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RESEARCH ARTICLE

Formation of Carbon Dioxide Attached Fragment Ions in the Fragmentation of Deprotonated Tolfenpyrad and Tebufenpyrad

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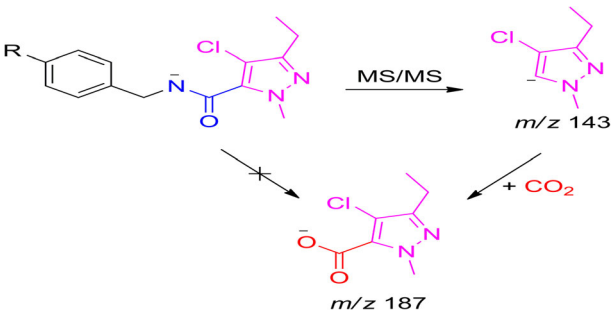

Abstract. The in-source collision-induced dissociation (CID) and MS/MS mass spectra of deprotonated tolfenpyrad and tebufenpyrad both showed an unusual fragment ion at *m/z* 187, but its fragmentation pattern and structure could not be explained by logical neutral losses. Accurate mass measurement indicated that the mass difference between this fragment ion and the dominant fragment ion at *m/z* 143 equaled to a carbon dioxide (CO_2) molecule. The isolation of the fragment ion *m/z* 143 in the mass analyzer could spontaneously give rise to the ion *m/z* 187. The Gibbs free energy of carbon dioxide addition to deprotonated pyrazole ion was significantly negative from the computational results. According to these results, we derived a proposal for the formation and structure of the ion *m/z* 187, which was an attachment of molecular carbon dioxide to the fragment ion *m/z* 143 to produce a carboxylate anion. The trace carbon dioxide was speculated to be derived from the residual atmosphere or collision gas in the instrument. This study is valuable for the qualitative and quantitative mass spectrometry analysis of pesticides containing the pyrazole functional group.

Keywords: Carbon dioxide addition, Tebufenpyrad, Tolfenpyrad, Fragmentation

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Introduction

Mass spectrometry (MS) has been a technical cornerstone in determining the molecular weight (even elemental composition using high-resolution MS) of a molecule and in gaining partial structural insights using multistage mass spectral fragmentations. For the analysis of thermolabile and nonvolatile polar compounds, the electrospray ionization mass spectrometry (ESI-MS) is a prior choice. Especially the coupling of high-performance liquid chromatography (HPLC) to ESI-MS serves as a routine tool in dealing with mixture analysis. As a soft ionization method, ESI mostly yields quasimolecular ion including protonated ion, deprotonated ion, and other ion adducts of the intact molecule. There is none or very little fragmentation information that can reveal the structure of the analyte of interest. Therefore, ion activation/fragmentation techniques such as tandem mass spectrometry (MS/MS), multistage mass spectrometry (MS^n), and in-source collision-induced dissociation (CID) are used to induce the fragmentation of the analyte of interest to produce abundant product ions that can be applied for the structural analysis. The

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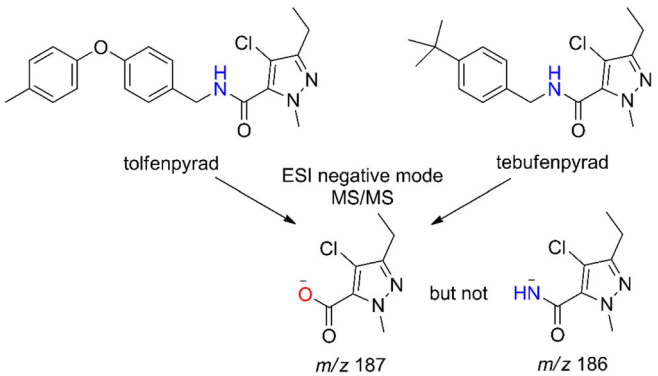

Figure 1. The chemical structures of tebufenpyrad and tolfenpyrad and the unusual fragment ion generated in the fragmentation of their deprotonated ions

ion activation/fragmentation in MS/MS or MS^n occurs under high vacuum gas-phase conditions, so the fragmentation reaction can exclude the interference of other compounds or solvents and clearly present the structural characteristics of the target ions. The improved knowledge on the fragmentation of protonated or deprotonated ions in the past two decades has enabled tremendous advances in the structural elucidation of small molecules using electrospray ionization-based mass spectrometry [1, 2].

