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Collision induced dissociation of deprotonated glycolic acid

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Abstract

Glycolic acid has been recently found to be a contaminant in a drinking water sample from Canada. An in-depth study was conducted to establish a mechanism of the unique fragmentation patterns of deprotonated glycolic acid by using ion trap and Q-TOF tandem mass spectrometry. Tandem mass spectrometry information from analysis of isotopically labeled (^{13}C and D) glycolic acids revealed two general dissociation pathways of glycolate. Major fragmentation patterns, initiated by nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon, proceed through an α-lactone intermediate ion and result in formation of glyoxalate, hydroxymethanolate, formate, and hydroxyl anions. The hydroxyl anion was detected as a species solvated by a molecule of water or methanol. Minor dissociation patterns originate from the initial proton transfer from the α-carbon to a negatively charged oxygen of the carboxylic group and lead to formation of hydroxymethanolate and hydrated hydroxyl ion. Proposed mechanisms of all fragmentation patterns of glycolate are presented in detail. Postulated gas phase dissociation reactions are described in terms of charge redistribution following collisional excitation. This approach has facilitated elucidation of the unique fragmentation pathways of glycolate and provided explanation for significant differences observed in dissociation of structurally similar hydroxycarboxylic acids.

Keywords: Glycolic acid; Glycolate; CID; Ion trap; Fragmentation patterns

1. Introduction

Glycolic acid or α-hydroxyacetic acid is a widely used chemical in skincare. It is used to reduce wrinkles and to treat acne in many patients around the world. Multiple studies have focused on optimization of the application of glycolic acid [1–3]. Current studies are evaluating the inhibitory effect of glycolic acid on UV induced skin tumor development [4]. Glycolic acid is also a useful compound in organic synthesis reactions including long chain polymerization processes [5]. The acute effects of the compound include possible irritation or burns upon contact with skin or eyes, as well as irritation or burns upon inhalation or ingestion [6]. The chronic effects of glycolic acid are relatively unknown. However, glycolic acid in lab rats was found to be toxic to kidneys and ingestion of glycolic acid on a daily basis was found to be associated with moderate maternal toxicity [7,8]. In a recent study conducted on highly polar non-target contaminants in drinking water hydroxycarboxylic acids have been identified as contaminants in a drinking water sample from Canada. Glycolic acid, not registered on EPA's regulated or candidate contaminant list, was found to be the most abundant contaminant in that particular drinking water at high ppm concentrations [9]. The identification of glycolic acid in drinking water was based on matching the CID spectrum of the unknown contaminant detected in drinking water with the CID spectrum the glycolic acid standard. Although the identification of glycolic acid was feasible, the identity of its dissociation products was poorly understood due to the fact that glycolic acid has exhibited different fragmentation patterns than larger hydroxycarboxylic acids. To gain understanding of fragmentation patterns of this small, highly polar compound, we used a combination of negative mode electrospray ionization with an ion trap mass analyzer and Q-TOF tandem mass spectrometry to analyze isotopically labeled standards of glycolic acid. Our goal was to establish a detailed mechanism for the fragmentation of glycolic acid in order to explain why dissociation patterns of glycolic acid are completely different from those observed in larger hydroxycarboxylic acids.

2. Experimental

Ammonium acetate, HPLC grade water, HPLC grade methanol and isotopically unlabeled glycolic acid were all pur-

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chased from Fisher Scientific (Nepean, ON). The $^{13}C_2$ and $^{13}C_1$ labeled glycolic acid standards were ordered from Sigma Aldrich (Oakville, ON). The 2,2-D_2 labeled glycolic acid standard was purchased from Cambridge Isotope (Andover, MA). Glycolic acid sample solutions at 100 μM concentration were prepared in buffer containing 0.1 mM ammonium acetate in 90/10 (v/v) HPLC grade methanol/HPLC grade water. The glycolic acid solutions were directly infused to an electrospray ionization source operated in the negative mode by a syringe pump at a flow rate of 3 μL/min.

