Fragmentation of the Metastable Molecular Ion of Methyl Lactate: The Formation of Oxygen-Protonated Methanol $[\text{CH}_3\text{OH}_2]^+$ Involving Double Hydrogen Atom Transfers

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The spontaneous unimolecular dissociation reaction of methyl lactate (**1**) ionized by electron impact was investigated by a combination of mass-analyzed ion kinetic energy spectrometry and deuterium labeling. The metastable ions $1^{+\bullet}$ decompose in a variety of ways: four fragment peaks are observed at m/z 89, 76, 61, and 45, which correspond to the losses of CH_3 , CO , $\text{CH}_3\dot{\text{C}}\text{O}$, and COOCH_3 , respectively. Double hydrogen atom transfer occurs in the third reaction.

The source-generated m/z 61 ions decompose into oxygen-protonated methanols at m/z 33 ($[\text{CH}_3\text{OH}_2]^+$) by the loss of CO with double hydrogen atom migration. Both hydroxyl and methyne hydrogen atoms in $1^{+\bullet}$ are present in the resultant protonated methanols. (*J Am Soc Mass Spectrom* 1995, 6, 202–206)

Information about the mechanism of double hydrogen atom transfer 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 [1–7]. Double hydrogen atom transfer is also observed during the fragmentations of the molecular ions of isobutanol [8–11], 1,2-ethanediol [12–14], and hydroxyacetone [15, 16]. In the mass spectra of isobutanol and 1,2-ethanediol, a fairly intense oxygen-protonated methanol ($[\text{CH}_3\text{OH}_2]^+$; m/z 33) is generated by double hydrogen atom transfers. The sizable m/z 33 ion also is observed in the mass spectrum of methyl glycolate [12a, 14]. The mechanism of these hydrogen migrations has been explained by an ingenious idea, namely, ion–neutral complexes [12, 17–20].

Recently, we have noticed that the ion at m/z 33 also is observed in the mass spectrum of methyl lactate (**1**), which exhibits an interesting hydrogen atom rearrangement. Tsuchiya and Adachi [21] have measured the kinetic energy mass spectrum of **1** and Tal'rose and co-workers [22] have examined the ion–molecule reaction of $1^{+\bullet}$ with diisopropyl tartrate. However, little is known about the fragmentation of $1^{+\bullet}$.

In this work, we investigate the fragmentation processes of $1^{+\bullet}$, with attention to the formation of CH_3OH_2^+ (m/z 33), by a combination of mass-analyzed ion kinetic energy (MIKE) spectrometry and deuterium labeling.

Experimental

The mass and MIKE spectra were obtained with a Hitachi M-80A double focusing mass spectrometer and a modified Hitachi RMU-7M instrument of reversed geometry, respectively.

The sample **1**, obtained from Tokyo Kasei Kogyo, was reagent grade and was used without further purification.

The D-labeled isomer $\text{CH}_3\text{CH}(\text{OD})\text{COOCH}_3$ (**1-d₁**) was obtained by repeated exchange of **1** with D_2O . $\text{CH}_3\text{CH}(\text{OH})\text{COOCD}_3$ (**1-d₃**) was prepared by esterifying lactic acid with CD_3OD . $\text{CH}_3\text{CD}(\text{OH})\text{COOCH}_3$ (**1-d₁**) was obtained by partial reduction of methyl pyruvate ($\text{CH}_3\text{COCOOCH}_3$) with NaBD_4 .

Results and Discussion

Fragmentation of Molecular Ion

Figure 1 shows the mass spectra of **1**, **1-d₃**, and **1-d₁**.

The molecular ion of **1** is very weak, similar to that of methyl glycolate, which is one of its lower homologs

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Figure 1. 70-eV electron ionization mass spectra of (a) 1, (b) $1-d_3$, and (c) $1-d_1$.

