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Unimolecular gas-phase reactions of methyl and ethyl trifluoroacetoacetates upon electron ionization

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Dedicated to Dr. Yannik Hoppilliard on the occasion of her 60th birthday and in recognition of her contributions and service to mass spectrometry.

Abstract

The unimolecular metastable decompositions of methyl and ethyl trifluoroacetoacetates, $CF_3COCH_2COOCH_3$ (MW: 170 (**1**)) and $CF_3COCH_2COOCH_2CH_3$ (MW: 184 (**2**)) induced by electron ionization, have been investigated by use of mass-analyzed ion kinetic energy (MIKE) spectrometry and D-labeling. In the metastable time window, the molecular ions $\mathbf{1}^{\bullet+}$ decompose to give exclusively the ions at *m/z* 101 $[M - CF_3]^+$. However, the metastably decomposing ions $\mathbf{2}^{\bullet+}$ lead not only to the formation of the major fragment ion *m/z* 115 $[M - CF_3]^+$, but also to three minor fragment ions *m/z* 164 $[M-HF]^+$, *m/z* 156 $[M-C_2H_4]^+$ and *m/z* 87. A large part of the metastably decomposing ions $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ has the enol form.

The loss of CO_2 from the ions *m/z* 101 and *m/z* 115 occurs through migration of the methyl and ethyl groups, respectively. The source-generated *m/z* 69 ions from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are most abundant and consist of both $CF_3{}^+$ and $OCCHCO^+$. The latter ion, a protonated carbon suboxide, is generated by at least three and four different fragmentation routes from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, respectively. The *m/z* 43 ion, $C_2H_3O^+$, from $\mathbf{2}^{\bullet+}$ is formed by at least two different routes. (Int J Mass Spectrom 219 (2002) 475–483)

Keywords: Alkyl trifluoroacetoacetate; MIKE spectrometry; Protonated carbon suboxide; Tautomer; Isobaric ions

1. Introduction

Many fluorine-containing organic compounds are used in industry or in medical science, for example, as detergents of semi-conductors, refrigerants or medicine. However, their extraordinary stability causes serious environmental problems. The fundamental properties of organofluoro compounds should therefore be investigated.

Unimolecular gas-phase reactions of ionized methyl acetoacetate have been extensively studied by the group of Audier [1–4]. This group reported that the molecular ions of methyl acetoacetate consist of a mixture of keto and enol tautomers which eliminate CO and $^\bullet CH_3$, respectively [2]. The group of Audier also reported that protonated carbon suboxide $OCCHCO^+$ (*m/z* 69) is generated by the loss of CH_3OH from the enol type *m/z* 101 ion $COCH{=}C(OH)OCH_3{}^+$ [4]. Carbon suboxide, OCCCO, has been postulated to be one of the key intermediates in the formation of

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interstellar species [5–7]. The kinetic energy release value for the loss of CO from the molecular ion of methyl acetoacetate has also been measured [8,9].

To the authors knowledge, the fragmentation mechanisms of methyl trifluoroacetoacetate, CF_3COCH_2-$COOCH_3$ (MW: 170 (**1**)), a fluorine derivative of methyl acetoacetate, have not been discussed earlier. In this paper, the influence of fluorine on the fragmentation pattern of this compound and of its homologue ethyl trifluoroacetoacetate, $CF_3COCH_2COOCH_2CH_3$ (MW: 184 (**2**)), has been investigated by use of mass-analyzed ion kinetic energy (MIKE) spectrometry and D-labeling. Particular attention has been paid to the possible formation of protonated carbon suboxide from these compounds.

2. Experimental

The standard mass and the MIKE spectra were obtained by using a JEOL JMS HX-100 tandem mass spectrometer. The electron energy was 70 eV, and the ion accelerating voltage was 5 kV.

Samples **1** and **2** were research grade products from Tokyo Kasei Co., Ltd., and were used without further purification. The D-labeled isotopomer of **2** ($CF_3COCD_2COOCD_2CD_3$, MW: 191, **2**-d_7) was obtained by stirring a mixture of **2** and a large excess of CD_3CD_2OD. From the mass spectrum, the percentage of labeling was estimated to be about 51% for **2**-d_7. Although this percentage is low, this was sufficient to investigate the fragmentation processes because, taking into account the naturally occurring ^{13}C contribution, the purity of the selected precursor ion beams for recording their MIKE spectra is more than 95%.

