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On the chemistry following methoxy migration in the metastably decomposing $(M - COOCH_3)^+$ ions (m/z 135) from dimethyl phthalate, isophthalate and terephthalate

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Dedicated to Professor Helmut Schwarz for his friendship and outstanding contributions to gas-phase ion chemistry on the occasion of his 60th birthday

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Abstract

The metastable ion dissociations of the $(M - COOCH_3)^+$ ions (m/z 135) generated upon electron ionization from dimethyl phthalate (**1**), isophthalate (**2**) and terephthalate (**3**), have been studied by use of mass-analyzed ion kinetic energy (MIKE) spectrometry and D-labeling. These ions all show as primary fragmentation channels the losses of methyl and carbon monoxide to give the ions m/z 120 and 107, respectively. The latter ions decompose further by the losses of another molecule of carbon monoxide or a molecule of formaldehyde to generate the ions at m/z 79 and 77, respectively. An additional dissociation channel is observed for the $(M - COOCH_3)^+$ ions from $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, the loss of methanol to give the ions m/z 103. The dissociation mechanism of the $(M - COOCH_3)^+$ ions from $\mathbf{1}^{\bullet+}$ is shown to be identical to that of the $(M - CH_3)^+$ ions from ionized 2-methoxyacetophenone. The latter ions have the 2-methoxybenzoyl cation structure demonstrating a methoxy migration in the $(M - COOCH_3)^+$ ions from $\mathbf{1}^{\bullet+}$ precedes their metastable ion dissociations. Part of the $(M - COOCH_3)^+$ ions from $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ has also rearranged to the 2-methoxybenzoyl cation structure prior to dissociation, but the significantly enhanced loss of methyl and the loss of methanol from these ions occur from the unrearranged structures as indicated by comparison with the dissociation behavior of the $(M - CH_3)^+$ ions from ionized 3- and 4-methoxyacetophenones.

Keywords: Benzenedicarboxylic acid dimethyl ester; MIKE; CH_3O migration; Isomerization

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1. Introduction

Dialkyl phthalates are used extensively as plasticizers in a variety of plastics, such as polyvinyl chloride and polyvinyl acetate. Their electron ionization mass spectra and those of the isomeric dialkyl isophthalates

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and terephthalates were recorded many years ago [1–4]. Later the unimolecular decompositions of several ions from dialkyl phthalates were studied by mass spectrometry–mass spectrometry (MS–MS) [5]. Ion kinetic energy (IKE) spectrometry has also been applied to study the unimolecular metastable decompositions of various ions generated from dimethyl phthalate ($C_6H_4(COOCH_3)_2$ (**1**), M_w: 194), isophthalate (**2**) and terephthalate (**3**) [6]. However, these studies did not deal with the unimolecular decompositions of the *m/z* 135 ions ($^+C_6H_4COOCCH_3$), which are the third most abundant in the mass spectrum of **1** and the second most abundant in the mass spectra of **2** and **3** [6].

In this paper, the unimolecular metastable decompositions of $^+C_6H_4COOCCH_3$ (*m/z* 135) ions which are generated by the consecutive eliminations of $CH_3O^\bullet$ and CO from $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$, will be reported based on mass-analyzed ion kinetic energy (MIKE) spectrometry, D-labeling and thermochemical considerations.

2. Experimental

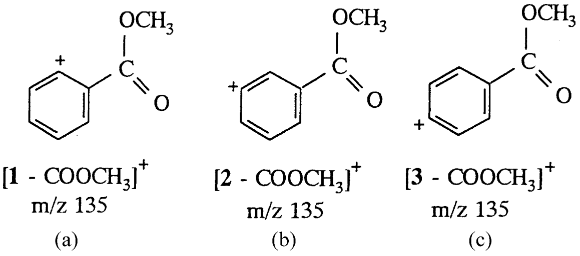
The standard mass, MIKE and collision-induced dissociation (CID) spectra were obtained at 70 eV electron energy by using a JEOL JMS HX-100 EBE type tandem mass spectrometer. The ion accelerating voltage was 5 kV. The lower energy (19–15 eV) MIKE spectra were obtained at nominal 1.0 eV intervals. In order to minimize the effect of the repeller voltage on the electron energy, its voltage was set as low as possible. The amount of kinetic energy release (KER) was estimated from the MIKE peak width at half-height, after correction for the width of the main beam of the stable ions [7].

