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Routes of Formation and Decomposition of the *m*/*z* 59 Ions with Elemental Composition C_3H_7O Generated upon Electron Impact Ionization of Methyl Propanoate

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It is shown that the peaks at *m*/*z* 31, 29 and 15 in the mass-analyzed ion kinetic energy spectrum of the *m*/*z* 59 ions generated from methyl propanoate upon electron impact ionization originate from decompositions of *m*/*z* 59, i.e. $C_2H_3O_2{}^+$ ions having the $O{=}C{=}O^+CH_3$ structure, and of *m*/*z* 59, i.e. $C_3H_7O^+$ ions having the $CH_3CH{=}O^+CH_3$ structure. The latter ions contribute <1% to the total abundance of the *m*/*z* 59 ions in the standard mass spectrum. However, these *m*/*z* 59 $C_3H_7O^+$ ions are responsible for the relatively significant amounts of the *m*/*z* 31 and 29 ions generated in the microsecond time frame. Based upon deuterium labelling and supported by calculations at the ROHF/6–31G* level of theory, the *m*/*z* 59 $C_3H_7O^+$ ions are suggested to be formed via a complex skeletal rearrangement of the molecular ions of methyl propanoate and subsequent loss of a formyl radical. © 1997 by John Wiley & Sons Ltd.

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INTRODUCTION

It is well known that usually a rich chemistry takes place upon electron impact ionization (EI) of gas-phase molecules in a mass spectrometer. One of the molecules which for various reasons has been studied repeatedly is methyl propanoate, $CH_3CH_2COOCH_3$ (**1**). Its molecular ion loses a methoxy radical, as shown by collision induced dissociation ionization (CIDI) experiments,[1] leading to the formation of the propanoyl cation. This cation has been established to be a structurally distinct species,[2] has served as a reference ion in CID studies[3,4] and has been studied by use of photoionization mass spectrometry to obtain its heat of formation.[5]

Other EI studies of **1** have shown that the oxygen atoms in the molecular ion retain their identity[6] and have provided the heat of formation of its $[M - \dot{C}_2H_5]^+$ ion, that is, $COOCH_3{}^+$.[7]

MNDO calculations more than a decade ago were carried out[8] on a possible 1,2-$CH_3OC(O)H$ migration in the distonic ion of **1**, that is, $^{\bullet}CH_2CH_2C(OH)OCH_3{}^+$, which has been found to be more stable than its conventional isomer.[8] CID studies of protonated **1** with the use of a triple-quadrupole mass spectrometer have also been reported.[9]

More recently, it has been shown that the long-lived molecular ions of **1** isomerize from the keto to the more stable enol form via two different pathways, being initiated by a 1,4-H shift of a methyl hydrogen from both the alcohol moiety and the acid moiety to the carbonyl oxygen atom.[10]

EXPERIMENTAL

The mass-analyzed ion kinetic energy (MIKE) spectra were obtained with a modified Hitachi RMU-7M reversed-geometry double-focusing mass spectrometer. A Hitachi M-80B double-focusing mass spectrometer was used to obtain the 70 eV EI mass spectra.

Compounds **1**, methyl fluoroacetate ($CH_2FCOOCH_3$, **2**) and 1,1-dimethoxyethane ($CH_3CH(OCH_3)_2$, **3**), obtained from Tokyo Kasei Kogyo, were of reagent grade and were used without further purification. The last two were used as reference compounds. The deuterated compounds **1-*d*$_2$** ($CH_3CD_2COOCH_3$), **1-*d*$_3$** ($CH_3CH_2COOCD_3$) and **1-*d*$_5$** ($CH_3CD_2COOCD_3$) were prepared by the esterification of labelled or unlabelled propanoic acid and methanol or trideuteromethanol, and were purified by gas chromatography. The degree of labelling, estimated from the peak heights at the appropriate mass to charge ratio in the standard mass spectrum of **1-*d*$_2$**, **1-*d*$_3$** and **1-*d*$_5$**, was better than 98%.