However, we often encountered a number of difficulties in MS/MS or MS^n spectra interpretation because they usually contained peaks which could not directly arisen from the precursor ion. On the one hand, a large part of them arose from the rearrangement of precursor/intermediate ions. On the other hand, a few peaks were found to be due to reaction of the fragment ions with the residual gas/solvent molecules in the collision cell. The formation of water adduct ions in MS/MS or MS^n was commonly observed [3–8], because water molecules had been found to be accessible to be delivered to the CID region from the collision gas or electrospray solvent. Other small molecules (methanol, acetonitrile, etc.) attachment also could be observed if the corresponding molecule was used as the electrospray solvent [9, 10]. In some special cases, intriguing association

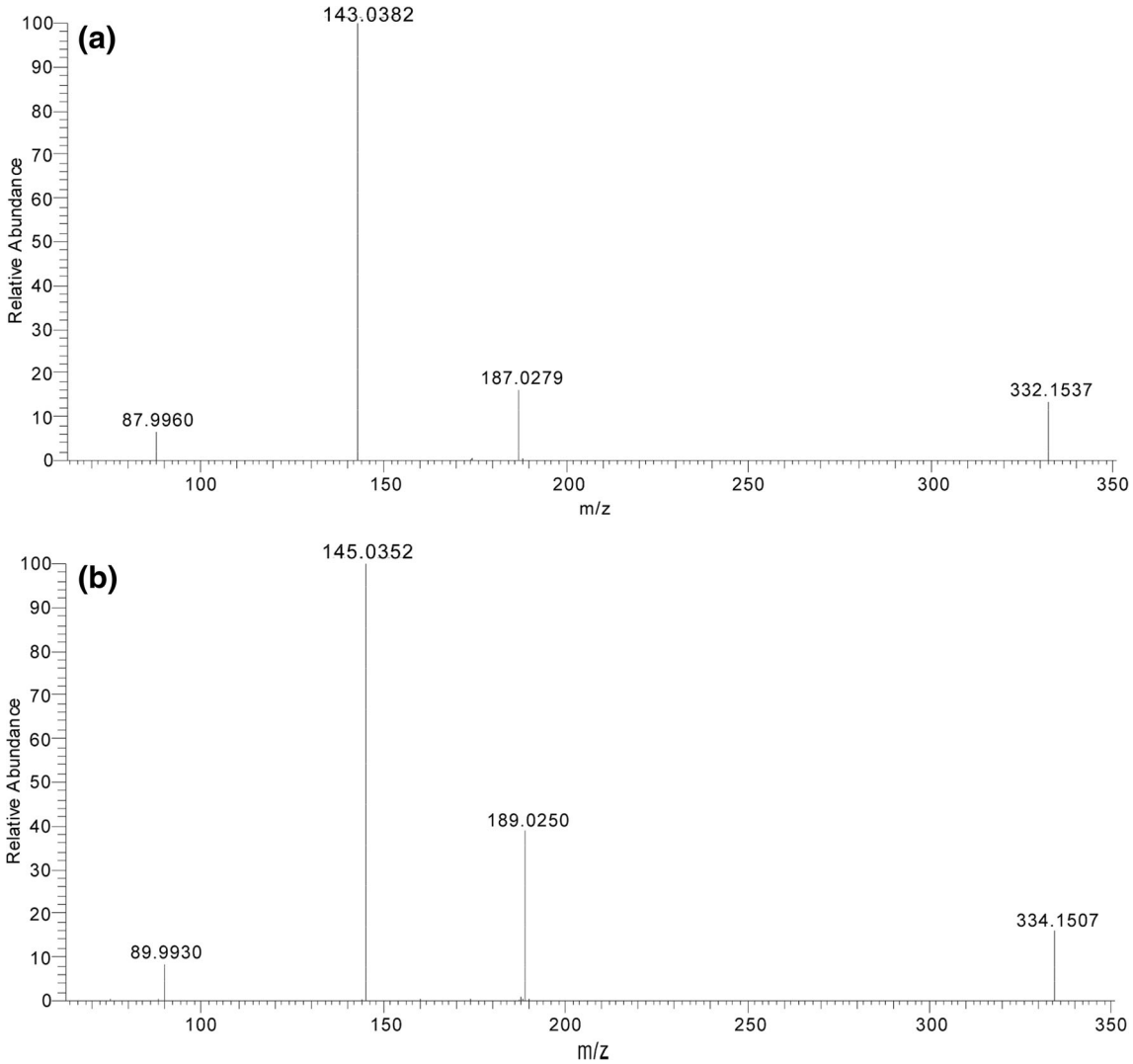

Figure 2. The MS/MS mass spectra of the $[M–H]^-$ ions of Cl^{35}-tebufenpyrad (**a**) and Cl^{37}-tebufenpyrad (**b**)