3. Results and discussion

The standard mass spectra of **1** and **2** are shown in Fig. 1, in which the moderately abundant molecular ions of **1** and **2** are observed as peaks at *m/z* 170 and 184, respectively. In both spectra, the base peak is at *m/z* 69. Although compounds containing a trifluoromethyl group in general give a peak at *m/z* 69, the present peak partly corresponds to the mass-to-charge ratio of protonated carbon suboxide as will be shown below. Undoubtedly, the fragment ion *m/z* 139 can be assigned to the loss of the $^{\bullet}OR$ (R = CH_3 or CH_2CH_3) group from the molecular ions $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. The loss of $^{\bullet}CF_3$ from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ gives rise to the moderately large peaks at *m/z* 101 and 115, respectively.

3.1. *Methyl trifluoroacetoacetate, $CF_3COCH_2COOCH_3$ (MW: 170 (**1**))*

In the metastable time window, the molecular ion of methyl acetoacetate (**3**), the fluorine-free analogue of **1** and known to be a mixture of keto and enol tautomers, eliminates CO in addition to $^{\bullet}CH_3$ to give the peaks at *m/z* 88 and 101, respectively [2,8,9]. The fragment ion *m/z* 88 originates from dissociation of the keto form, $CH_3COCH_2COOCH_3^{\bullet+}$, while the enol form, $CH_3COCH{=}C(OH)OCH_3^{\bullet+}$ or $CH_3C(OH){=}CHCOOCH_3^{\bullet+}$ generates a larger part of the fragment ion *m/z* 101 [2].

Metastable $\mathbf{1}^{\bullet+}$ eliminates essentially exclusively a trifluoromethyl radical, $CF_3^{\bullet}$, to give rise to the peak at *m/z* 101 and not CO, in contrast to metastable $\mathbf{3}^{\bullet+}$. According to the results obtained by Audier and co-workers [2], a large part of metastable $\mathbf{1}^{\bullet+}$ would be in the enol form, $CF_3COCH{=}C(OH)OCH_3^{\bullet+}$ or $CF_3C(OH){=}CHCOOCH_3^{\bullet+}$, especially because the very electronegative fluorine atom enhances the acidity of the methylene hydrogens.

Fig. 2 shows the MIKE spectra of the *m/z* 139 and 101 ions from $\mathbf{1}^{\bullet+}$.

According to the results obtained by Audier and co-workers [2], the former ions are generated by the loss of $^{\bullet}OCH_3$ from the enol form of $\mathbf{1}^{\bullet+}$, and the latter by the loss of $^{\bullet}CF_3$ from both the keto and in a larger part the enol form of $\mathbf{1}^{\bullet+}$. Thus, the structure of the *m/z* 139 ions is $CF_3COCH{=}C(OH)^+$ and/or $CF_3C(OH){=}CHCO^+$, and that of the *m/z* 101 ions is $COCH_2COOCH_3^+$, $COCH{=}C(OH)OCH_3^+$ and/or $C(OH){=}CHCOOCH_3^+$.