A Q-TOF "Micro" mass spectrometer operated in the ion product mode was implemented to determine elemental compositions of dissociation products of glycolate. Tandem mass spectrometry MS^2 and MS^3 experiments of glycolic acid were carried out using a Finningan LCQ Deca Ion Trap mass spectrometer. An efficient transmission of fragile molecular ions of glycolic acid into the ion trap required setting the capillary voltage and tube lens offset voltage to 0 V and using the following ion optics parameters: multipole 1 offset = 5.5 V, lens voltage = 24.0 V, multipole 2 offset = 8.0 V, multipole Rf amplitude 120.0 V (p–p), and entrance lens = 50.0 V. The ion trap dissociation experiments were carried out, if not stated otherwise, at a q_z of 0.300, a normalized collision energy of 26 V, an isolation window of 1 a.m.u., and an activation time of 30 ms for MS^2 experiments and likewise for MS^3 experiments with the exception of a q_z of 0.420. The instrument was operated in the low mass setting to allow for detection of low mass ions.

3. Results and discussion

Fig. 1A shows the ion trap collision induced dissociation (CID) spectrum of deprotonated glycolic acids with five fragment ions detected at *m/z* 73, *m/z* 49, *m/z* 47, *m/z* 45 and *m/z* 35. A similar CID spectrum (not shown) of glycolate at *m/z* 75 was acquired on the Q-TOF mass spectrometer to establish elemental compositions of the detected dissociation products. The elemental formula of *m/z* 73 ($C_2HO_3^-$), *m/z* 47 ($CH_3O_2^-$), and *m/z* 45 (CHO_2^-) indicates that the fragment ions were generated from the molecular ion by elimination of H_2, CO, and CH_2O, respectively. The elemental composition of *m/z* 49 ($CH_5O_2^-$) and *m/z* 35 ($H_3O_2^-$), on the other hand, does not correspond to any logical neutral loss from the molecular ion ($C_2H_3O_3^-$). Dissociation patterns observed for *m/z* 75 glycolate or α-hydroxyacetate (Fig. 1A) are quite different from those established for *m/z* 89 lactate or α-hydroxypropanoate [9]. Only two common CID features are observed for glycolate and lactate: a lack of elimination of CO_2 from the molecular ion and formation of a fragment ion by elimination of H_2. However, the dissociation products of glycolate (Fig. 1A) generated by elimination of CO (*m/z* 47) and CH_2O (*m/z* 45) as well as the intriguing fragment ions at *m/z* 49 and *m/z* 35 have not been observed in the dissociation process of lactate. Finally, a common CID process of elimination of H_2O from hydroxycarboxylates [9] was not observed for glycolate. In order to explain such a distinctive behavior of two homologs, an in-depth study of the unique fragmentation patterns of glycolic acid was carried out using the sequential tandem mass spectrometry capabilities of an ion trap for analysis of isotopically labeled standards of glycolic acid. Fig. 1 represents MS^2 spectra of glycolate (Fig. 1A) and three isotopically labeled analogs containing ^{13}C carboxylic carbon (Fig. 1B), $^2D_2$ at the α-carbon (Fig. 1C), and two ^{13}C isotopes (Fig. 1D).