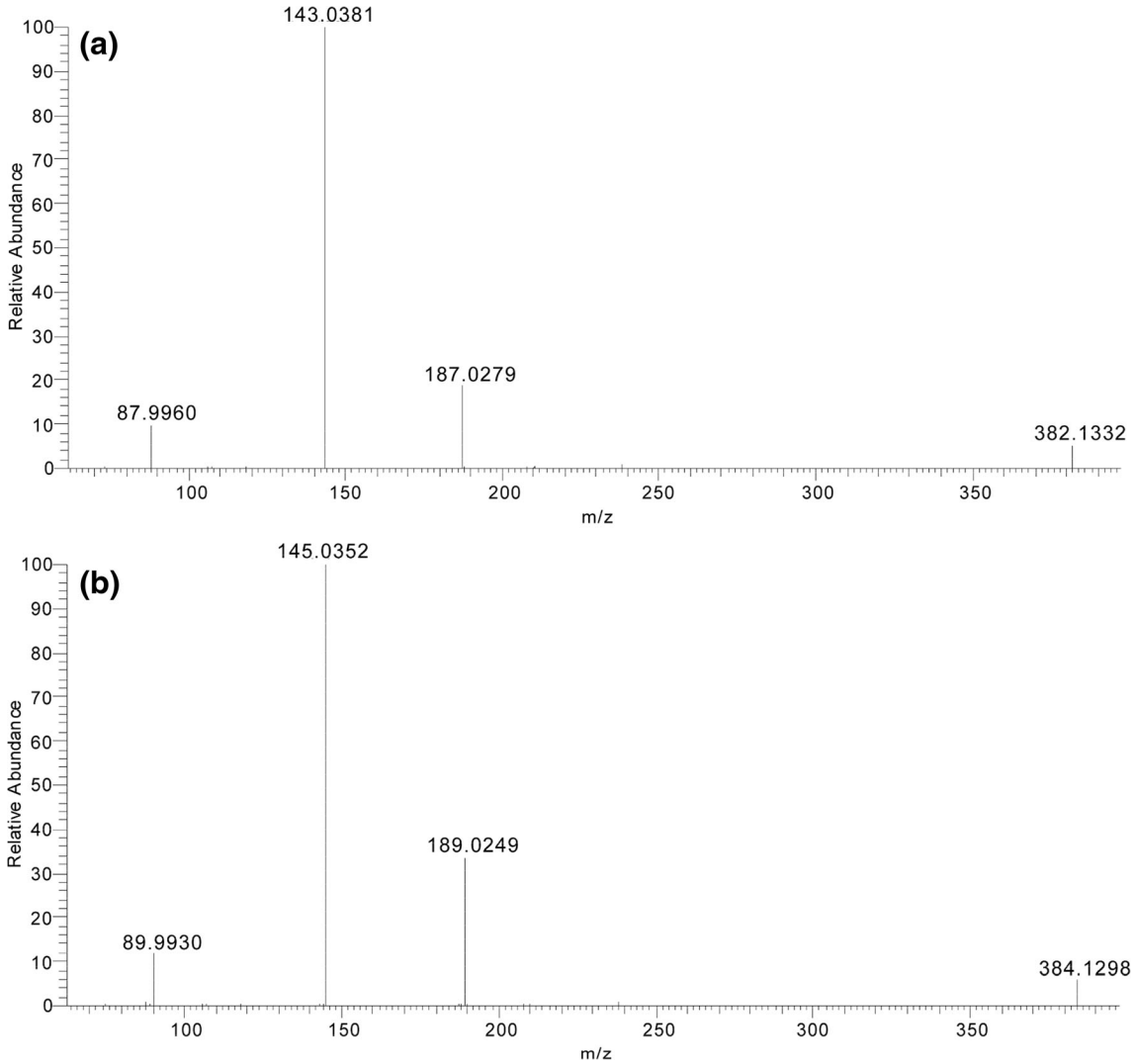

Figure 3. The MS/MS mass spectra of the $[M–H]^-$ ions of Cl^{35}-tolfenpyrad (**a**) and Cl^{37}-tolfenpyrad (**b**)

products of N_2 or O_2 addition to fragment ions had been reported [11–13]. These abnormal product ions would interfere with structural analysis and even led to obscure results.

Tebufenpyrad and tolfenpyrad are broad-spectrum pyrazole acaricides used in the control of tetranychus and panonychus in fruits, tea, vegetables, and other crops. High-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) is a routine method to determine the residue of these two pesticides in products [14, 15]. In our recent study, we found their fragmentation patterns in negative mode were almost the same to generate the same fragment ions. It was intriguing that one of the fragment ions at *m/z* 187 contained two oxygen atoms which was confirmed by high-resolution mass spectrometry (Figure 1). This abnormal fragment ion (*m/z* 187 but not *m/z* 186) seemed impossible to be produced directly from the precursor ion. Thus, the focus of the present study was to gain insight into the source of this abnormal fragment ion and its formation mechanism.

Table 1. Accurate Masses and Elemental Compositions of Product Ions Observed in the MS/MS Spectra of the $[M–H]^-$ Ions of Cl^{35}- and Cl^{37}-Tebufenpyrad

Observed *m/z*	Elemental composition	Theoretical *m/z*	Error (ppm)
332.1537	$C_{18}H_{23}Cl^{35}N_3O$	332.1535	0.6
187.0279	$C_7H_8Cl^{35}N_2O_2$	187.0280	−0.5
143.0382	$C_6H_8Cl^{35}N_2$	143.0381	0.7
87.9960	$C_3H_3Cl^{35}N$	87.9960	0
334.1507	$C_{18}H_{23}Cl^{37}N_3O$	334.1506	0.3
189.0250	$C_7H_8Cl^{37}N_2O_2$	189.0250	0
145.0352	$C_6H_8Cl^{37}N_2$	145.0352	0
89.9930	$C_3H_3Cl^{37}N$	89.9930	0

Experimental

Materials

