1**$^{+\cdot}$ consists of at least three different ionic species, which are $CH^+(OH)OCH_2CH_3$ (protonated ethyl formate), $CH_3CH(OH)O^+{=}CH_2$ and $CH^+(OH)COOH$ (protonated glyoxylic acid). The first ion decomposes into the *m/z* 47 ion by the loss of ethylene, the second ion decomposes into the ion *m/z* 45 by the loss of formaldehyde and the third ion decomposes to give the *m/z* 19 ion by the spontaneous loss of two CO molecules.

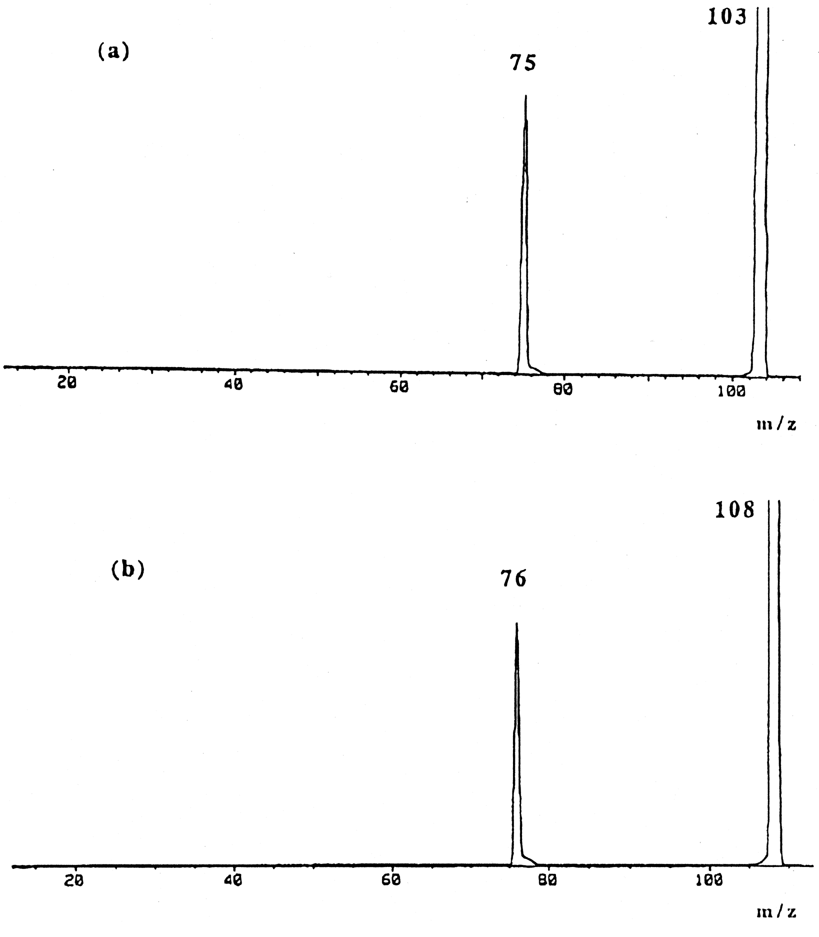
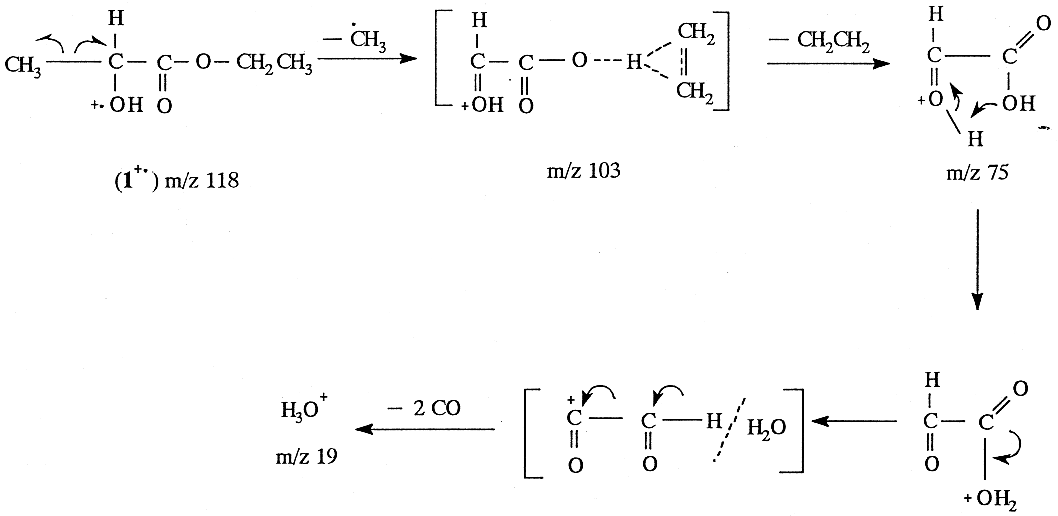
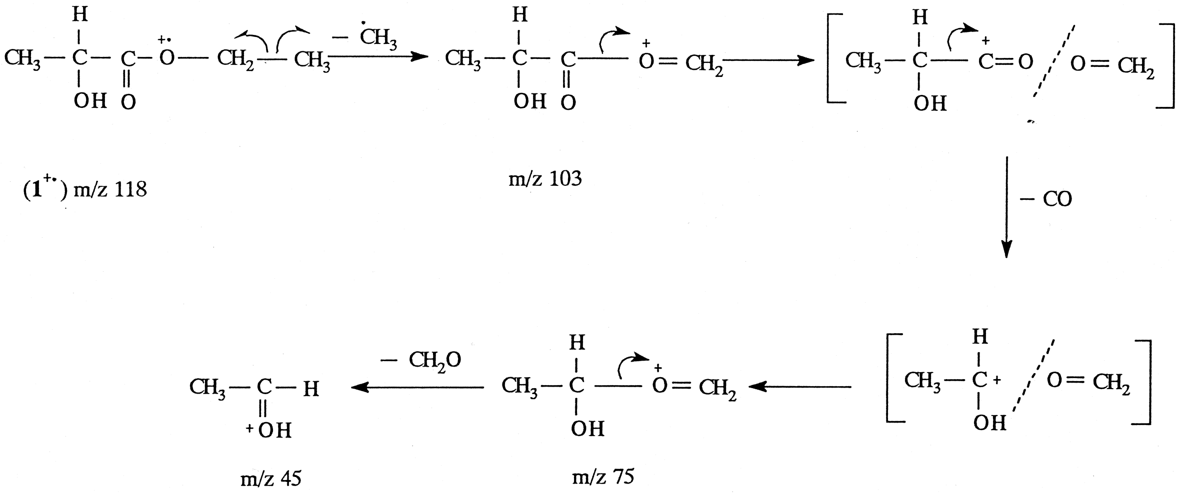