Compounds **1**–**3** and 2-methoxy- (**4**), 3-methoxy- (**5**) and 4-methoxyacetophenones ($CH_3OC_6H_4COCH_3$ (**6**), M_w: 150) were research grade products from Tokyo Kasei Co. Ltd., and were used without further purification. The last three compounds were used a source for the reference *m/z* 135 ions. Compounds **1**-d_6 and **2**-d_6, ($C_6H_4(COOCD_3)_2$, M_w: 200), were prepared by esterification of the corresponding acid chlorides with CD_3OD, and were purified by the distillation. From the mass spectra, the percentage of labeling was estimated to be about 98%.

3. Results and discussion

The standard electron ionization mass spectra of **1**–**3** contain peaks at *m/z* 135 with relative intensities of 7.1, 31.4 and 24.3%, respectively [6]. Each corresponding ion, which has the initial structure shown in Scheme 1, is generated by the consecutive eliminations of $CH_3O^\bullet$ and CO from the respective molecular ions [6].

The MIKE spectra of the *m/z* 135 ions from **1** to **3** are shown in Fig. 1a–c. Fig. 1a shows that the source-generated *m/z* 135 ions from **1** decompose in the metastable time window in a variety of ways: in addition to the relatively narrow peaks at *m/z* 120 (loss of 15 Da) and *m/z* 77 (loss of 58 Da), two broad peaks are observed at *m/z* 107 (KER: 217 meV) and 79 (KER: 166 meV), which correspond to the losses of 28 and 56 Da, respectively. The first peak does not shift and the other three peaks shift to *m/z* 78, 110 and 82, respectively, in the MIKE spectrum of the *m/z* 138 ion ($^+C_6H_4COOCD_3$) from **1**-d_6 (see Fig. 2a). Therefore, each peak can be assigned unambiguously to be due to the elimination of a $^\bullet CH_3$, ($CO + CH_2O$), CO and 2CO, respectively. The losses of 2CO (or C_2O_2) have been reported also in the decompositions of protonated glyoxylic acid [8], squaric acid [9] and **4** [10]. Peak (A) in Fig. 2 is due to the metastably-generated ion in the second field-free region before the magnetic sector in the reaction *m/z* 200 → *m/z* 166 + CD_3O, which has the apparent mass of 137.8 ($166^2/200$ =



Scheme 1. Nominal ion structures of the ion at *m/z* 135 from $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$.