Tolfenpyrad, tebufenpyrad, and 1-methylpyrazole-5-carboxylic acid standards used in this study were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China),

respectively. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, USA). Water-O^{18} (97% atom, O^{18}) was purchased from Beijing InnoChem Science and Technology Co., Ltd. (Beijing, China). Deionized water was purified with a Millipore Milli-Q plus ultrapure water purification system (Billerica, MA, USA). The tolfenpyrad and tebufenpyrad were prepared in different solvents (methanol, 1:1 methanol/water, 1:1 acetonitrile/water, and 1:1 acetonitrile/water-O^{18}) at a final concentration of 10 μg mL^{-1}.

Instrumentation and MS Conditions

The MS/MS experiments were performed on a Q Exactive hybrid quadrupole-orbitrap mass spectrometer equipped with a heated electrospray ionization source (Thermo Fischer Scientific, Bremen, Germany). Ionization in ESI negative mode was performed using the following settings: spray voltage 3.1 kV, sheath gas (N_2) flow rate 35 arb (arbitrary units), auxiliary gas (N_2) flow rate 10 arb, heated capillary temperature 320 °C, S-lens radio frequency (RF) level 50, max injection time 100 ms, and AGC target 1×10^6. The fore vacuum, high vacuum, and ultra-high vacuum of the instrument were 1.5 mbar, 3.6×10^{-5} mbar, and 1.8×10^{-10} mbar, respectively. In MS/MS experiments, the precursor ions were selected with an isolation window of ± 0.5 Da. The MS/MS spectra were obtained with nitrogen (99.99%) as the collision gas. The normalized collision energy (NCE) was set at 20%. A solution containing the tolfenpyrad or tebufenpyrad (10 μg mL^{-1}) was infused to the mass spectrometer with a syringe pump at a flow rate of 20 μL min^{-1}. The data were processed using Thermo Xcalibur 3.0 software.

