Fragmentation of Organosulfur Compounds upon Electron Impact. II. Metastable Decomposition of Methyl and Ethyl Thiolactates

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The unimolecular decomposition of the molecular ions of methyl thiolactate (1) and ethyl thiolactate (2) upon electron impact was investigated. The metastable fragmentation of 1^{+} is dominated by the loss of methanol. The molecular ions 2^{+} decompose in a variety of ways: the loss of water, the loss of ethylene, as well as the loss of ethanol are prominent. Both methyl and ethyl thiolactates do not show the fragmentation with double hydrogen transfer, which is observed in methyl lactate (3) and ethyl lactate (4).

1. Introduction

Fragmentations of some esters of α -hydroxycarboxylic acids have been investigated.¹⁻⁶⁾ Methyl glycolate shows an interesting fragmentation in which double hydrogen transfer plays an important role to produce $[\text{C}_2\text{H}_5\text{O}_2]^+$.^{1), 6)} Methyl lactate (3) also decomposes with double hydrogen transfer to produce $[\text{C}_2\text{H}_5\text{O}_2]^+$, which further decomposes into protonated methanol with double hydrogen transfer.⁵⁾

A fragmentation with double hydrogen transfer is also observed in the molecular ions of 1,2-ethanediol in the metastable time region.^{3), 4), 7-11)} Recently, we have investigated the fragmentation mechanism of sulfur analogs of 1,2-ethanediol, *i.e.*, 2-mercaptoethanol and 1,2-ethanedithiol, upon electron impact.¹²⁾ Although these sulfur compounds produced protonated methanethiol with double hydrogen transfer in the ion source, it was not observed in the metastable time region. Further the abundance of protonated methanethiol in the mass spectra of these sulfur compounds was rather low compared with that of protonated methanol in the case of 1,2-ethanediol. In addition, completely different fragmentation pathways to the case of 1,2-ethanediol were found in the case of these sulfur compounds.

Thus the substitution of oxygen with sulfur severely affects the fragmentation mechanism. This kind of information serves for understanding the principle of the fragmentation reaction. In this context, we have studied the fragmentation of esters of α -mercaptocarboxylic acids. Detailed study on the fragmentation of this type of organosulfur compounds is rather scarce.¹³⁾ In this paper, we report the metastable fragmentation of the molecular ions of methyl thiolactate (1) and ethyl thiolactate (2). The results are compared with those of the corresponding oxygen analogs, *i.e.*, methyl lactate (3) and ethyl lactate (4). Particular attention is paid to the fragmentations with double hydrogen transfer observed in 3⁵⁾ and 4.¹⁴⁾

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2. Experimental

The mass spectra and the B/E linked scan spectra were measured with a Hitachi M-80B double focusing mass spectrometer, and the mass analyzed ion kinetic energy (MIKE) spectra were obtained with a modified Hitachi RMU-7M instrument of reversed geometry.

The samples used are shown below.

(1)

(1-*d*₁) (1-*d*₃) (1-*d*₄)

(2)

(2-*d*₁) (2-*d*₅) (2-*d*₆)

(3)

(4)

All the compounds except for 3 and 4 were synthesized in our laboratory by esterifying thiolactic acid (from Tokyo Kasei Kogyo) with appropriate alcohols. The S-deuterated and O-deuterated compounds were obtained by repeated H-D exchange of the original esters with D₂O.

3. Results and Discussion

3.1 Methyl thiolactate

In the mass spectra of 1, the base peak is located at *m/z* 61 (CH₃CHSH⁺, vide infra). Other prominent peaks appear at *m/z* 120 (M⁺, P. C. 34.9) and 88 (P. C. 18.0) due to methanol loss, as described below.