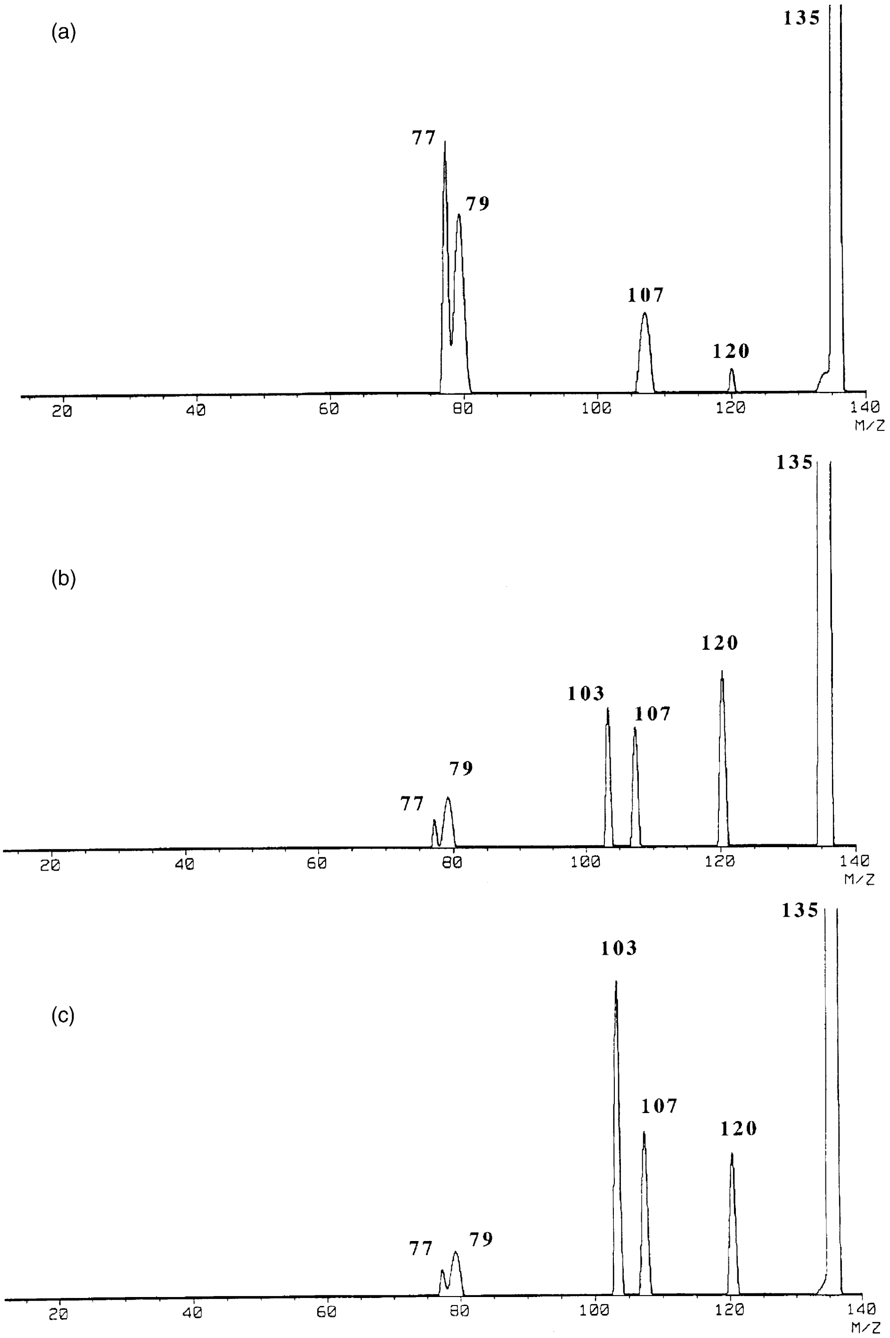


Fig. 1. MIKE spectra of the ions *m/z* 135 from (a) $\mathbf{1}^{\bullet +}$, (b) $\mathbf{2}^{\bullet +}$ and (c) $\mathbf{3}^{\bullet +}$.