Fig. 3. MIKE spectra of (a) the *m/z* 103 ion from **1**$^{+\cdot}$ and (b) the *m/z* 108 ion from **1**-$d_5^{+\cdot}$.



Scheme 2. Proposed mechanism for the formation and decomposition of the ions *m/z* 75 in the protonated glyoxylic acid structure generated from $\mathbf{1}^{+\cdot}$.



Scheme 3. Proposed mechanism for the formation and decomposition of the ions *m/z* 75 generated by the successive loss of methyl from the ester group and carbon monoxide from $\mathbf{1}^{+\cdot}$.

References

[1] Y. Takahashi, T. Higuchi, O. Sekiguchi, M. Hoshino, S. Tajima, Int. J. Mass Spectrom. 181 (1998) 89.

[2] S. Tajima, Y. Nagai, O. Sekiguchi, M. Fujishige, N. Uchida, J. Am. Soc. Mass Spectrom. 6 (1995) 202.

[3] K. Levsen, Fundamental Aspects of Organic Mass Spectrometry, Verlag Chemie, Weinheim, 1978, p. 159.

[4] R.D. Bowen, Org. Mass Spectrom. 28 (1993) 1577.

[5] C.E. Hudson, D.J. McAdoo, J. Am. Soc. Mass Spectrom. 9 (1998) 138.

[6] S. Tajima, A. Fujizuka, S. Nakajima, Y. Takahashi, O. Sekiguchi, Rapid Commun. Mass Spectrom. 14 (2000) 1195.

[7] D. Sülzle, T. Weiske, H. Schwarz, Int. J. Mass Spectrom. Ion Processes 125 (1993) 75.

[8] D. Schroeder, C. Heinemann, H. Schwarz, J.N. Harvey, S. Dua, S.J. Blanksby, J.H. Bowie, Chem. Eur. J. 4 (1998) 2550.