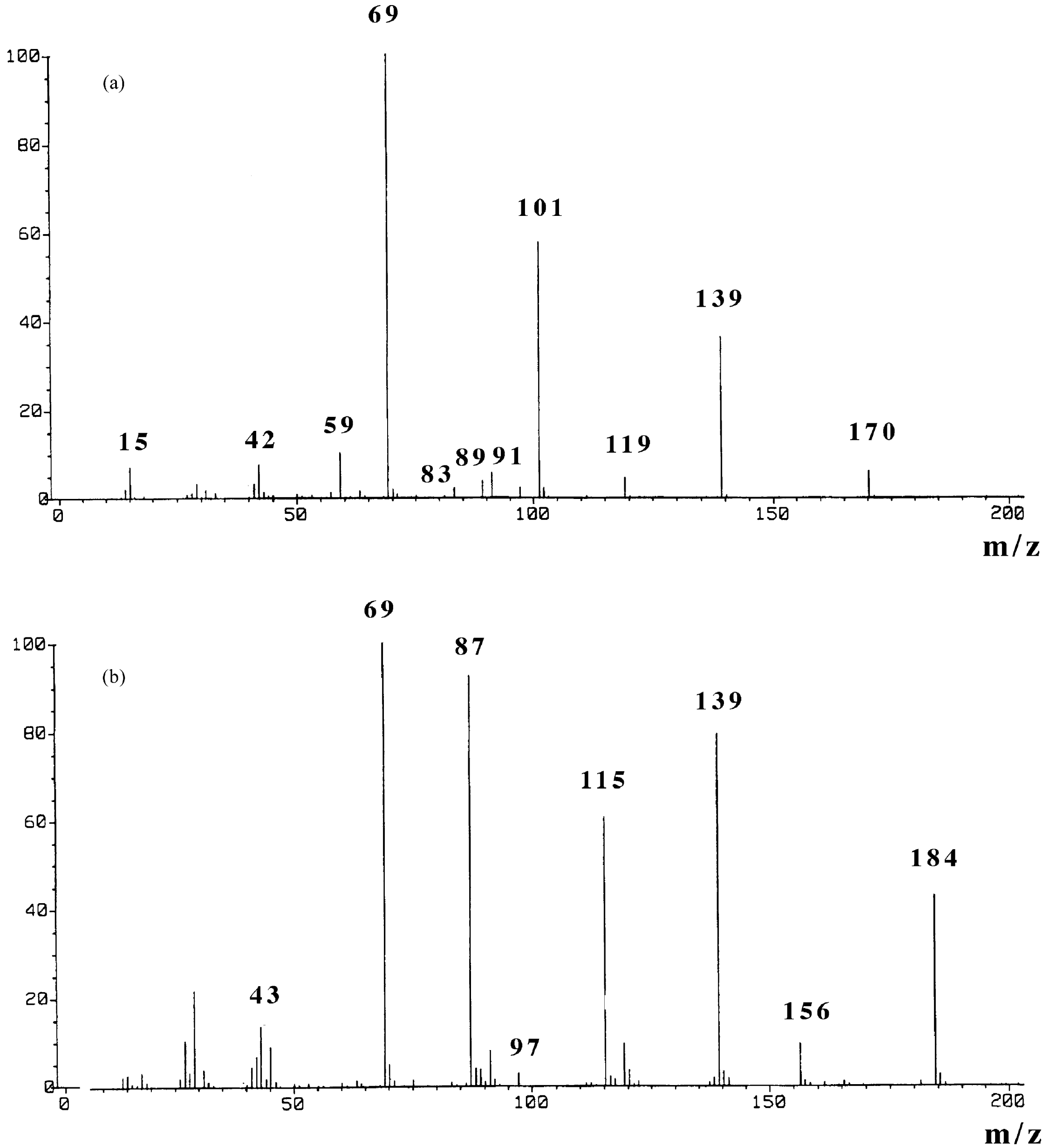


Fig. 1. Mass spectra of (a) methyl trifluoroacetoacetate (**1**) and (b) ethyl trifluoroacetoacetate (**2**).

In Fig. 2a, a significant peak is observed at *m*/*z* 119, corresponding to the loss of a 20 Da neutral species, in addition to a moderately large and small peak at *m*/*z* 111 and 89, corresponding to the losses of 28 and 50 Da neutral species, respectively. These peaks can be assigned to the losses of HF, CO and CF_2. The first and last fragmentations are common reactions for organofluoro compounds [10–13]. The *m*/*z* 119 ions further decompose by loss of CF_2 and the generated ions *m*/*z* 69 are protonated carbon suboxide,