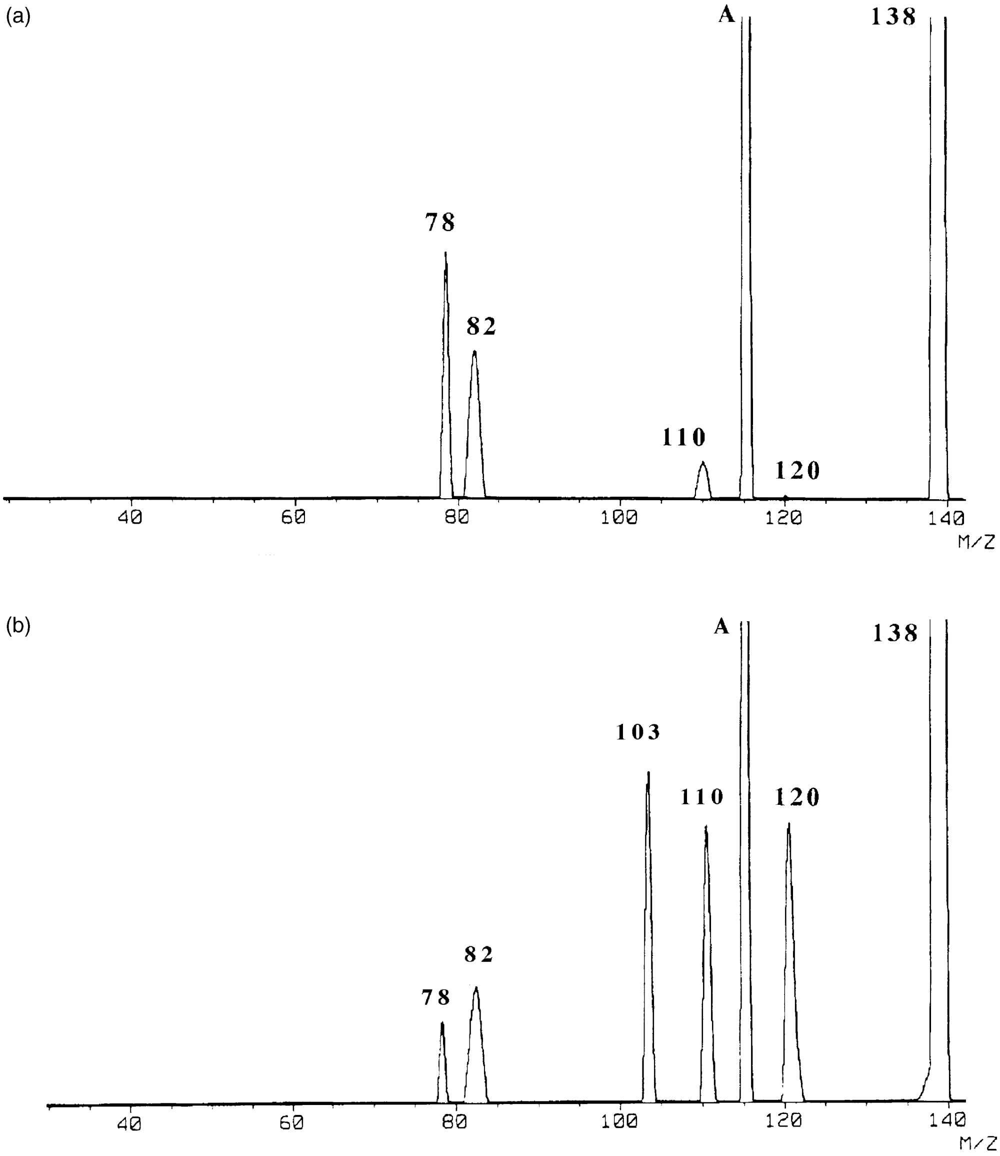


Fig. 2. MIKE spectra of the ions *m/z* 138 from (a) **1**-d$_6^{\bullet+}$ and (b) **2**-d$_6^{\bullet+}$. The peak (A) at about *m/z* 115 is due to the reaction *m/z* 200 → *m/z* 166 + CD_3O in the second field-free region.

137.8). When the *m/z* 138 ion was selected by the magnetic sector, a part of the apparent *m/z* 137.8 ions must pass through the sector. Thus, these strayed ions will be observed at about 115 mass to charge ratio ((166/200) × 137.8 ≑ 115), because this ion has a kinetic energy of (166/200) × 5 kV.

Fig. 1b and c show that the *m/z* 135 ions from **2**$^{\bullet+}$ and **3**$^{\bullet+}$ further decompose into the *m/z* 103 ions by the loss of a 32 Da neutral species in addition to the four ions mentioned above. In the following, the results obtained for **1** and **2** will be discussed, because as shown in Fig. 1, the fragmentation patterns of the *m/z*

135 ions for **2** and **3** were very similar. The peak at *m*/*z* 103 in Fig. 1b does not shift in the MIKE spectrum of the *m*/*z* 138 ion ($C_6H_4{}^+COOCD_3$) from **2**-d$_6$ (see Fig. 2b). Therefore, the corresponding ion is generated by the loss of methanol containing one hydrogen atom of the benzene ring. The peak width associated with the *m*/*z* 107 ions from **2** and **3** in Fig. 1b and c is relatively narrow (KER: 5 and 15 meV, respectively), in contrast with that for the *m*/*z* 107 ions from **1** (KER: 217 meV) in Fig. 1a. The KER values associated with the fragmentation of the *m*/*z* 135 ions from **2** and **3** into the *m*/*z* 79 ions are 100 and 130 meV, respectively.

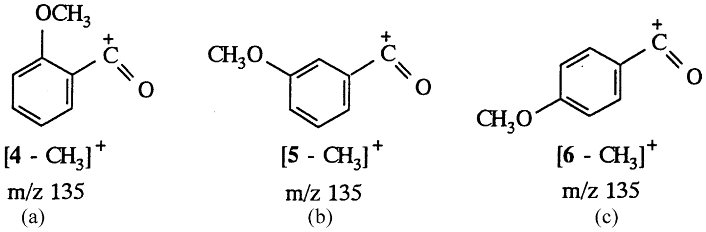
In order to rationalize the losses of CO (*m*/*z* 107 ion) and 2CO (*m*/*z* 79 ion) from the *m*/*z* 135 ion, at least a migration of the methoxy group (CH_3O) from the methoxycarbonyl group ($COOCH_3$) to the benzene ring must be considered. The MIKE spectra of the source-generated *m*/*z* 135 ions from the reference compounds **4**–**6** are shown in Fig. 3a–c. These *m*/*z* 135 ions, which have initial structures shown in Scheme 2, are generated by the loss of $^\bullet CH_3$ from the acetyl group of the corresponding molecular ions [10]. If the CH_3O group migrates from each $COOCH_3$ group in the *m*/*z* 135 ions from **1** to **3** to the original charge site in the benzene ring (see Scheme 1), then the structures would result as shown in Scheme 2.