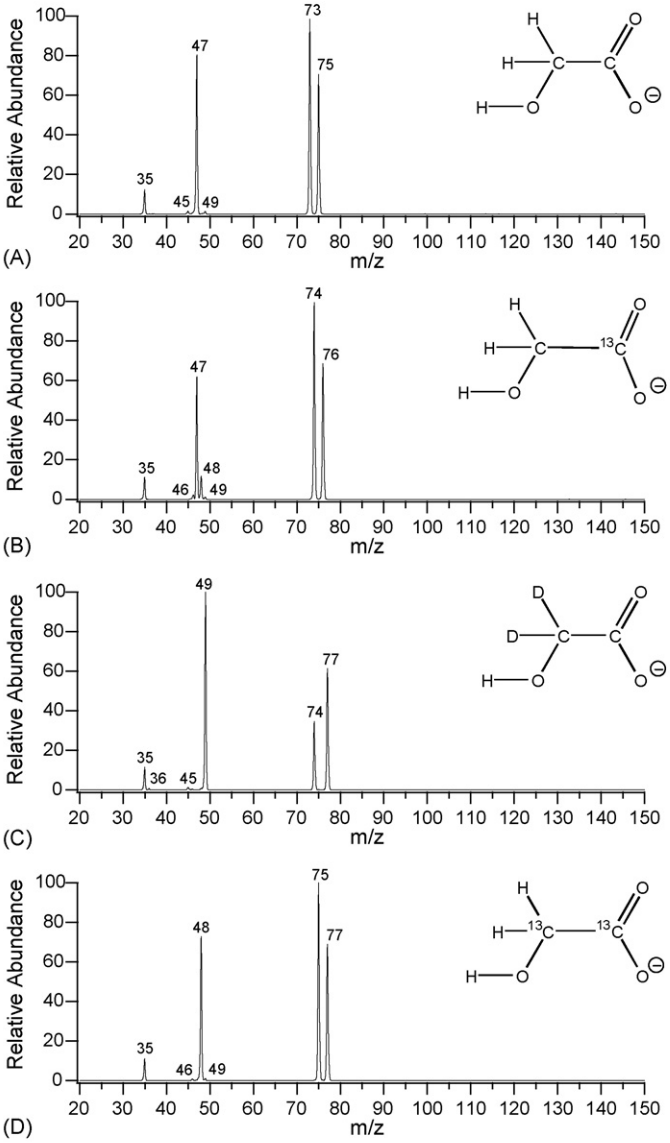

Fig. 1. Ion trap MS^2 spectra of deprotonated glycolic acids. (A) Glycolic acid, (B) 1-^{13}C labeled glycolic acid, (C) 2,2-D_2 labeled glycolic acid, (D) $^{13}C_2$ labeled glycolic acid.

The most abundant dissociation product of glycolate (*m/z* 75 in Fig. 1A) is the *m/z* 73 ion, which exhibits a loss of H_2 from the molecular ion. The MS^2 spectrum of isotopically labeled glycolate (*m/z* 77), with two deuterium atoms located on the α-carbon (Fig. 1C), clearly shows that elimination of molecular hydrogen involves the loss of the hydroxyl hydrogen along with a hydrogen from the α-carbon. This information was crucial to propose the mechanism of H_2 elimination from glycolate (Fig. 2A). The dissociation process is initiated by the nucleophilic attack of negatively charged carboxylic oxygen on the α-carbon fol-