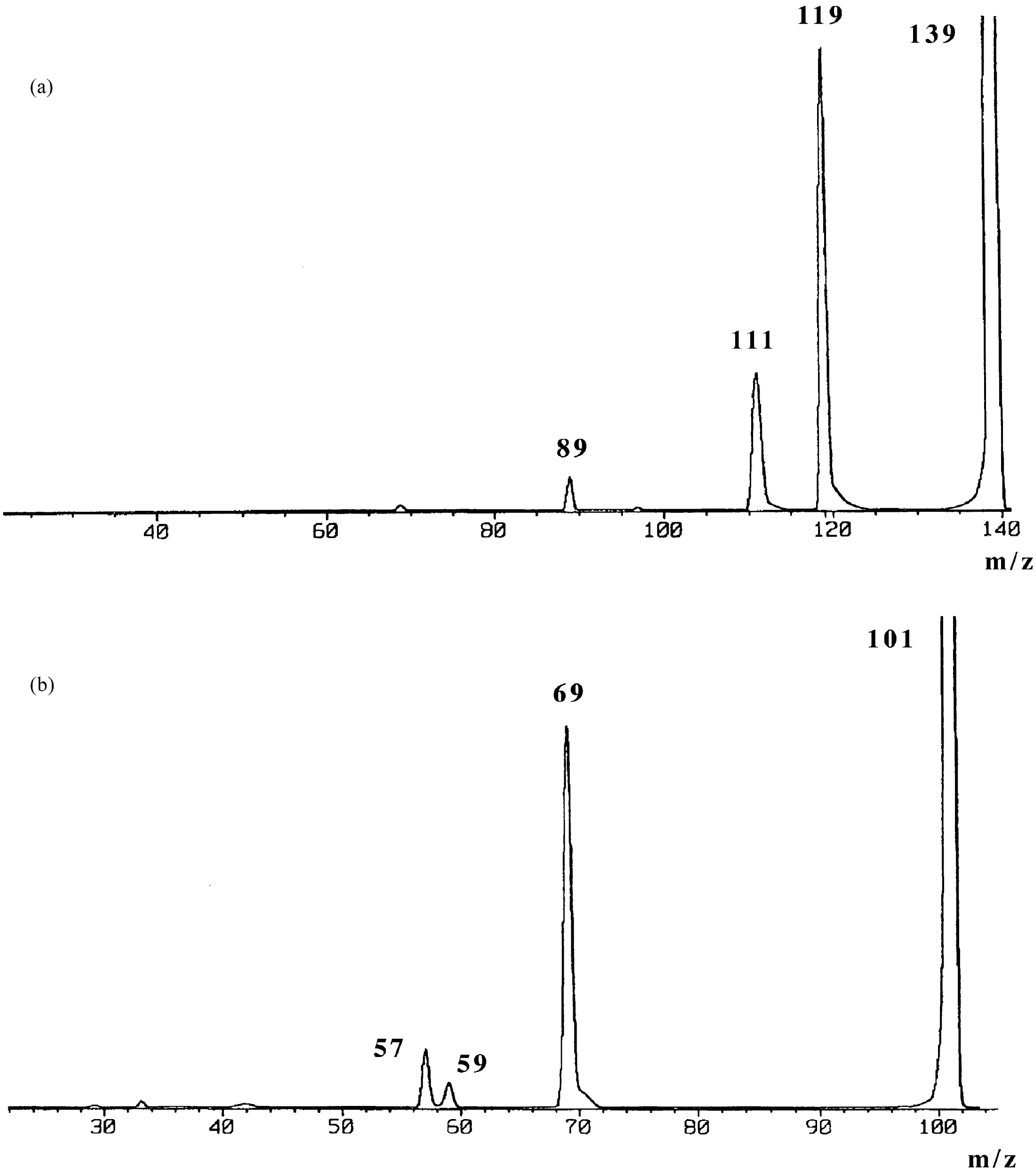


Fig. 2. MIKE spectra of the ions at (a) *m/z* 139 and (b) *m/z* 101 from $\mathbf{1}^{\bullet+}$.

$OCCHCO^+$ [4,7]. The *m/z* 111 ions decompose into *m/z* 91 and 83 by losses of HF and CO, respectively (MIKE spectrum not shown). Protonated carbon suboxide (*m/z* 69) is also generated by the loss of HF from the *m/z* 89 ions.

In metastable time window, the source-generated *m/z* 69 ions eliminate predominantly a 28 Da neutral species, yielding the ions *m/z* 41. Usually a peak due to CF_3^+ ion is observed at *m/z* 69 in the mass spectra of the compounds containing a trifluoromethyl group. Therefore, it can be concluded that the *m/z* 69 ions from $\mathbf{1}^{\bullet+}$ consist of two nominally isobaric ions, that is $OCCHCO^+$ and CF_3^+. The latter fragment ions do not decompose at all in the metastable time window. Thus, we can conclude that the *m/z* 41 ions are generated by the loss of CO from protonated carbon suboxide, $OCCHCO^+$ [7].

The relatively rich chemistry of the *m/z* 139 ions and its fragment ions, discussed above, is thus quite different from that of the corresponding fluorine-free ions $CH_3C(OH)CHCO^+$ (*m/z* 85) which eliminate essentially exclusively CH_2CO to give the ions *m/z* 43 [1,3].

The MIKE spectrum of the source-generated *m/z* 101 ions (Fig. 2b) turns out to be the same as that of the *m/z* 101 ions from $\mathbf{3}^{\bullet+}$. The fragmentation mechanism of the *m/z* 101 ions from $\mathbf{3}^{\bullet+}$, especially to form the *m/z* 57 ions by CO_2 loss and accompanying methyl group migration, has been reported already in detail [4]. As shown in Fig. 2b, loss of CH_3OH occurs from the *m/z* 101 ions in the enol form to give the *m/z* 69 ion which is also protonated carbon suboxide, $OCCHCO^+$ and not $CF_3{}^+$ [4]. Thus, protonated carbon suboxide is generated from $\mathbf{1}^{\bullet+}$ by at least three different fragmentation routes, which have been summarized in Scheme 1.