Although the relative intensities of the corresponding peaks are different, the MIKE spectra in Figs. 1a and 3a show similar peak patterns (and peak shape) at *m*/*z* 120, 107, 79, and 77. The KER values associated with the fragmentation of the *m*/*z* 135 ions from **4** into the *m*/*z* 107 and 79 ions are 255 and 149 meV, respectively, and are not much different from those for the fragmentation of the *m*/*z* 135 ions from **1** (217 and 166 meV as shown above). Therefore, it may be concluded that the *m*/*z* 135 ions decompose into the *m*/*z* 120, 107, 79 and 77 ions following the migration of CH_3O from the $COOCH_3$ group to the charge site at the *ortho* position in the benzene ring. This migration is supported by the fact that the heat of formation of the *o*-$CH_3OC_6H_4CO^+$ ion (583 kJ mol^{-1}) is lower than that of $^+C_6H_4COOCH_3$ (912 kJ mol^{-1}), which values were calculated by use of the PM3 method [11,12].

On the other hand, the MIKE spectra in Fig. 1b and c are quite different from the corresponding reference MIKE spectra in Fig. 3b and c. Instead of the five peaks observed for ions $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, only one is found in the MIKE spectra of ions $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ (*m*/*z* 107, loss of CO, KER: 17 and 22 meV, respectively). The MIKE spectra in Fig. 1b and c, except for the peak at *m*/*z* 103, the intensity of the peak at *m*/*z* 120 and the different peak shape for the signal at *m*/*z* 107, are similar to that of Fig. 3a.

Consequently, it may be concluded that in the cases of **2** and **3** the four ions (*m*/*z* 120 (part), *m*/*z* 107 (part), *m*/*z* 79 and 77 ions) are generated following charge migration to the *ortho* position of the benzene ring via the so-called hydrogen "ring-walk" [13,14] prior to the migration of CH_3O from the $COOCH_3$ group as occurring in the $(M - COOCH_3)^+$ ions from **1**.

The widths of the *m*/*z* 107 peaks in Fig. 1b and c are narrower than that in Fig. 1a, as described above. A part of the *m*/*z* 107 ions may be generated via other process, for example, migration of CH_3O to the original charge site, followed by the loss of CO. This migration may be initiated via an ion–neutral complex [15–22]. The moieties composing the ion–neutral complex can rotate with respect to each other before



$[\mathbf{4} - CH_3]^+$ m/z 135 (a)

$[\mathbf{5} - CH_3]^+$ m/z 135 (b)

$[\mathbf{6} - CH_3]^+$ m/z 135 (c)

Scheme 2. Nominal ion structures of the ion at *m*/*z* 135 from $\mathbf{4}^{\bullet+}$ to $\mathbf{6}^{\bullet+}$.