Results and Discussion

The MS/MS spectra of the $[M–H]^-$ ions of tebufenpyrad (*m/z* 332) and tolfenpyrad (*m/z* 382) are almost the same (Figures 2A and 3A). They yield three major product ions at *m/z* 87, 143, and 187. When the $[M–H]^-$ ions are generated from different ESI solvents (methanol, 1:1 methanol/water, 1:1 acetonitrile/water, and 1:1 acetonitrile/water-O^{18}), their MS/MS spectra and the relative abundances of product ions have no obvious difference (Figures S1 and S2 in the supporting information). Both tebufenpyrad and tolfenpyrad contain a chlorine atom, so significant $[M+2–H]^-$ ions at *m/z* 334 and 384 (~30%) can be observed respectively in their full-scan mass spectra. The mass-to-charge (*m/z*) value of the fragment ions generated from the Cl^{37} isotopes are all 2 larger than that from the Cl^{35} isotopes (Figures 2B and 3B) that indicates the three fragment ions all contain a chlorine atom. The accurate masses and simulated elemental compositions of product ions observed in the MS/MS spectra of the $[M–H]^-$ ions of tebufenpyrad are shown in Table 1. It is interesting that the fragment ion *m/z* 187 contains two oxygen atoms which is even one more oxygen atom than the parent ion (*m/z* 332), so it is difficult to figure out the structure of this fragment ion.

The dominant fragment ion *m/z* 143 is a deprotonated substituted pyrazole ion which is produced by loss of an isocyanate neutral molecule. Neutral loss of isocyanate is a common fragmentation pattern for the dissociation of deprotonated amides [16, 17]. Comparison of the simulated elemental compositions of fragment ions *m/z* 143 and 187 shows that the latter ion has one more carbon atom and two oxygen atoms than the former ion. Therefore, we proposed that the ion *m/z* 187 was formed from the fragment ion *m/z* 143 by

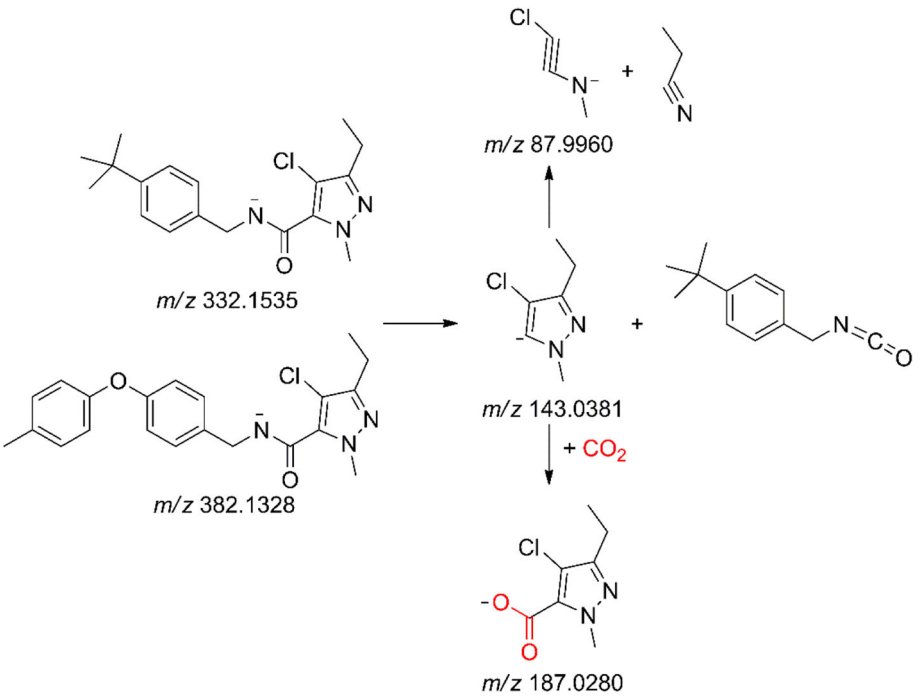

Figure 4. The proposed fragmentation mechanism of deprotonated tebufenpyrad and tolfenpyrad

attachment of a molecular carbon dioxide (CO_2). The formation mechanism of the product ions in the fragmentation of deprotonated tebufenpyrad is proposed in Figure 4. Residual gas (N_2, O_2) or solvent (H_2O, CH_3OH, CH_3CN) adduct