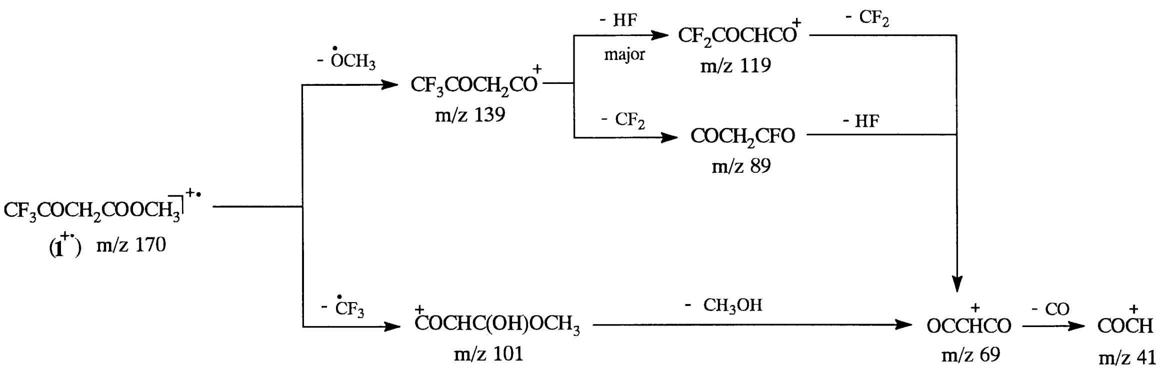
The *m/z* 59 ions generated by the loss of CH_2CO from the *m/z* 101 ions ($C(OH){=}CHCOOCH_3{}^+$ or $COCH_2COOCH_3{}^+$) are $COOCH_3{}^+$, because they decompose only into the ions *m/z* 15 [14].

3.2. *Ethyl trifluoroacetoacetate, $CF_3COCH_2COOCH_2CH_3$ (MW: 184 (**2**))*

The MIKE spectra of the molecular ions of **2** and **2**-d_7 are shown in Fig. 3. A significant peak is observed at *m/z* 115 in Fig. 3a, in addition to two small peaks at *m/z* 164, and 156, corresponding to the losses of 20 and 28 Da neutral species, respectively. These peaks are assigned to be due to the losses of $^{\bullet}CF_3$, HF and C_2H_4 because they shift to *m/z* 122, 170 and 159 in the MIKE spectrum of **2**-$d_7{}^{\bullet+}$, respectively (see Fig. 3b). The difference in the relative intensities of corresponding peaks in Fig. 3a and b shows that a fairly large isotope effect is operative [15,16]. The absence of the peak, corresponding to the loss of CO, means that a large part of metastable $\mathbf{2}^{\bullet+}$ would also be in the enol form, $CF_3COCH{=}C(OH)OCH_2CH_3{}^{\bullet+}$ and/or $CF_3C(OH){=}CHCOOC_2CH_3{}^{\bullet+}$ [2]. The very small peak at *m/z* 87 in Fig. 3a could not be assigned as being due to loss of either CF_3CO or $CF_3{+}C_2H_4$ from the molecular ion of **2**, because the corresponding peak cannot be detected in Fig. 3b.

The MIKE spectrum of the *m/z* 164 ions could not be measured, because their abundance was too low (see Fig. 1b). The MIKE spectrum of the source-generated *m/z* 139 ions is essentially identical to that of the *m/z* 139 ions from $\mathbf{1}^{\bullet+}$, indicating that these ions are $CF_3COCH{=}C(OH)^+$ or $CF_3C(OH){=}CHCO^+$.

The MIKE spectra of the *m/z* 156 and 115 ions from $\mathbf{2}^{\bullet+}$ and the *m/z* 122 ions from **2**-$d_7{}^{\bullet+}$ are shown in Fig. 4. In the metastable time window, the 156 ions eliminate essentially exclusively a 69 Da neutral species to give the *m/z* 87 ion (Fig. 4a). Undoubtedly, this reaction can be assigned to the loss of a $^{\bullet}CF_3$



Scheme 1. The formation pathways of protonated carbon suboxide from $\mathbf{1}^{\bullet+}$.