[12b, 14, 23]. The MIKE spectrum of this ion, however, shows two narrow peaks at m/z 61 and 45 in addition to the relatively broad peaks at m/z 89 and 76, as shown in Figure 2a. As will be described, these peaks correspond to the losses of $\dot{C}_2H_3O$, $\dot{C}_2H_3O_2$, $\dot{CH}_3$, and CO, respectively. The MIKE spectra of $1-d_3^{+}$ (m/z 107) and $1-O-d_1^{+}$ (m/z 105) are also given in Figure 2, but that of $1-d_1^{+}$ is not shown because the spectrum was nearly the same as that of $1-O-d_1^{+}$.

The ions at m/z 89 and 45 stay at the same mass, whereas the ions at m/z 76 and 61 shift to m/z 79 and 64 in the MIKE spectrum of $1-d_3$ (Figure 2b). These results indicate that the latter two ions contain the methyl group of the ester function and that the former two ions do not contain this methyl. In other words, the m/z 89 ion is generated by the loss of the methyl group of the ester function, not the other methyl.

Figure 2. MIKE spectra of the molecular ions of (a) 1 (m/z 104), (b) $1-d_3$ (m/z 107), and (c) $1-O-d_1$ (m/z 105).

A broad metastable peak [a large kinetic energy release (KER)] is observed for the loss of $\dot{CH}_3$ from the methoxy group. This is similar to the case of the loss of $\dot{CH}_3$ from the metastable molecular ions of tetramethoxysilane [24]. The m/z 89 ion in Figure 1a, however, shifts to m/z 92 in the source spectrum of $1-d_3$ (Figure 1b), which indicates that the source-generated m/z 89 ion is formed by the loss of the lactic acid methyl group. This observation demonstrates that the methyl loss from the ester function is favored in the molecular ions of 1 with a low internal energy, whereas in the ions with a high energy, the other methyl loss is favored. The former reaction, which includes the cleavage of the oxygen-carbon bond, is, in general, a disfavored reaction, and is accompanied by a large KER [25]. This metastable $\dot{CH}_3$ loss would be initiated from the ion that possesses the formal positive charge on the oxygen atom of the methoxy group [pathway (a) in Scheme II] [24, 25]. On the other

Scheme I. Proposed mechanisms for CHO loss from the molecular ion of methyl glycolate.

hand, the high energy $\dot{\text{C}}\text{H}_3$ loss occurs by α -cleavage at the ionized hydroxyl group [pathway (b) in Scheme II].

The ions in the MIKE spectrum of **1** (Figure 2a) shift to m/z 90, 77, 62, and 46 in the spectrum of **1-O-d₁** (Fig. 2c), which indicates that all of these ions contain the hydroxyl hydrogen.

The foregoing results lead to the conclusion that the ion at m/z 76 is generated by the loss of CO, not C₂H₄, from **1**⁺. According to Grützmacher and Masur [20], this fragmentation will be initiated at the ions in which the formal positive charge resides on the oxygen atom of the carbonyl group, and may be explained by proposing involvement of an ion-neutral complex [pathway (d) in Scheme II] [12, 17-20].

As shown in Figure 2c, the ion at m/z 61 for **1** shifts to m/z 62 for **1-O-d₁**⁺. This result indicates that one hydrogen atom in the m/z 62 ion generated from **1-O-d₁**⁺ comes from the hydroxyl group. Furthermore, it is concluded that another hydrogen atom in the m/z 61 ion generated from **1**⁺ comes from the methyne group, because this ion shifted to m/z 62 in the MIKE spectrum of **1-d₁**⁺ (not shown for the reason as described previously). Thus, the ion at m/z 61 is generated by the loss of CH₃CO from **1**⁺ that accompanies the transfer of both hydroxyl and methyne hydrogen atoms [pathway (e) in Scheme II]. According to Schwarz and co-workers [26], the resulting m/z 61 product ions will be the carbonyl oxygen-protonated methyl formate.