RESULTS AND DISCUSSION

Notwithstanding the many mass spectrometric studies of **1**,[1–10] an interesting, surprising and not previously

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reported observation was made here with regard to the MIKE spectrum of its *m/z* 59 fragment ion. This MIKE spectrum, shown in Fig. 1(a), exhibits peaks at *m/z* 31, 29 and 15, whereas the MIKE spectrum of the *m/z* 59 fragment ion from **2**, shown in Fig. 2(a), only contains a peak at *m/z* 15. The latter is expected for the *m/z* 59 ion $COOCH_3{}^+$, which can decompose by expulsion of carbon dioxide to give the methyl cation $CH_3{}^+$.

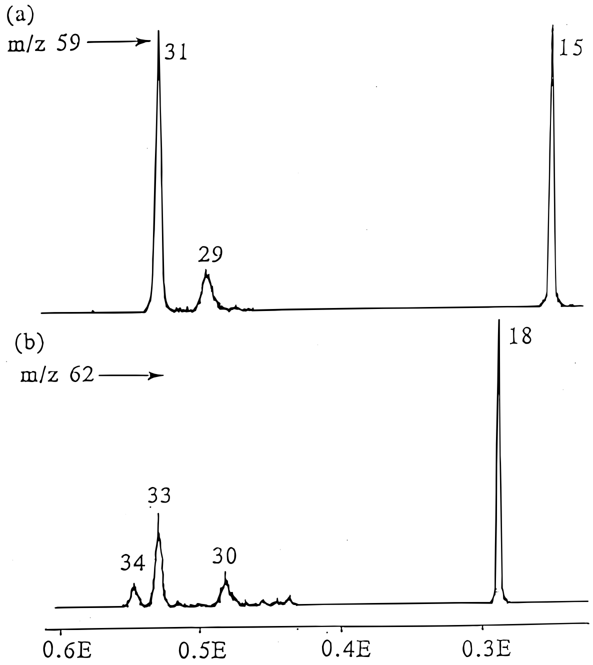


Figure 1. MIKE spectra of (a) the *m/z* 59 ion from methyl propanoate ($CH_3CH_2COOCH_3$, **1**) and (b) the *m/z* 62 ion from trideuteromethyl propanoate ($CH_3CH_2COOCD_3$, **1-*d*₃**).

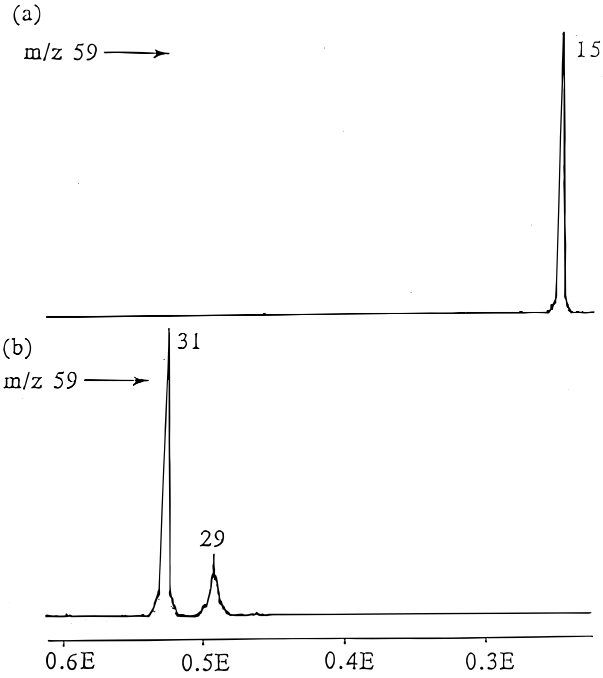


Figure 2. MIKE spectra of (a) the $[M-\dot{C}H_2F]^+$ ion (*m/z* 59) from methyl fluoroacetate ($CH_2FCOOCH_3$, **2**) and (b) the $[M-\dot{O}CH_3]^+$ ion (*m/z* 59) from 1,1-dimethoxyethane ($CH_3CH(OCH_3)_2$, **3**).