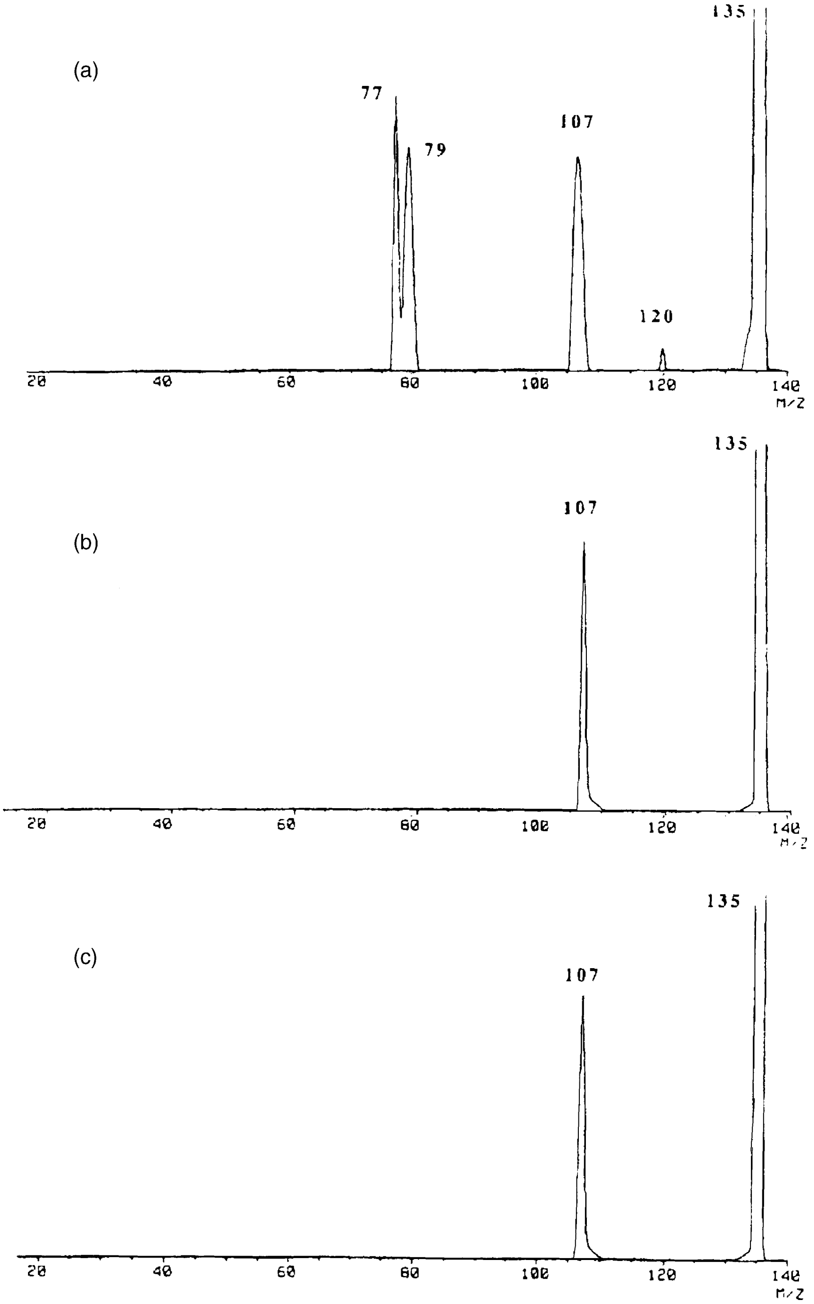
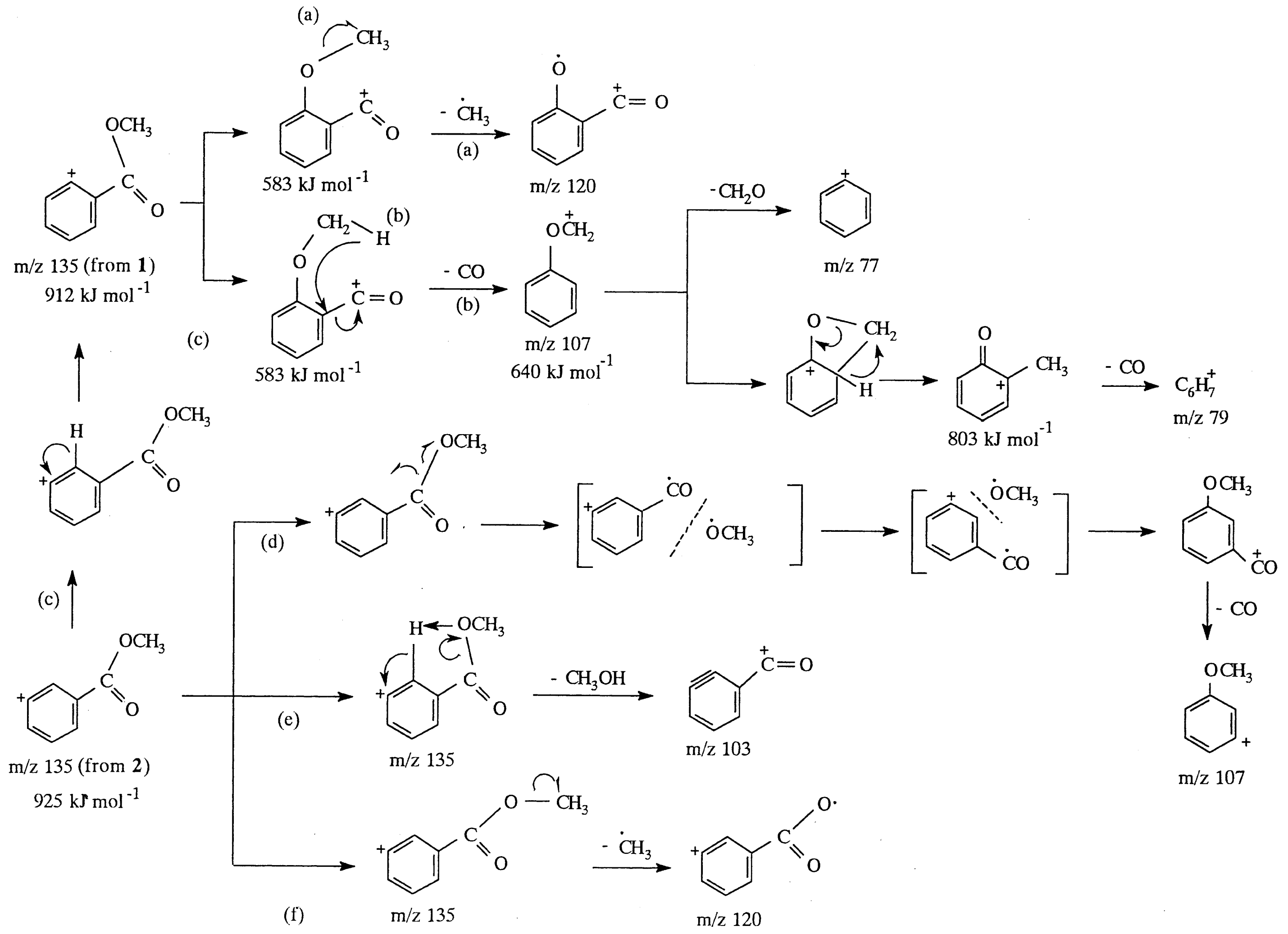