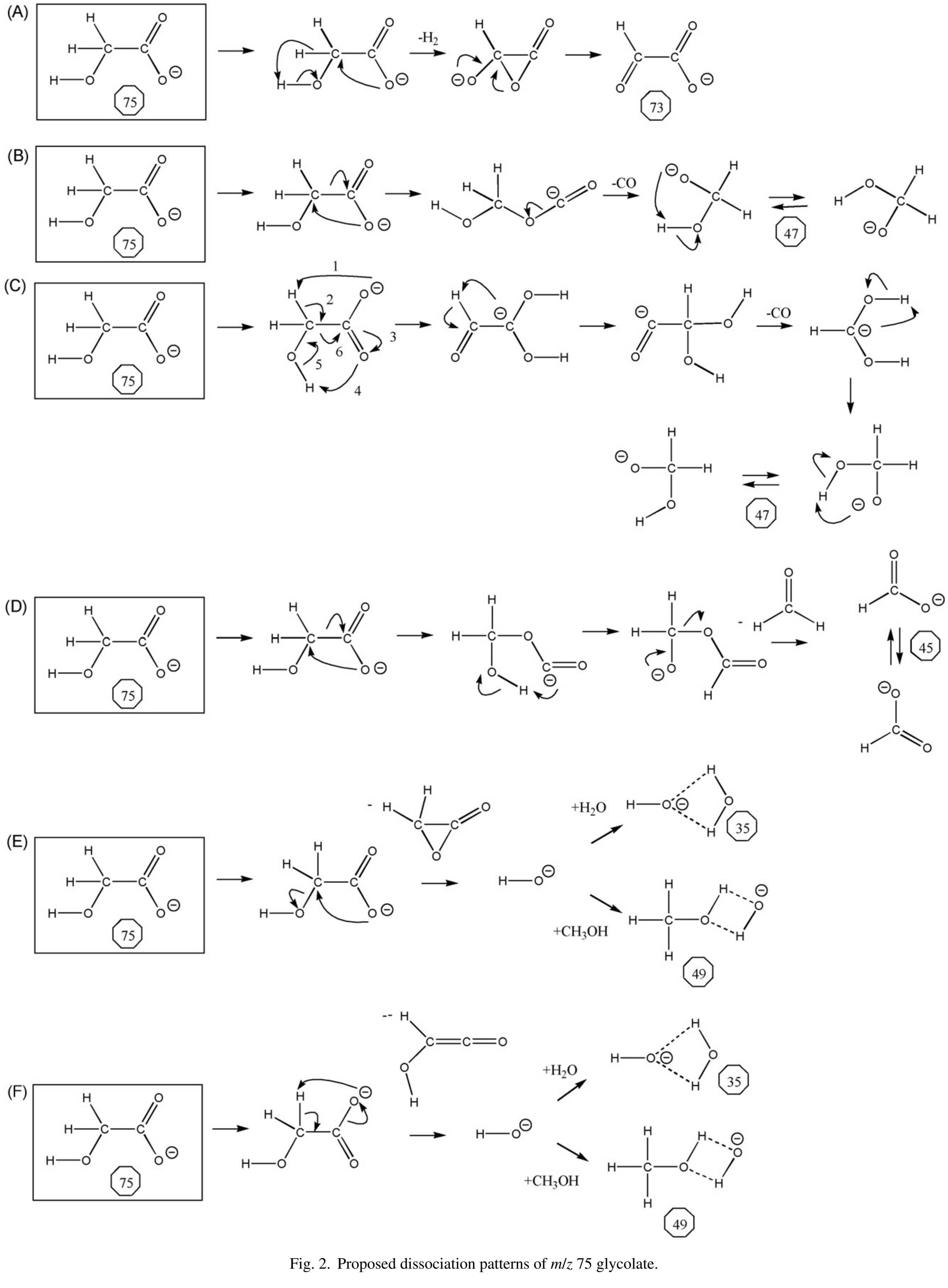

Fig. 2. Proposed dissociation patterns of *m*/*z* 75 glycolate.

lowed by the elimination of both a α-carbon hydrogen and the hydroxyl hydrogen in the form of H_2. The redistribution of negative charge in the structure of the α-lactone intermediate ion results in formation of glyoxalate (*m*/*z* 73). The mechanism for the formation of the *m*/*z* 73 ion demonstrates that the loss of a neutral molecule, such as the hydrogen molecule in this case, is feasible only when hydrogen atoms involved in H_2 elimination are located at adjacent atoms (vicinal elimination). An elimination of H_2, involving hydrogen atoms located at same atom (geminal elimination), does not occur. Such a general rule of neutral elimination was also observed in dissociation reactions of larger hydroxycarboxylic acids involving elimination of neutral molecules following a nucleophilic attack at an elimination site [9]. This important observation explains the lack of a dissociation reaction of glycolate that would lead to the formation of an *m*/*z* 57 fragment ion by the elimination of H_2O following the nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon. This was found to be possible when the hydrogen and hydroxyl group were located on different carbons (vicinal elimination). The process of H_2O elimination from glycolate, therefore, does not occur because it would have to involve a hydrogen and the hydroxyl group located at the same α-carbon.