In the MIKE spectrum of the *m/z* 62 ions from **1-*d*₃** ($CH_3CH_2COOCD_3$), the peaks due to the ions at *m/z* 31, 29 and 15 from the *m/z* 59 ions of **1** [see Fig. 1(a)] are shifted to *m/z* 34 and 33, 30 and 18, respectively, as shown in Fig. 1(b). The shift from *m/z* 15 to 18 is expected for the *m/z* 62 ion $COOCD_3{}^+$, which upon loss of carbon dioxide should give the trideuteromethyl cation $CD_3{}^+$.

The dominant shift from *m/z* 31 [Fig. 1(a)] to *m/z* 33 [Fig. 1(b)], however, means that most of the *m/z* 31 ions contain only two hydrogen atoms from the original methoxy group and that their third hydrogen atom must originate from the ethyl group, that is, the *m/z* 33 ions generated from the *m/z* 62 ions of **1-*d*₃** have the composition CHD_2O^+. Consequently, the ions at *m/z* 31 and also *m/z* 29 must originate from *m/z* 59 ions of **1** which do not have the elemental composition of $C_2H_3O_2$ due to loss of $\dot{C}_2H_5$ but instead C_3H_7O due to loss of $H\dot{C}O$ from $\mathbf{1}^{+\cdot}$ The corresponding *m/z* 62 $C_3H_4D_3O^+$ ions due to loss of $H\dot{C}O$ from $\mathbf{1\text{-}d_3^{+\cdot}}$ can then account easily for the peaks due to the ions at *m/z* 34, 33 and 30 in the MIKE spectrum given in Fig. 1(b), as will be shown below.

Accurate mass measurements under high-resolution conditions confirmed that the *m/z* 59 ions generated from **1** consist of two species with different elemental compositions, i.e. $C_2H_3O_2$ (99.2%) and C_3H_7O (0.8%), in full agreement with the tabulated high-resolution data of the mass spectrum of **1** reported more than three decades ago.[11]

It should be noted that within the limits of detection, no peak is observed at *m/z* 59 in the MIKE spectrum of the molecular ion of **1**. Instead, peaks are observed at *m/z* 57 and 56 in a ratio of ~ 14:1 due to loss of $CH_3O^{\cdot}$ and CH_3OH, respectively [see Fig. 3(a)]. The MIKE spectra of the molecular ions of **1-*d*₂**, **1-*d*₃** and **1-*d*₅** show that an extensive hydrogen–deuterium exchange occurs prior to expulsion of the methoxy radical in which all hydrogen atoms in metastably decomposing $\mathbf{1}^{+\cdot}$ participate (see Fig. 3; for complete hydrogen–deuterium exchange the expected peak intensities for methoxy radical loss would be *m/z* 59:58:57 = 20:30:6 for **1-*d*₂**, *m/z* 60:59:58:57 = 10:30:15:1 for **1-*d*₃** and *m/z* 62:61:60:59 = 1:15:30:10 for **1-*d*₅**). For the first steps in this exchange the recently reported[10] initial 1,4-H shifts in $\mathbf{1}^{+\cdot}$ can be invoked.

A mechanism for the formation of *m/z* 59 ions with the elemental composition C_3H_7O from $\mathbf{1}^{+\cdot}$ is proposed in Scheme 1. It involves reaction steps which are common in the field of gas-phase ion chemistry and which lead in a straightforward way to the loss of a formyl radical from $\mathbf{1}^{+\cdot}$ to give the $CH_3CH{=}O^+CH_3$ species. To confirm the proposed structure of the latter ion, the MIKE spectrum of the *m/z* 59 ions generated from ionized **3** by the loss of a methoxy radical and known to give the $CH_3CH{=}O^+CH_3$ species[12] was measured. It is shown in Fig. 2(b) and exhibits peaks at *m/z* 31 and 29 in an abundance ratio nearly equal to that in Fig. 1(a). Comparison of the MIKE spectrum in Fig. 1(a) with those in Fig. 2 nicely illustrates that the spectrum of the *m/z* 59 ions generated from $\mathbf{1}^{+\cdot}$ is a superposition of the spectra of the *m/z* 59 ions generated from $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$.