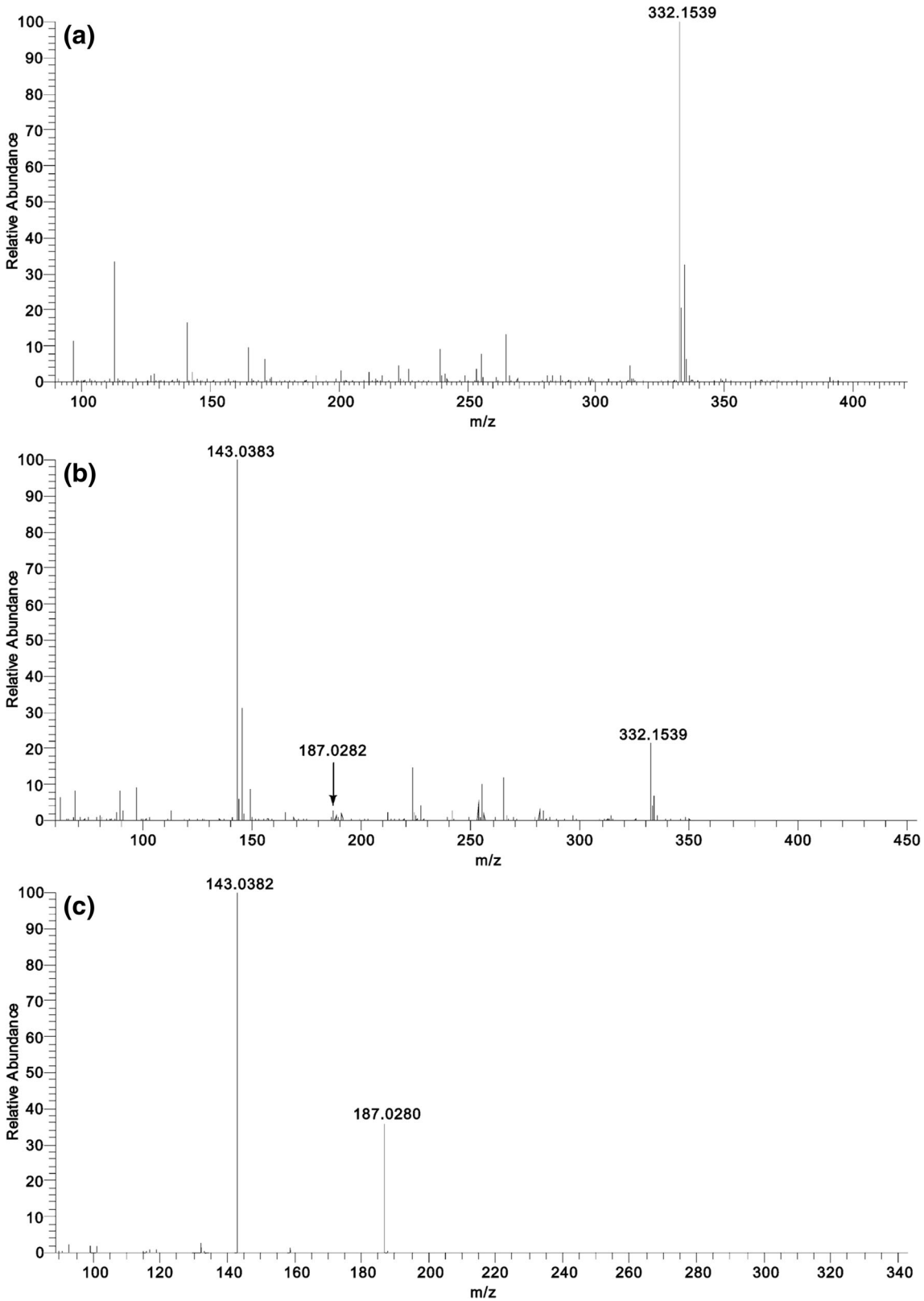

Figure 5. The full-scan mass spectrum of deprotonated tebufenpyrad (**a**), in-source CID mass spectrum of deprotonated tebufenpyrad (20 eV) (**b**), and MS/MS mass spectrum of the fragment ion *m/z* 143 (NCE 10%) (**c**)