Figure 1 shows the MIKE spectra of the molecular ions of 1, 1-*d*₁, 1-*d*₃, and 1-*d*₄. In the metastable time region, the molecular ions of 1 decompose mainly into the *m/z* 88 ion. On substituting the mercapt hydrogen atom with deuterium, the corresponding peak splits into two peaks at *m/z* 89 and 88 with an intensity ratio of 1:1.3. The molecular ions of methyl-*d*₃ thiolactate (1-*d*₃⁺) eliminate the species with the 35 mass unit to produce *m/z* 88 ions. From these results, the species lost in these reactions can be assigned to methanol molecule. In the case of 1-*d*₁⁺, both peaks due to the loss of

Fig. 1. MIKE spectra of the molecular ions of (a) 1, (b) 1- d_1 , (c) 1- d_3 , and (d) 1- d_4 , respectively.

CD_3OH and CD_3OD are observed with an intensity ratio of 1 : 1.2. These observations indicate that the hydroxy hydrogen in the methanol lost originates both from the mercapto hydrogen and the other hydrogen in the mercaptoethyl group. The following two mechanisms are able to explain the observation: (a) The hydrogen randomization in the mercaptoethyl group occurs prior to methanol loss. (b) The loss of methanol occurs through the extraction not only of the mercapto hydrogen but also of the other hydrogen atom in the mercaptoethyl group, *i.e.*, two or more different fragmentation pathways exist. Unfortunately, we cannot obtain any evidence which, such as that observed in the case of esters of thioglycolate,¹⁴ can deduce either the mechanism (a) or (b) is the case.

In Fig. 1(a), besides the peak at m/z 88, very weak peaks at m/z 92, 61, and 60 are observed, and these are owing to CO loss, COOCH_3 loss (*vide infra*), and HCOOCH_3 loss, respectively. In the mass spectrum of 1, the peak at m/z 61 is the base peak, as

Fig. 2. B/E linked scan spectrum of the m/z 61 ion from **1**.

mentioned above. The peak at m/z 61 in Fig. 1(a) arises our interest. In the case of **3**, the molecular ions decompose metastably into ions with m/z 89, 76, 61, and 45. The ions with m/z 61 in **3** is produced through CH_3CO loss with double hydrogen transfer.⁵⁾ If CH_3CS elimination with double hydrogen transfer occurs in **1**, the peak at m/z 61 will be observed. However, the peaks at m/z 61 in the mass spectrum and in Fig. 1 remain at the same m/z value on substituting hydrogen atoms in the methoxy group with deuterium. This indicates that the ion with m/z 61 in Fig. 1(a) is produced by the loss of the methoxycarbonyl group. Figure 2 shows the B/E linked scan spectrum of the m/z 61 ion from **1**. This spectrum shows that the m/z 61 ion decomposes into the m/z 35 ion corresponding to H_3S^+ (C_2H_2 loss). Thus the m/z 61 ion contains sulfur, and is not produced through CH_3CS loss. This fragmentation of the m/z 61 ion from **1**⁺ is different from that of the corresponding ion (m/z 45) from **3**⁺, except for the loss of C_2H_2 . In the latter case, the m/z 45 ion, produced by the loss of methoxycarbonyl group, decomposes into the ions at m/z 29 (CH_4 loss), 27 (H_2O loss), and 19 (C_2H_2 loss).⁵⁾ In conclusion, the fragmentation with the double hydrogen transfer observed in **3**⁺ is not observed in **1**⁺.

3.2 Ethyl thiolactate

The mass spectrum of **2** is similar to that of **1**: the base peak at m/z 61 (CH_3CHSH^+) is produced through the C–C bond fission as in the case of **1**, and other prominent peaks appear at m/z 134 (M^+ , P. C. 32.6) and 88 (P. C. 22.9) due to ethanol loss.

Figure 3 shows the MIKE spectra of the molecular ions of **2**, **2**- d_1 , **2**- d_5 , and **2**- d_6 . The molecular ion of **2** decomposes metastably in a variety of ways to produce fragment ions of m/z 116, 106, 88, 74, 61, and 60.