The *m*/*z* 47 peak, observed in the MS^2 spectrum of glycolate in (Fig. 1A), represents a fragment ion generated by CO loss. The MS^2 spectrum of the *m*/*z* 76 glycolate standard, labeled with a ^{13}C carboxylic carbon (Fig. 1B), shows that either carbon can be lost in the form of CO leading to *m*/*z* 47 (loss of the carboxylic carbon) or *m*/*z* 48 (loss of the α-carbon) ions. These ions are produced in a 6:1 ratio, respectively. Fig. 2B and C illustrates two proposed fragmentation pathways involving the elimination of CO. The major process of CO elimination, engaging the loss of the carboxylic carbon (Fig. 2B), proceeds through the nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon, breaking the carbon–carbon bond, and forming the intermediate ion which eliminates CO to produce the *m*/*z* 47 hydroxymethanolate ion. The minor process of CO elimination, engaging the loss of the α-carbon (Fig. 2C), requires a series of proton transfers from the α-carbon site to the carboxylic moiety. The initial proton transfer from the α-carbon to a negatively charged oxygen of the carboxylic group leads to the second proton transfer from the hydroxylic oxygen to the carboxylic oxygen and subsequent formation of the resonance-stabilized intermediate ion. The proton transfer from carbon-2 to carbon-1 results in CO loss. The product of CO elimination rearranges by transferring a proton from a hydroxylic group to carbon-1 to form the *m*/*z* 47 hydroxymethanolate ion. Both dissociation pathways of glycolate by CO elimination produce fragment ions of the same structure, which differ only by which carbon atom they contain. The loss of a carboxylic CO, initiated by the nucleophilic attack of a carboxylic oxygen on the α-carbon is favored over the competitive, but minor process of CO loss originating from a proton transfer from the α-carbon to a carboxylic oxygen. The proposed mechanisms of CO elimination from glycolate suggest that the *m*/*z* 47 hydroxymethanolate ion, produced in the major pathway (Fig. 2B), would retain the identity of the two hydrogen atoms located at carbon-2 and the initial hydroxylic hydrogen would be shared by the two equivalent hydroxyl oxygens. The *m*/*z* 47 hydroxymethanolate ion, produced in the minor pathway involving a series of proton transfers (Fig. 2C), is represented by two equivalent structures in which either the initial hydroxylic hydrogen or an initial α-carbon hydrogen would be shared by the two equivalent hydroxyl oxygens. The proposed structures of the above mentioned *m*/*z* 47 ions have been verified by results of sequential (MS^3) tandem mass spectrometry experiments which will be discussed later.

The low intensity peak at *m*/*z* 45 (Fig. 1A) corresponds to a product generated by the loss of formaldehyde. The MS^2 spectra of isotopically labeled glycolates (Fig. 1B–D) provide evidence that the formaldehyde loss involves the elimination of the α-carbon moiety (carbon-2 plus two hydrogens at carbon-2). This observation is consistent with the proposed mechanism of the formation of *m*/*z* 45 illustrated in Fig. 2D. The nucleophilic attack of the negatively charged carboxylic oxygen on the α-carbon results in breaking the carbon–carbon bond and forming the intermediate ion. This intermediate ion then undergoes the intramolecular proton transfer from the hydroxyl group to carbon-1 producing the *m*/*z* 45 formate ion. The formation of the *m*/*z* 45 (H_2CO loss) is a competitive process with respect to the major pattern of the formation of the *m*/*z* 47 ion (CO loss involving carbon-1) because both reactions proceed through the same intermediate ion. The relative intensity of the *m*/*z* 47 and the *m*/*z* 45 peaks in the spectrum in Fig. 1A clearly indicates that the direct loss of CO from the intermediate ion (Fig. 2B) is much more favorable than the proton transfer form the hydroxyl group to the negatively charged carbon-1 at the CO elimination site (Fig. 2D). The proposed structure of the *m*/*z* 45 was supported by results of MS^3 experiments of this fragment ion. The *m*/*z* 45 ion did not produce dissociation products in CID and this result is consistent with the structure of formate.