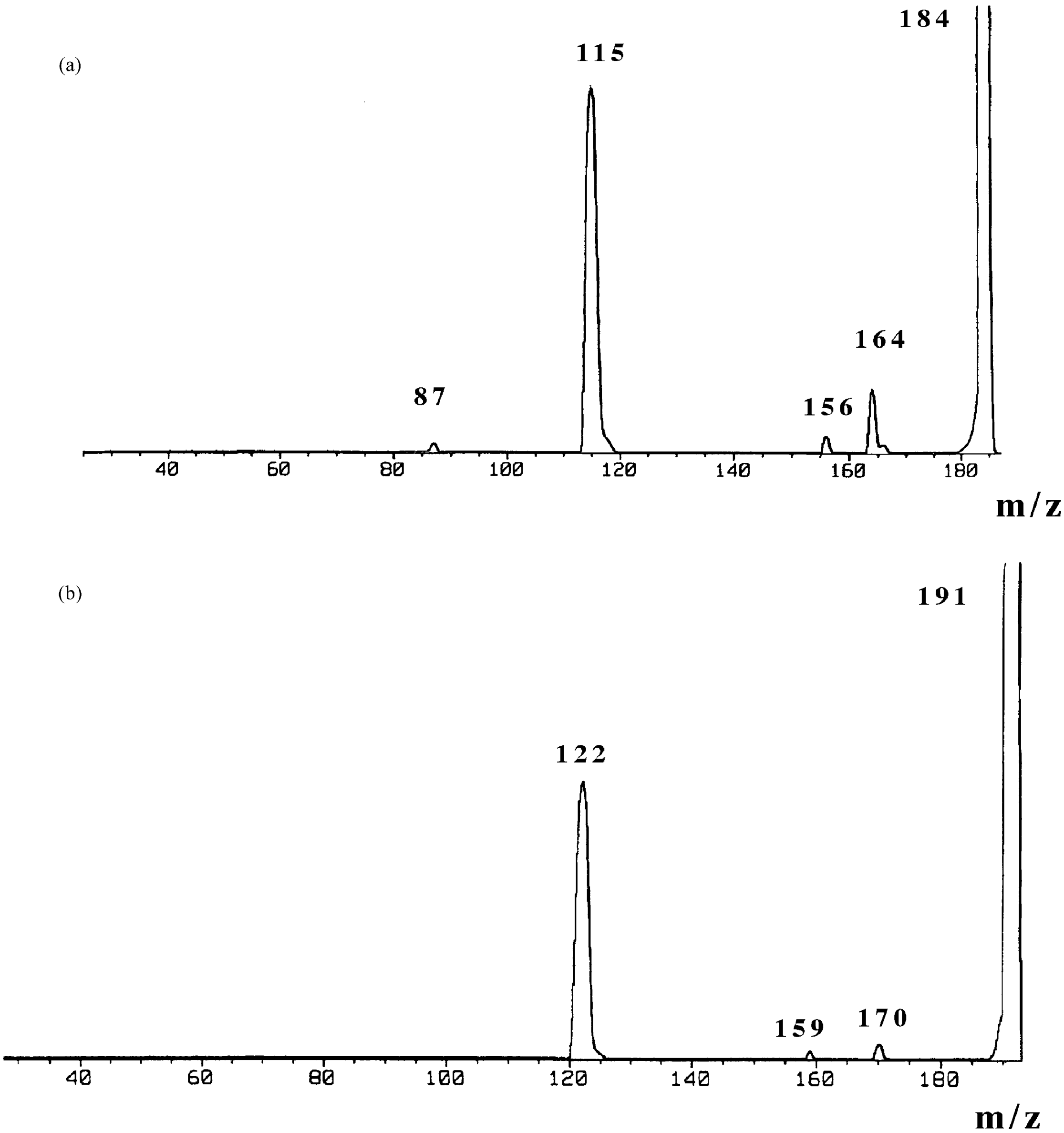


Fig. 3. MIKE spectra of the ions at (a) *m/z* 184 from $\mathbf{2}^{\bullet+}$ and (b) *m/z* 191 from $\mathbf{2}$-$d_7^{\bullet+}$.

radical to give the $COCHC(OH)OH^+$ ions, because they eliminate an H_2O molecule to give the *m/z* 69 ions, as described below.

In Fig. 4b, a significant peak is observed at *m/z* 87, in addition to a moderately large peak at *m/z* 43 and a small peak at *m/z* 71. The first two peaks shift to *m/z* 90 and 46 in Fig. 4c, while the peak, corresponding to *m/z* 71, is not observed due to a large isotope effect [15,16]. However, considering the fragmentation of *m/z* 101 ions from $\mathbf{1}^{\bullet+}$ into *m/z* 57 ions, the *m/z* 71 ions should be generated by loss of CO_2 with accompanying $^{\bullet}C_2H_5$ group migration [4]. The