The peak at m/z 116 will correspond to water loss. We have also observed that the water loss from ethyl thioglycolate takes place in a similar fashion to, say, ethyl acetate.¹⁴⁾ However, the water loss from **2** is not the same as that in ethyl thioglycolate or ethyl acetate. In general, both the hydrogen atoms participating in the water loss from ethyl esters originate from the ethoxycarbonyl group,¹⁵⁾ if the hydrogen randomization does not occur prior to water loss. Thus the water lost from ordinary ethyl- d_5 esters will be D_2O . In this case of ethyl- d_5 thiolactate (**2**- d_5), however, the water lost is

Fig. 3. MIKE spectra of the molecular ions of (a) 2, (b) 2- d_1 , (c) 2- d_5 , and (d) 2- d_6 , respectively.

mainly H_2O , as seen from Fig. 3(c). The contribution of DHO and D_2O is very small, if any. This cannot be rationalized with the general mechanism of water loss from the ethoxycarbonyl group, even invoking hydrogen randomization.¹⁵⁾ Even if all the hydrogen atoms in 2- d_5^+ is randomized completely, the probability for the loss of DHO is more than twice larger than that of H_2O , with ignoring isotope effects. Hence we must conclude that the hydrogen atoms in the water loss from 2 originate not from the ethoxycarbonyl group but from the mercaptoethyl group. In the case of 2- d_1^+ and 2- d_6^+ , the peak due to the loss of HDO is more intense than that due to the loss of H_2O . Hence the mercaptohydrogen is more likely involved in the water lost than the other hydrogen atoms in the mercaptoethyl group.

As shown in Fig. 3, the peak at m/z 106 in Fig. 3(a) shifts to 107 in Figs. 3(b) and 3(c) and to 108 in Fig. 3(d). These results indicate that the fragmentation is owing to the loss of ethylene: 2 $^{+}$ and 2- d_1^+ lose C_2H_4 , whereas 2- d_5^+ and 2- d_6^+ lose C_2D_4 . This fragmentation is the most prominent pathway of the metastable molecular ions of 2, and is common to usual ethyl esters. This occurs through a McLafferty rearrangement in the ethoxycarbonyl group. Further, it can be concluded that any hydrogen randomization does not occur prior to ethylene loss.

The peak at m/z 88 in 2 $^{+}$ retains the same m/z in 2- d_5^+ , so this peak corresponds to

Fig. 4. MIKE spectrum of the m/z 74 ion from **2**.

the loss of ethanol. Ethanol loss in **2** will be, in principle, similar to methanol loss in **1**. As can be seen from Fig. 3, $2^{+\cdot}$ gives rise to the peak at m/z 88, and this peak splits into two peaks at m/z 89 and 88 (with an intensity ratio of 1.0 : 1.7) on substituting the mercapto hydrogen with deuterium, as in the case of **1**. Similarly, the peak at m/z 88 of $2-d_s^{+\cdot}$ splits into two peaks at m/z 89 and 88 with an intensity ratio of 1.0 : 1.4 in $2-d_s^{+\cdot}$. These observations are rationalized with two plausible mechanisms as in the case of **1**. In this case also, we cannot conclude which mechanism is the case.

Figure 3(a) also shows a peak at m/z 74. This fragmentation is unique to **2**, and is owing to the loss of C_2H_4S , $C_2H_4O_2$, or C_3H_8O . Although the intensity of the peak at m/z 74 in the normal mass spectrum is fairly weak, we can measure the MIKE spectrum of the m/z 74 ion, and is shown in Fig. 4. In the MIKE spectrum, the peak at m/z 56 due to the ion produced by the loss of water is observed. Thus the m/z 74 ion must contain oxygen atom. Hence the loss of $C_2H_4O_2$ can be ruled out. In Fig. 3(d), the corresponding peak appears at m/z 76, although the intensity is very weak. If this fragmentation is owing to the loss of methyl ethyl ether, not only the loss of $C_3D_4H_4O$ giving rise to the peak at m/z 76 but also the loss of $C_3D_5H_3O$ giving rise to the peak at m/z 75 must be observed. However only the peak at m/z 76 is observed in Fig. 3(d). This means that the neutral species lost from $2^{+\cdot}$ is C_2H_4S , and the C_2H_4 moiety in it originates from the ethoxy group, although such a fragmentation pathway seems to be entropically unfavorable.