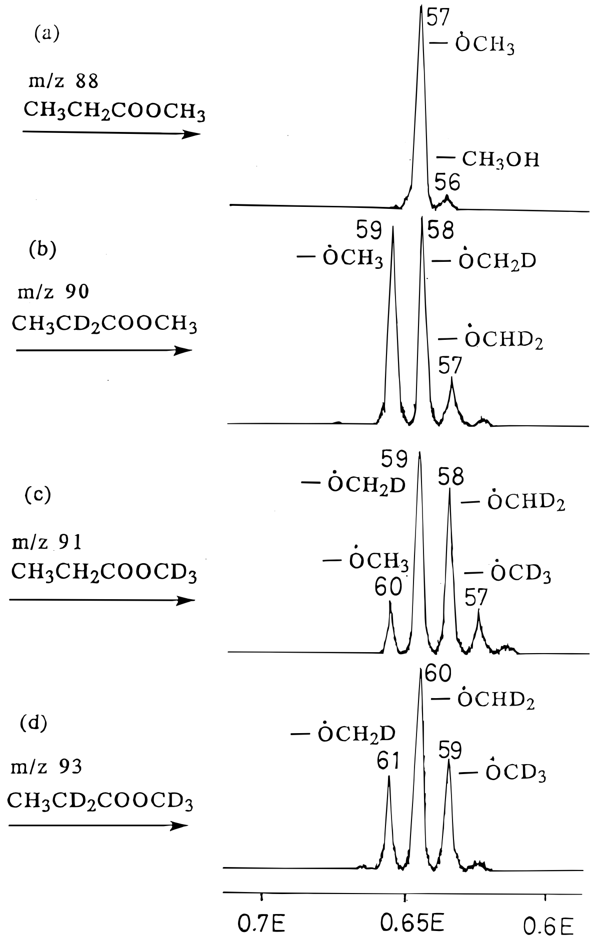


Figure 3. MIKE spectra of the molecular ions of (a) **1**-d_0 (m/z 88), (b) **1**-d_2 (m/z 90), (c) **1**-d_3 (m/z 91) and (d) **1**-d_6 (m/z 93).

With reference to the mechanism for C_2H_4 loss from $C_3H_7O^+$ ions proposed by Tsang and Harrison[12] and Holmes *et al.*,[13] fragmentation pathways for the m/z 62 ions with the elemental composition $C_3H_4D_3O$, generated from **1**-d_3, are given in Scheme 2 to account for the peaks observed at m/z 34, 33 and 30 in Fig. 1(b).

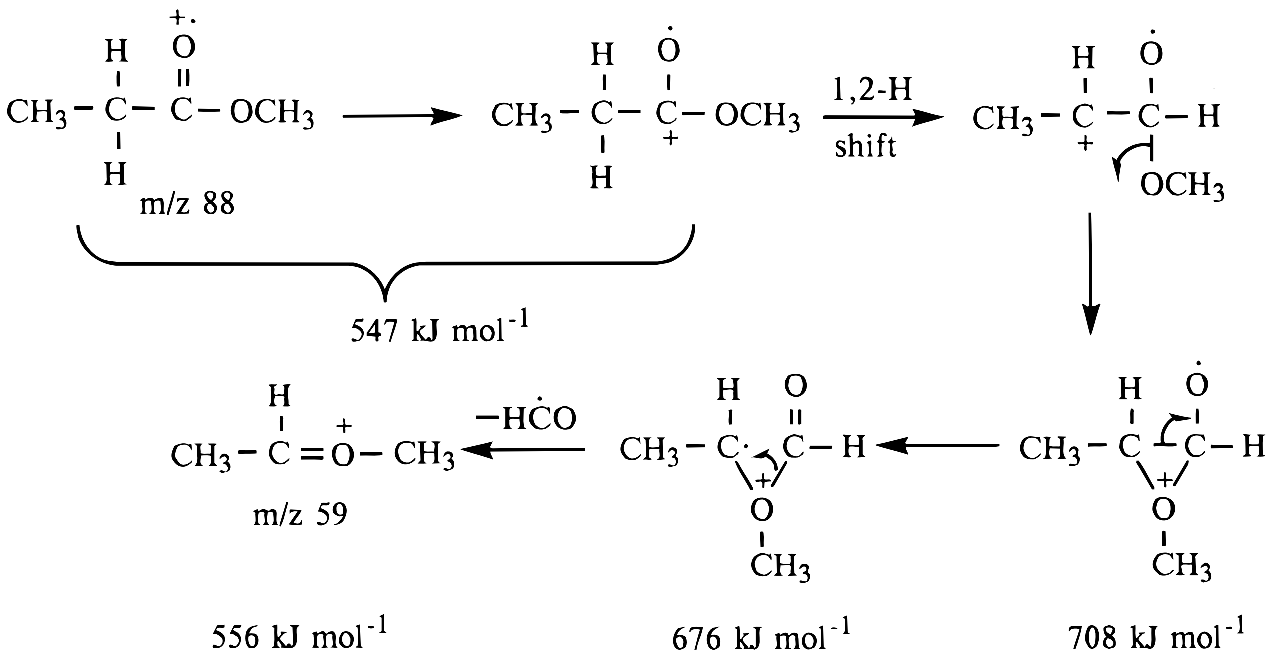
Finally, we would like to comment on the observations made with reference to the available[14,15] or calculated (ROHF/6–31G*)[16] heats of formation of the species involved in the reaction pathways which are summarized in Table 1 and given in Scheme 1, respectively.