Fig. 3. MIKE spectra of the ions *m*/*z* 135 from (a) $\mathbf{4}^{\bullet+}$, (b) $\mathbf{5}^{\bullet+}$ to (c) $\mathbf{6}^{\bullet+}$.

migration, as shown in Scheme 3 (process (d)). One of the reasons the peaks at *m*/*z* 107 in Fig. 1b and c are not composite may be that the abundance of the ions generated via migration of CH_3O to the charge site in the *ortho* position is too low to result in a composite peak. Further, it can be concluded that the loss of methanol from the *m*/*z* 135 ions ($^+C_6H_4COOCH_3$) from **2** and **3** occurs prior to migration of CH_3O to the



Scheme 3. Proposed fragmentation pathways of the *m/z* 135 ions from $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$.

benzene ring, because no *m*/*z* 103 ion peak is observed in Fig. 3a. Similarly, the significantly enhanced loss of methyl from the *m*/*z* 135 ions ($^{+}C_6H_4COOCH_3$) from **2** and **3** most probably occurs from their unrearranged structure by a homolytic cleavage of the O–CH_3 bond to give the distonic [23] ions $^{+}C_6H_4COO^{\bullet}$ (Scheme 3 (process (f)). This is in agreement with the critical energy for the decompositions of $^{+}C_6H_4COOCH_3$ ions to the *m*/*z* 120 and 103 being lower than that of the same ions to the *m*/*z* 79 and 77, as described later.

The losses of the second CO and CH_2O from the *m*/*z* 107 ions occur following the sequential methoxy group migration to the charge site in the *ortho* position of the benzene ring. Hydride migration occurs from the migrated methoxy group to the incipient charge site upon loss of the first CO. This rearrangement results in the formation of the $C_6H_5OCH_2{}^{+}$ ion, which is much more stable than the isomeric $CH_3OC_6H_4{}^{+}$ ion (640 and 845 kJ mol^{-1}, respectively [24]), and explains the peak broadening of *m*/*z* 107. The $C_6H_5OCH_2{}^{+}$ ion is known to decompose into the *m*/*z* 79 and 77 ions [24]. The elimination reactions of CO and CH_2O from the *m*/*z* 107 ions appear to be very fast because they occur in the same field-free region where the *m*/*z* 107 ions are both generated and decompose into the *m*/*z* 79 and 77. This is also supported by the fact that the peak at *m*/*z* 107 is very small in the mass spectrum of **4** (<0.5%), in contrast to that in the spectrum of **5** (14.5%).