The *m*/*z* 35 and *m*/*z* 49 ions observed in the spectrum in Fig. 1A appear not to be the direct fragmentation products of glycolate. The elemental compositions of these intriguing species suggest that both the *m*/*z* 49 $[(CH_3OH)OH^-]$ and *m*/*z* 35 $[(H_2O)OH^-]$ are non-covalent complexes of hydroxyl ions with methanol and water, respectively. It is expected and it has been shown [10] that CID regions (e.g., an ion trap or a quadrupole collision cell) contain enough solvent molecules (introduced with a collision gas or electrospray solvents) to facilitate ion solvent reactions in gas phase. The *m*/*z* 49 and *m*/*z* 35 species exhibited a fragile nature in MS^3 experiments when it was not possible to select these ions in the ion trap. Even the most gentle ion isolation conditions (a large *m*/*z* isolation window, a short duration of an isolation waveform) seemed to provide enough collisional energy to decompose these labile ions. Consequently, no tandem mass spectrometry information could be obtained. The spectra of isotopically labeled glycolates (Fig. 1) support the formation of hydroxyl ions solvated by water (*m*/*z* 35) and methanol (*m*/*z* 49). The mass spectrum of the deuterium labeled glycolate (Fig. 1C) shows that there are at least two dissociation mechanisms leading to hydroxyl ion adducts. The major process entails the formation of the hydroxyl ion water complex (*m*/*z* 35) incorporating the hydrogen from the hydroxyl group, whereas the minor process necessitates the formation of the hydroxyl ion complex (*m*/*z* 36) containing a hydrogen from the α-carbon. Fig. 2E illustrates the major dissociation pathway leading to formation of *m*/*z* 35 and *m*/*z* 49 ions from glycolate. The nucleophilic attack of a carboxylic oxygen on the α-carbon results in the formation of a hydroxide ion and the loss of α-lactone which may decompose further to formaldehyde and CO. The hydroxide ion is solvated in situ by a molecule of water or methanol to form a more stable adduct ion. Fig. 2F shows the minor dissociation pathway which leads to the formation of the *m*/*z* 35 water adduct from glycolate. A proton transfer from the α-carbon to a negatively charged oxygen of the carboxyl group results in the formation of a hydroxide ion and the loss of hydroxyketene. The hydroxide ion is solvated in situ by a water molecule. A similar process for the formation of the methanol adduct is likely to take place. However, the peak of the diagnostic product of this reaction (the *m*/*z* 50 ion in the spectrum of the deuterium labeled glycolate in Fig. 1C) could not be distinguished from spectral noise. The relative signal intensity of *m*/*z* 35 and *m*/*z* 36 ions in the same spectrum (Fig. 1C) indicates that the hydroxyl ion is preferentially generated in the reaction initiated by the nucleophilic attack on the α-carbon.

Attempts to isolate (select) and fragment ions observed in the MS^2 spectra (Fig. 1) were successful for *m*/*z* 73-like ($C_2HO_3^-$) and *m*/*z* 47-like ($CH_3O_2^-$) ions. *m*/*z* 45-like (CHO_2^-) ions could be isolated in the trap but did not generate dissociation products which would be observed above the *m*/*z* cut-off limit (*m*/*z* 15) of the detector. *m*/*z* 49-like ($CH_5O_2^-$) and 35-like ($H_3O_2^-$) ions could not survive an ion trap isolation process. Although no tandem mass spectrometry information was obtained with respect to *m*/*z* 45, *m*/*z* 49, and *m*/*z* 35 ions, their characteristic behavior in ion trap tandem mass spectrometry demonstrates that the *m*/*z* 45 ion is stable, whereas *m*/*z* 49 and *m*/*z* 35 species are very labile. This observation is in agreement with the proposed structures of these ions.

The postulated mechanism of H_2 elimination from glycolate (Fig. 2A) suggests formation of glyoxalate at *m*/*z* 73. MS^3 data for *m*/*z* 73-like ions (Fig. 3) support the proposed structure. The *m*/*z* 73 glyoxalate (Fig. 3A) produces the *m*/*z* 35 hydrated hydroxyl ion and *m*/*z* 45 fragment by CO loss. The MS^3 spectrum of the $^{13}C_1$ labeled glyoxalate at *m*/*z* 74 (Fig. 3B) shows that the elimination of CO involves at least two processes responsible for the detection of *m*/*z* 45 and *m*/*z* 46 ions. The *m*/*z* 46 peak is more intense than the *m*/*z* 45 peak, which means that for CO elimination the α-carbon is more readily lost than the carboxylic carbon. The major pathway of CO loss (Fig. 4A) involves nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon, breaking the carbon–carbon bond, and formation of the intermediate ion with a negative charge initially localized on carbon-1. If the intramolecular proton transfer between carbon-2 and carbon-1 of the intermediate ion is fast with respect to a rate of CO elimination, the abundance of each of two equivalent intermediate ions (Fig. 4A) should be the same at this stage of the dissociation process. A subsequent elimination of a CO from an intermediate ion should lead to equal formation of two types of formate ions retaining a different carbon atom in their structure. The second and less favorable loss of CO (Fig. 4B) originates from a proton transfer from the α-carbon to a negatively charged oxygen of the carboxyl group. This is followed by the formation of formate through a rearrangement involving a proton transfer from the hydroxyl group to carbon-1. The MS^3 spectrum of the $^{13}C_1$ labeled glyoxalate at *m*/*z* 74 (Fig. 3B) supports the postulated patterns of CO elimination. The intensity of the *m*/*z* 46 ion from the minor process of CO elimination involving carbon-1 adds only slightly to intensities of the *m*/*z* 45 (loss of CO involving carbon-1) and the *m*/*z* 46 (loss of CO involving carbon-2) ions from the major processes of CO elimination. Fig. 4C illustrates the dissociation pathway of glyoxalate which results in the formation of a hydrated hydroxyl ion observed in all MS^3 spectra of isotopially labeled species (Fig. 3). The proton transfer from the α-carbon to a negatively charged oxygen of the carboxyl group leads to formation of the hydroxyl ion