Table 1 shows that the thermochemical threshold for the formation of the m/z 59 ion with elemental composition $C_2H_3O_2$ is 63 kJ mol^{-1} higher than that for formation of the m/z 57 propanoyl cation $C_2H_5CO^+$ from $1^{+\cdot}$. Both reactions are simple cleavage reactions, corresponding to loss of an ethyl and a methoxy radical from

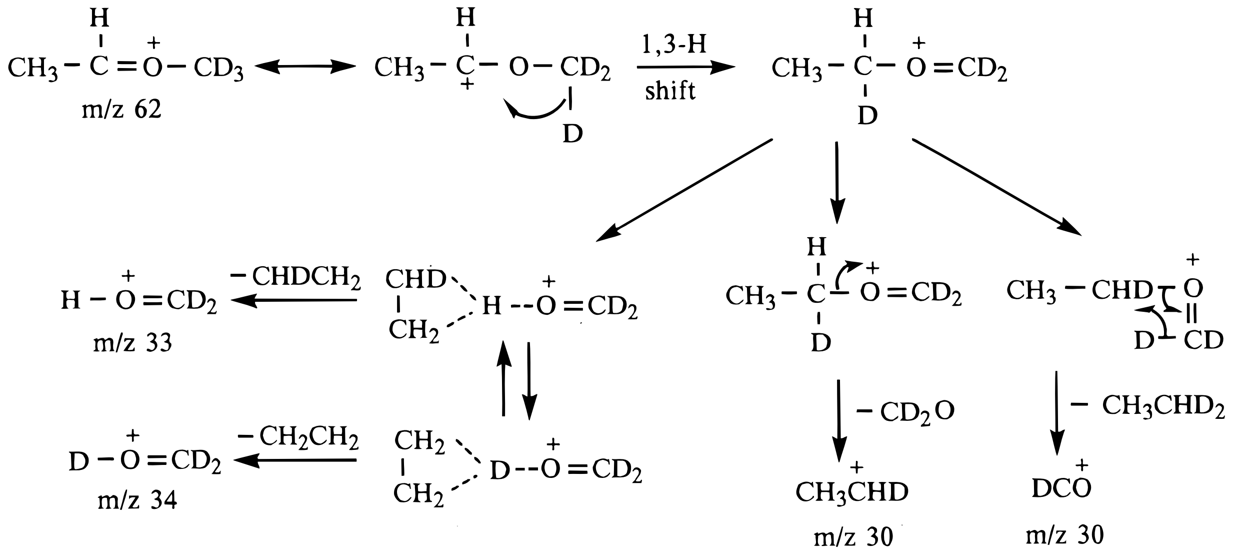
Table 1. Sums of the heats of formation of possible product ions and neutral fragments generated upon unimolecular decomposition of ionized methyl propanoate (1) in kJ mol^{-1} (taken from Ref. 14 unless stated otherwise)