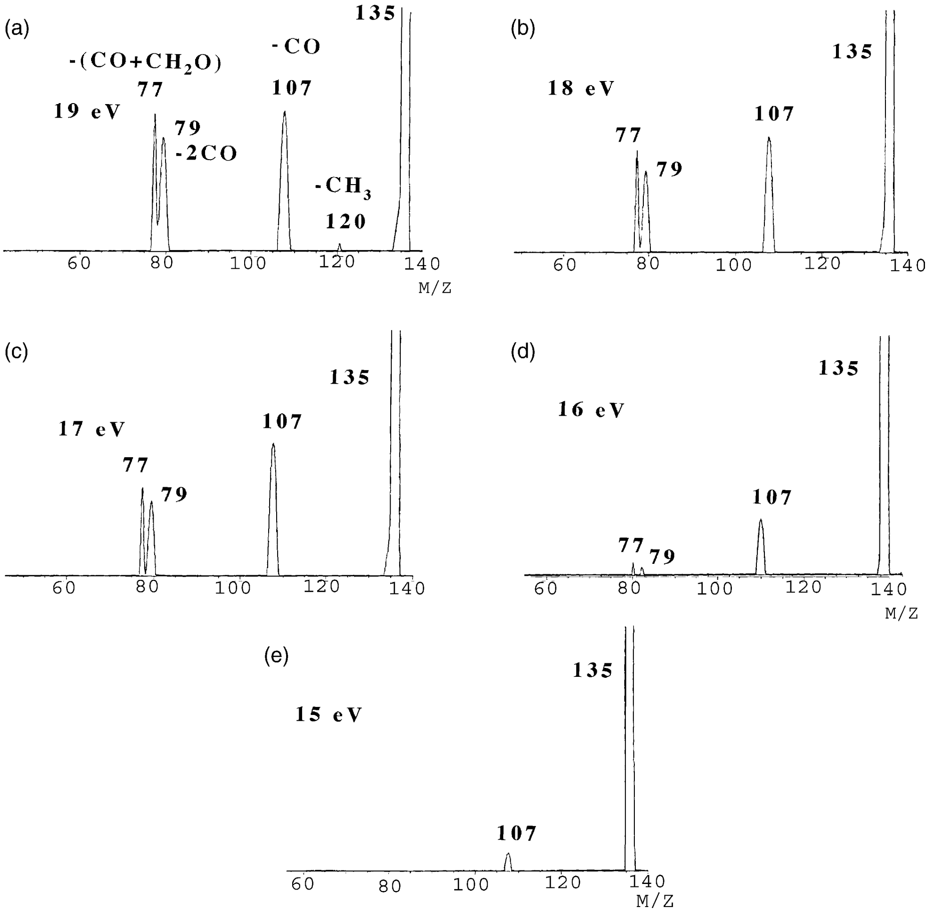


Fig. 4. MIKE spectra of the ions at *m*/*z* 135 for $\mathbf{4}^{\bullet +}$ generated at nominal (a) 19 eV, (b) 18 eV, (c) 17 eV, (d) 16 eV, and (e) 15 eV.

The proposed fragmentation pathways of the *m*/*z* 135 ions from **1** and **2** are summarized schematically in Scheme 3 on the basis of the experimental observations described above. The heats of formation of several ions either available from the literature or calculated by the PM3 method are also given in Scheme 3.

Fig. 4 shows the MIKE spectra of the *m*/*z* 135 ions from **4**, not from **1**, which were obtained at nominal 19–15 eV electron energies and recorded at 1.0 eV intervals. This is because the abundance of the *m*/*z* 135 ions for **1** is too low to allow measurement of their low energy MIKE spectra. In the MIKE spectrum taken at 14 eV electron energy, no fragment ion peaks could be detected. From Fig. 4, we can estimate that the critical energies for decompositions of the *m*/*z* 135 ions from **4** decrease in the order $CH_3 > 2CO \doteqdot (CO + CH_2O) > CO$. From the low energy MIKE spectra of the *m*/*z* 135 ions from **2** (not shown), we can also estimate that the critical energies for decompositions of these 135 ions decrease in the order $(CO + CH_2O) > 2CO > CO \doteqdot CH_3OH > CH_3$. This is in line with the proposed decomposition pathways shown in Scheme 3 where the critical energy for the loss of CO (*m*/*z* 107) has been assumed to be lower than those for the losses of 2CO (*m*/*z* 79) and $CO + CH_2O$ (*m*/*z* 77), that is, the *m*/*z* 79 and 77 ions are generated from the *m*/*z* 107 ions.

4. Conclusions

(1) The decompositions of the *m*/*z* 135 $(M - COOCH_3)^+$ ions from **1** and a substantial part from **2** and **3** occur following the migration of CH_3O from the $COOCH_3$ group to the charge site in the *ortho* position of the benzene ring.

(2) In portions the *m*/*z* 135 ions from **2** and **3**, the charge site in the *ortho* position of the benzene ring is generated through the so-called hydrogen “ring-walk”. Part of the *m*/*z* 107 ions from **2** and **3** are generated via migration of CH_3O to the original charge site, followed by the loss of CO.

(3) The unrearranged *m*/*z* 135 ions from **2** and **3** eliminate both methanol and a methyl radical, the latter reaction leading to the formation of the distonic ions $^+C_6H_4COO^\bullet$.

(4) Both the generation of metastable *m*/*z* 107 ions from **1** (and part of the ions from **2** and **3**) and their further decomposition into the ions *m*/*z* 79 and 77 by the competing losses of CO and CH_2O, respectively, occur in the same field-free region.

(5) The critical energies for decompositions of *o*-$CH_3OC_6H_4CO^+$ ions (*m*/*z* 135) from **4** decrease in the order $CH_3 > 2CO \doteqdot (CO + CH_2O) > CO$.

(6) The critical energies for decompositions of $^+C_6H_4COOCH_3$ ions (*m*/*z* 135) from **2** decrease in the order $(CO + CH_2O) > 2CO > CO \doteqdot CH_3OH > CH_3$.

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