Table 2. The Relative Abundances of Product Ions *m/z* 143 and 187 by Setting Different Ion Injection Times in MS/MS Mode (NCE 10%) in Isolation of Ion *m/z* 143 Which Is Generated from In-source CID of Deprotonated Tebufenpyrad

Ion injection time (ms)	The relative abundance of *m/z* 143 ion (%)	The relative abundance of *m/z* 187 ion (%)
10	100	9
100	100	35
500	100	79
1000	28	100

formation to gas-phase ions in mass spectrometry has been reported several times [3–13]. However, to our knowledge, attachment of CO_2 to fragment ions in tandem mass spectrometry on a commercial instrument has rarely been reported. The presence of these adduct ions often complicates MS/MS spectra interpretation and leads to dubious identifications. After CO_2 addition, the deprotonated pyrazole ion (*m/z* 143) is transformed to a pyrazole carboxylate anion (*m/z* 187), which may mislead us to make a wrong identification that the parent ion contains a carboxyl group or an ester group.

Trapping carbon dioxide by adduct formation with organic molecules such as nitrogen heterocyclic carbenes has attracted much attention during the last decades due to the growing concern on the greenhouse effect of carbon dioxide and organic synthetic challenge to incorporate carbon from cheap and abundant sources [18–21]. It is known that some anions such as anilide anion [22], phenoxide anion [23], allenyl anion [24], and phenyl anion [25] act as nucleophiles and react with CO_2 in gas-phase ion/molecule reactions.

In the Q orbitrap instrument, the C-trap is used to collect and store ions from the Q until a certain amount is reached (collisional cooling of the ions with a bath gas), and then the ions are delivered into the orbitrap analyzer. The addition of CO_2 probably takes place in the C-trap. According to the degree of vacuum in different regions of the instrument, the pressure in the C-trap is about 3.6×10^{-5} mbar. The concentration of CO_2 in atmosphere is known to be about 0.04% by volume, and the purity of collision gas (N_2) is greater than 99.99%. So, the partial pressure of CO_2 in the C-trap is roughly estimated to be 1.4×10^{-8} mbar. This pressure is reasonable for the occurrence of gas-phase ion/molecule reactions in view of the collision rate [26] and a recent ion/molecule reaction study [27].

To further confirm that the ion at *m/z* 187 was formed from *m/z* 143 by addition of CO_2, an isolation experiment was performed. In the full-scan mass spectrum of deprotonated tebufenpyrad (Figure 5A), a dominant $[M–H]^-$ ion *m/z* 332 is observed, but the ions *m/z* 143 and 187 are not formed. By using in-source CID, the fragment ion *m/z* 143 is generated as a dominant ion, and the ion *m/z* 187 is also observed with a relative abundance of 3% (Figure 5B). When the ion *m/z* 143 is isolated in the C-trap (the normalized collision energy cannot be set to zero and its minimum value is 10%), the ion *m/z* 187 can spontaneously form with a relative abundance of 35% (Figure 5C). Many factors may affect the abundance of the CO_2 adduct ion. As shown in Table 2 (Figure S3 in the supporting information), as the ion injection time increases in isolation of ion *m/z* 143, the relative abundance of ion *m/z* 187 also increases. Longer injection times mean that the ion *m/z* 143 can be stored in the C-trap for a longer period of time, giving it more opportunity to react with trace CO_2. Although the max injection time in the in-source CID mode is set to be 100 ms, the actual ion injection time is only 7.6 ms, because in this mode, all the ions in the full-scan are injected into the mass analyzer, and it quickly reaches the upper limit of another parameter, AGC target. In the MS/MS mode, only one ion *m/z* 143 is injected into the C-trap, and it is unable to reach the upper limit of AGC target within the max injection time. So, the actual ion injection time is 100 ms in the MS/MS mode. This should be one of the important reasons that the observed relative abundance of *m/z* 187 in the MS/MS mode is higher than that in the in-source CID mode. We also repeated the