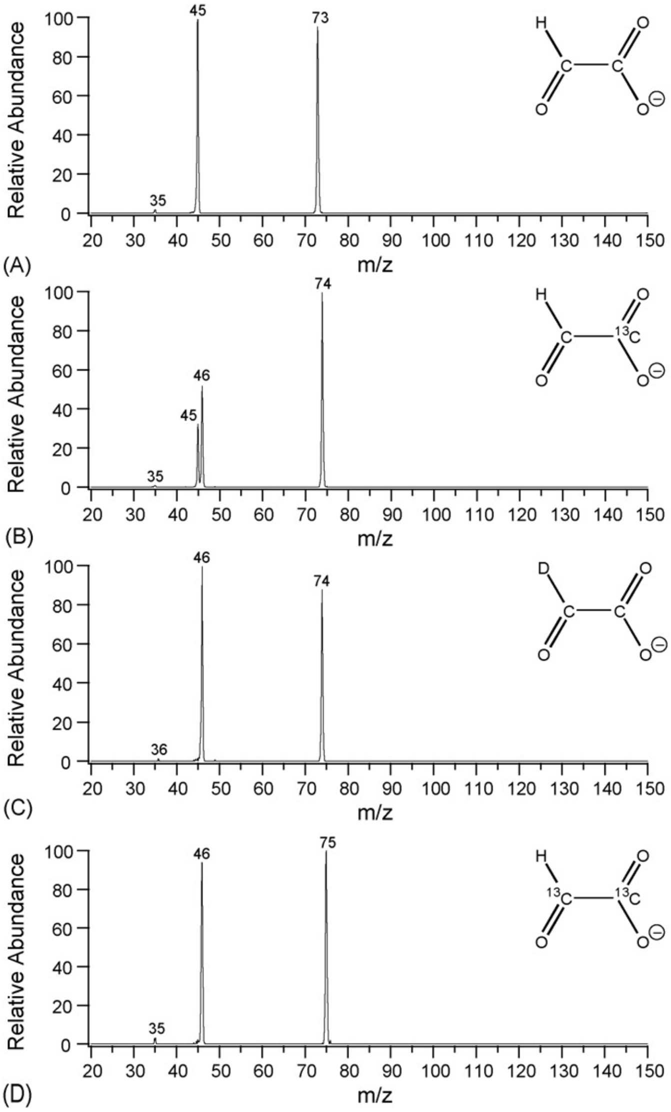

Fig. 3. Ion trap MS^3 spectra of fragment ions generated by H_2 elimination from: (A) glycolic acid, (B) 1-^{13}C labeled glycolic acid, (C) 2,2-D_2 labeled glycolic acid, (D) $^{13}C_2$ labeled glycolic acid.