The peaks at m/z 61 and 60 in Fig. 3(a) are similar to those in **1**, and correspond to the losses of $\dot{C}OOC_2H_5$ and $HCOOC_2H_5$, respectively.

3.3 Comparison with lactates

Fragmentation of the metastable molecular ions of methyl lactate has been reported.⁵⁾ Although the loss of CO and the loss of $\dot{C}OOCH_3$ are observed both from the molecular ions of **1** and **3**, the contribution of these fragmentations in **1** is negligibly small. Thus we can conclude that the molecular ions of **1** and **3** decompose in completely different ways. In particular, the fragmentation involving double hydrogen transfer observed in **3** is not observed in **1**.

Detailed study on the metastable decomposition of the molecular ion of **4** will be reported elsewhere.¹⁴⁾ The molecular ion of **4** decomposes mainly into ions with m/z 90, 89, 75, and 45, which are due to the losses of CO, $\dot{C}_2H_5$, $CH_3\dot{C}O$, and $\dot{C}OOC_2H_5$, respectively. The loss of $CH_3\dot{C}O$ involves double hydrogen transfer, and is akin to the case of **3**. On

Table 1. The Bond Order and the Bond Length of the Central C-C Bond Calculated with PM3 Method

		Bond order	Bond length/ 10^{-10}m
Methyl thiolactate	(1 ⁺ ·)	0.90	1.54
Ethyl thiolactate	(2 ⁺ ·)	0.89	1.54
Methyl lactate	(3 ⁺ ·)	0.014	2.46
Ethyl lactate	(4 ⁺ ·)	0.0013	3.33

the other hand, the molecular ions of **2** decompose into ions due to the losses of H_2O , C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_4\text{S}$, $\dot{\text{C}}\text{OOC}_2\text{H}_5$, and HCOOC_2H_5 . Although the losses of C_2H_4 and $\dot{\text{C}}\text{OOC}_2\text{H}_5$ are common processes, the fragmentation of the molecular ions of **2** and **4** is fairly different as a whole. As in the case of methyl esters, the fragmentation with double hydrogen transfer is observed in **4**, but not observed in **2**.

One of the reason why the loss of $\text{CH}_3\dot{\text{C}}\text{S}$ with double hydrogen transfer is not observed in **1** and **2** is as follows. We proposed an ion-neutral complex as an intermediate of the fragmentation with double hydrogen transfer from $3^{+\cdot}$.⁵⁾ We consider that the corresponding ion-neutral complex in **1** and **2** is hard to be formed. In order that an ion-neutral complex is formed, the internal energy of the incipient ion must be rather low,¹⁶⁾ and yet a bond in the incipient ion must be cleaved. Our preliminary MO calculations with PM3 method showed that the strength of the C-C bond between the hydroxyethyl group and the methoxy- or ethoxycarbonyl group is very weak in the molecular ions of **3** and **4**. Table 1 shows the bond orders and the bond lengths of the center C-C bonds calculated with PM3. Table 1 shows that in the molecular ions of **3** and **4**, the C-C bond is almost cleaved. The MO calculation is made for the ground state (with no excess energy) of the molecular ions. On the other hand, the C-C bonds between the mercaptoethyl group and the methoxy- or ethoxycarbonyl group in the molecular ions of **1** and **2** are not weak, as shown in Table 1. Thus in order to break the C-C bond in $1^{+\cdot}$ and $2^{+\cdot}$, the internal energy of the molecular ion must be high. Under these conditions, the intermediate such as an ion-neutral complex is exerted no barrier to decomposition, and the ion-neutral complex cannot exist stably. Hence the double hydrogen transfer *via* the ion-neutral complex is not observed in **1** and **2**. In our results of the MO calculation, for almost all the molecular ions which show the fragmentation with double hydrogen transfer similar to the case of **3**, the C-C bond concerned is weak.

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Keywords

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