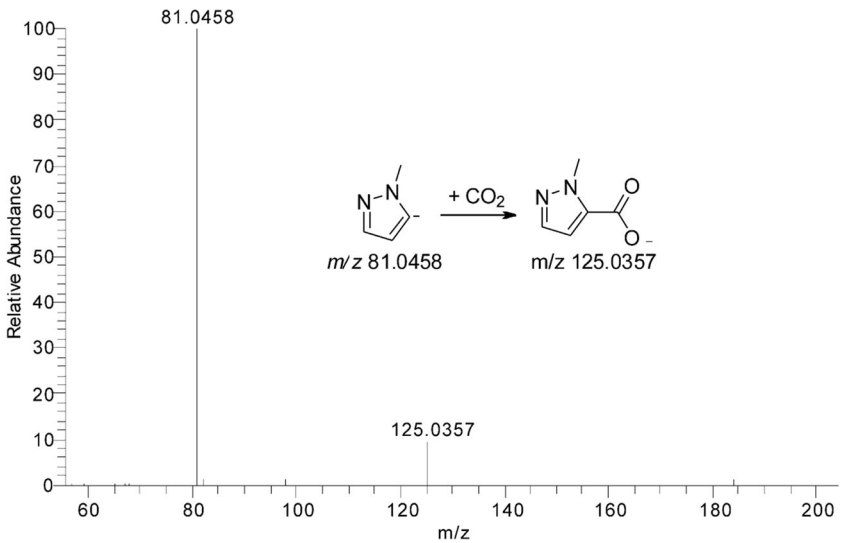

Figure 6. The MS/MS mass spectrum of the ion *m/z* 81 generated from deprotonated 1-methylpyrazole-5-carboxylic acid (*m/z* 125) in the full-scan mode (NCE 10%)

experiments on a LTQ orbitrap mass spectrometer, and the mass spectra are shown in Figure S4 in the supporting information. The CO_2 adduct ion (*m/z* 187) can be observed with a relative abundance of 0.7%. The lower relative abundance of *m/z* 187 formed in LTQ orbitrap than that in Q orbitrap is probably due to different sources of the collision gases, different instrumental parameters, etc.

Obviously, the spontaneous adduct formation of CO_2 to the deprotonated pyrazole ion indicates that it is an exothermic reaction. The Gibbs free energy of this reaction was calculated and estimated using the DFT method at the B3LYP/6-311++G(2d,p) level of theory. The computed ΔG was −98.5 kJ mol^{-1} that supported the occurrence of CO_2 adduct reaction in mass spectrometry.

The above study shows that the pyrazole anion has a strong nucleophilicity to CO_2, and it can capture a background CO_2 molecule in the commercial mass spectrometer. In order to verify whether this phenomenon has certain universality, we studied another compound containing a pyrazole functional group. A simple 1-methylpyrazole anion (*m/z* 81) can be readily formed from deprotonated 1-methylpyrazole-5-carboxylic acid (*m/z* 125) by loss of 44 u in the full-scan mode. The isolation of 1-methylpyrazole anion (*m/z* 81) in MS/MS mode can give rise back to the *m/z* 125 anion by CO_2 addition (Figure 6). In addition, there should be other anions having the same behavior as reported in this work, and we will continue to carry out such research.

Conclusions

In the fragmentation of the $[M–H]^-$ ions of tolfenpyrad and tebufenpyrad, an unusual product ion at *m/z* 187 was observed. Our experimental and computational investigations showed that this unusual product ion was rather an attachment of molecular carbon dioxide to the fragment ion *m/z* 143, which was the dominant fragment ion in the mass spectra. After CO_2 addition, a new structural fragment, carboxylate anion (*m/z* 187), was formed, which was not present in the precursor ion. Although the attachment of various small molecules from the residual gas to gas-phase ions in mass spectrometry has been reported, the CO_2 adduct formation is rarely observed. Our findings indicate that the pyrazole anion has a strong nucleophilicity to CO_2. Besides, the correct interpretation of such adduct ions in the mass spectra can help us avoid their interference with structural elucidation of relevant analytes containing the pyrazole functional group using multistage mass spectrometry.

Acknowledgements

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