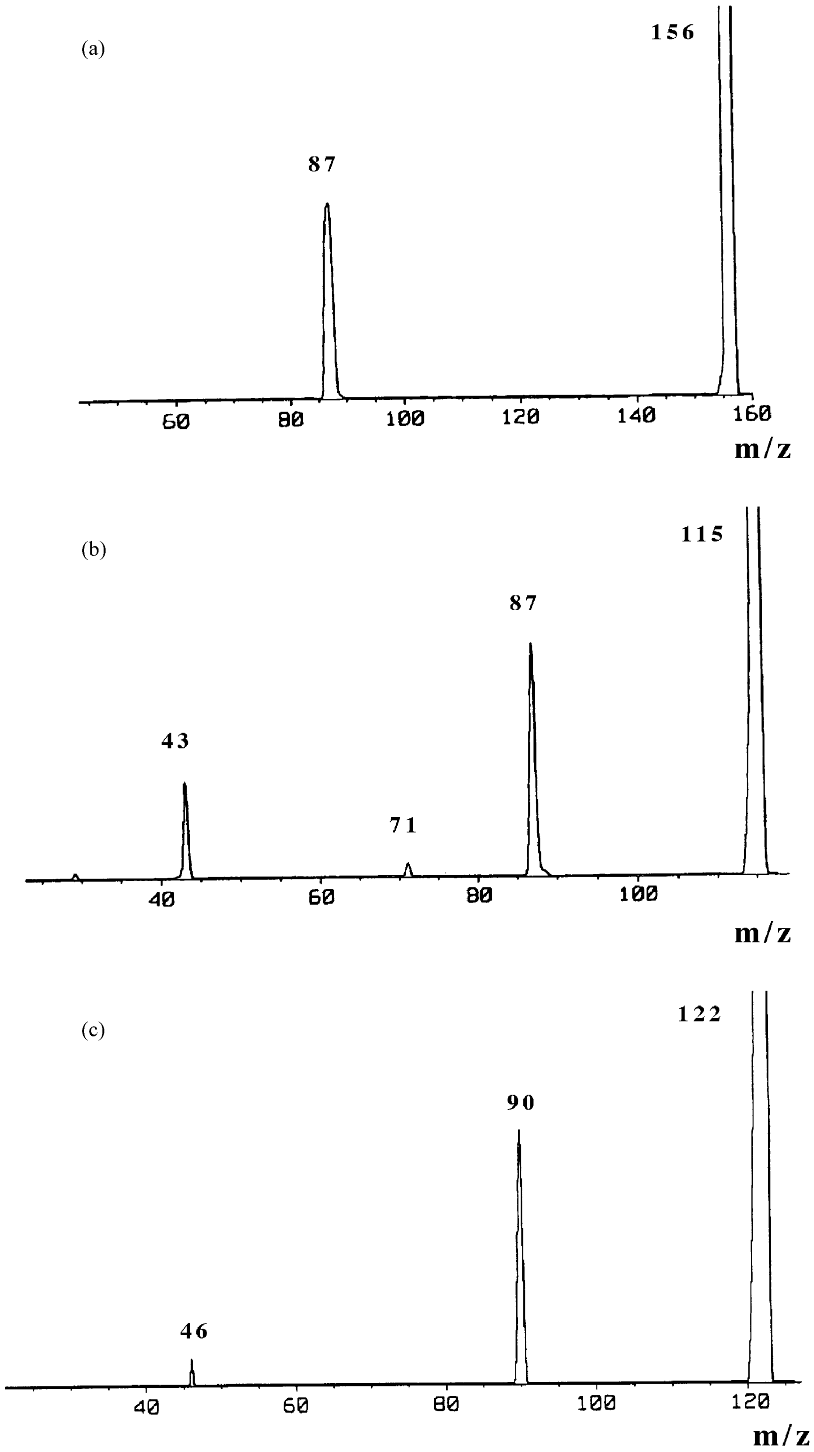


Fig. 4. MIKE spectra of the ions at (a) m/z 156 from $\mathbf{2}^{\bullet +}$, (b) m/z 115 from $\mathbf{2}^{\bullet +}$ and (c) m/z 122 from $\mathbf{2}$-$d_7^{\bullet +}$.