(1)	$CH_3CH_2^{\cdot}$	$+COOCH_3^+$	(m/z 59)	$118+522^a=670$
(2)	$CH_3O^{\cdot}$	$+CH_3CH_2CO^+$	(m/z 57)	$16+591=607$
(3)	$HCO^{\cdot}$	$+CH_3CH{=}O^+CH_3$	(m/z 59)	$45+556^b=601$
(4)	CH_2CH_2	$+HOCH_2^+$	(m/z 31)	$52+703=755$
(5)	CH_2O	$+CH_3CH_2^+$	(m/z 29)	$-109+902=793$
(6)	CH_3CH_3	$+CHO^+$	(m/z 29)	$-84+825=741$
(7)	CO_2	$+CH_3^+$	(m/z 15)	$-393+1083=700$

[a] See Ref. 7.
[b] See Ref. 15.



Scheme 1. Mechanism proposed for the loss of HĊO from the molecular ion of methyl propanoate (**1**). The values given under the structures are the heats of formation calculated at the ROHF/6–31G* level of theory[16] with reference to the heat of formation of $1^{+\cdot}$ (547 kJ mol^{-1}).[14] For the top-right structure no stable energy minimum has been obtained. The value of 556 kJ mol^{-1} for the bottom-left structure was taken from Ref. 15.



Scheme 2. Mechanisms proposed for the formation of the ions at *m/z* 30, 33 and 34 from the $[M - H\dot{C}O]^+$ ion (*m/z* 62) generated from the molecular ion of trideuteromethyl propanoate (**1**-d_3).

$\mathbf{1}^{+\cdot}$, respectively, for which the barriers of the reverse reaction are known to be generally small.[17] Consequently, the 63 kJ mol^{-1} higher energy required to form the $COOCH_3^+$ ion than to generate the $C_2H_5CO^+$ ion from $\mathbf{1}^{+\cdot}$ is too large for competition[18,19] between these two reaction channels in the metastable time frame. This explains the absence of a peak at *m/z* 59 due to $COOCH_3^+$ in the MIKE spectrum of the molecular ion of **1**. Similarly, the formation of *m/z* 59 ions with the elemental composition C_3H_7O from $\mathbf{1}^{+\cdot}$ cannot compete in the metastable time frame with that of the *m/z* 57 propanoyl cations, notwithstanding the similar endothermicity for both reaction channels (see Table 1). This is due to the relatively high barriers *en route* from $\mathbf{1}^{+\cdot}$ to the final products of the $CH_3CH{=}O^+CH_3$ and formyl radical species (see Scheme 1).

The observation that a significant fraction of the much less abundant *m/z* 59 ions with the elemental composition C_3H_7O decomposes in the metastable time frame compared with that of the *m/z* 59 ions with the elemental composition C_2H_3O can be explained in the following way.

The thermochemical threshold for decomposition of the $COOCH_3^+$ ion into carbon dioxide and the methyl cation is 700 kJ mol^{-1},as shown in Table 1. This simple cleavage reaction will have a small barrier for the reverse reaction[17] and therefore is significantly less endothermic than decomposition of the $C_3H_7O^+$ ion into either ethene and protonated methanal or methanal and the ethyl cation or ethane and the formyl cation, even ignoring energy barriers (see Table 1). Consequently, the more energetic $COOCH_3^+$ ions will have decomposed relatively more than the $C_3H_7O^+$ ions[19,20] before arriving in the second field-free region of the mass spectrometer used (see Experimental). This will increase the $C_3H_7O^+/COOCH_3^+$ abundance ratio as reflected in the abundances of the corresponding product ions at *m/z* 31 and 29 with respect to *m/z* 15, respectively, in the MIKE spectrum of the *m/z* 59 ions from $\mathbf{1}^{+\cdot}$ [see Fig. 1(a)].

CONCLUSIONS

The *m/z* 59 ions generated from the molecular ions of methyl propanoate (**1**) consist of species with two different elemental compositions, that is, $C_2H_3O_2$ and C_3H_7O. The $C_3H_7O^+$ ion is generated via a complex skeletal rearrangement and its decomposition is pronounced in the microsecond time frame.

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