The relative abundance of the ions at m/z 62 versus m/z 46 in Figure 2c is lower than those in Figure 2a and b. This is reasonably explained in terms of a primary isotope effect. The value of $k_{\text{H}}/k_{\text{D}} = 2.2$ was estimated from the relative abundance of the ions in Figure 2a and c. This value is consistent with the known value [27].

Goulden and Manning [23] have suggested two possible mechanisms (Scheme I) for the elimination of CHO from the molecular ions of methyl glycolate to yield the C₂H₅O₂⁺ ion at m/z 61. However, they have described nothing about the decomposition of the m/z 61 ion. Schwarz and co-workers [12a] also have reported the elimination of CHO from the molecular ion of methyl glycolate. To elucidate these mecha-

Scheme II. Plausible fragmentation pathways of **1**⁺.

Figure 3. MIKE spectrum of the $[C_2H_5O]^+$ (m/z 45) ion generated from 1^+ .

nisms, it is necessary to examine the fragmentation of the ^{13}C - or ^{18}O -labeled isomers.

In the case of 1^+ , the loss of $CH_3\dot{C}O$ is preferred to that of CHO (Figures 1a and 2a). This result indicates that the loss of $CH_3\dot{C}O$ from the molecular ion of **1** occurs by a reaction analogous to process (a) in Scheme I [pathway (e) in Scheme II]. This means that in this case the original carbonyl group is not included in the eliminated $CH_3\dot{C}O$.

Fragmentation of the Metastable Ion at m/z 45

The MIKE spectrum of the source-generated m/z 45 ion $[C_2H_5O]^+$ is shown in Figure 3. This spectrum is very similar to that of the m/z 45 ion generated by the loss of $\dot{C}H_3$ from the molecular ion of isopropanol (not shown). Consequently, we conclude that the m/z 45 ion is generated by α -cleavage relative to the hydroxyl group of 1^+ . The three peaks at m/z 29, 27, and 19 correspond to the competitive losses of CH_4 , H_2O and C_2H_2 , respectively [pathway (c) in Scheme II] [28].

Fragmentation of the Metastable Ion at m/z 61 to the Ion at m/z 33 ($CH_3OH_2^+$)

As shown in Figure 4a, the m/z 33 ion is formed by the loss of 28 u from the source-generated m/z 61 ion. The MIKE spectra of the ions at m/z 64 from $1-d_3^+$ and m/z 62 from $1-O-d_1^+$ are also shown in Figure 4. The spectrum of the m/z 62 from $1-d_1^+$ is not shown because it was similar to that of the ion at m/z 62 from $1-O-d_1^+$ (Figure 4c).

The ion at m/z 33 in Figure 4a shifts to m/z 36 and 34 in Figure 4b and c, respectively. These results lead to the conclusion that the m/z 33 ion is generated by the loss of CO , not C_2H_4 , from the m/z 61 ion. That is, the elemental composition of the ion at m/z 33 is CH_5O^+ . This reaction was accompanied by double hydrogen atom migration, too.

Although the peaks that correspond to the loss of H_2O from the protonated methyl formate ion are very low in Figure 4a and c, the MIKE spectrum of m/z 64

Figure 4. MIKE spectra of (a) the m/z 61 ion from 1^+ ; (b) the m/z 64 ion from $1-d_3^+$; and (c) the m/z 62 ion from $1-O-d_1^+$.

displays a peak at m/z 46 as shown in Figure 4b. Differences in intensity are attributable to isotope effects [27]. This reaction also occurs in the ion source (see Figure 1b).

Plausible dissociation pathways of 1^+ as deduced from the foregoing results are given in Scheme II.

Conclusions

Metastable molecular ions of methyl lactate (1^+) decompose into ions at m/z 89, 76, 61, and 45 by the losses of $\dot{C}H_3$, CO , $CH_3\dot{C}O$, and $\dot{C}OOCH_3$, respectively. The m/z 61 ion (protonated methyl formate) is generated by double hydrogen atom transfer. This m/z 61 ion decomposes into oxygen-protonated methanol (m/z 33) by loss of CO , again accompanied by double hydrogen atom migration.

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