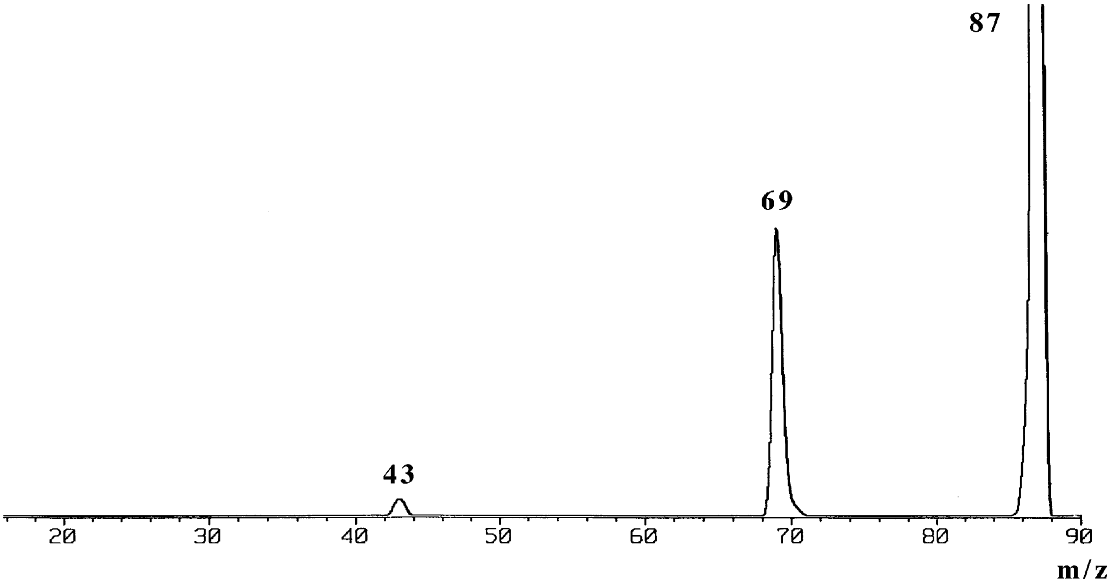
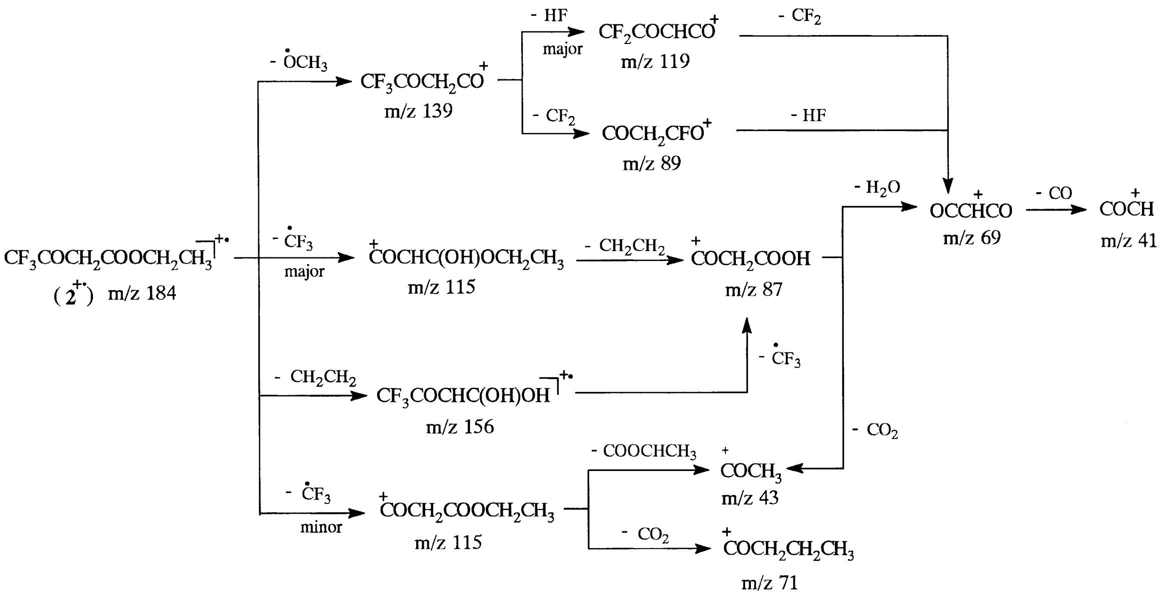


Fig. 5. MIKE spectrum of the ion at *m*/*z* 87 from $\mathbf{2}^{\bullet +}$.

fragmentation of the *m*/*z* 115 ions to give *m*/*z* 87 ions must be due to the loss of C_2H_4, not CO, because in the MIKE spectrum of Fig. 4c this peak shifts to *m*/*z* 90, not to *m*/*z* 94, as described above. This means that the structure of the *m*/*z* 87 ions is $COCHC(OH)OH^+$ and that they are generated via at least two different routes. Finally, the *m*/*z* 43 ions must be generated by the loss of $C_3H_4O_2$ from the *m*/*z* 115 ions through



Scheme 2. The formation pathways of protonated carbon suboxide from $\mathbf{2}^{\bullet +}$.

a hydrogen migration, according to the applied D-labeling.

As shown in Fig. 5, the protonated carbon suboxide *m*/*z* 69 ions, are also generated by the loss of H_2O from the *m*/*z* 87 ion. This means that protonated carbon suboxide from $\mathbf{2}^{\bullet+}$ is formed by at least four different routes which have been summarized in Scheme 2.

The *m*/*z* 87 ions also eliminate CO_2 to give the *m*/*z* 43 ions [4] so that they appear to be formed by at least two different routes, as given in Scheme 2.

From the results of the high-resolution measurement of the *m*/*z* 69 ion, the intensity ratio of CF_3^+ and $OCCHCO^+$ turned out to be 1:2.

4. Conclusion

A large part of the metastably decomposing molecular ions of methyl and ethyl trifluoroacetoacetates, **1** and **2**, is in the enol form. Protonated carbon suboxide with *m*/*z* 69 is generated by at least three and four different routes from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, respectively, which means that the source-generated *m*/*z* 69 ions from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are both CF_3^+ and $OCCHCO^+$. The fragmentation pathways of these fluorinated compounds are more complicated than those of the corresponding fluorine-free compounds.

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