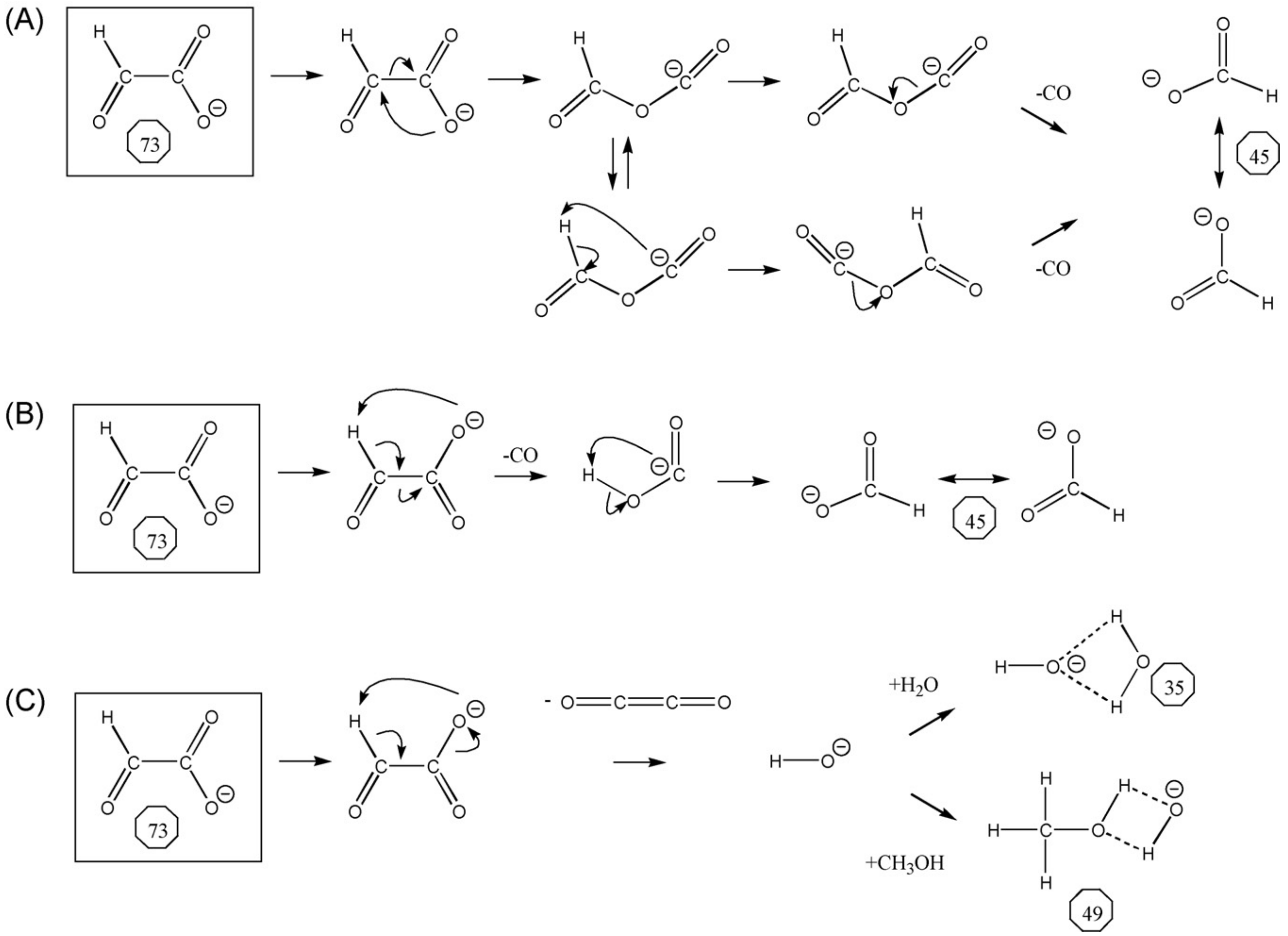

Fig. 4. Proposed dissociation patterns of *m/z* 73 glyoxatate.

which is solvated in situ by a water molecule. The low intensity of hydrated hydroxyl ions observed in dissociation of glyoxalate is dictated by a low rate of reactions proceeding through the initial proton transfer step. Moreover, the hydroxyl ion formation (Fig. 4C) and the minor process of CO elimination (Fig. 4B) are two competitive low rate processes of the dissociation of glyoxalate.

Fig. 5 shows dissociation spectra of *m/z* 47-like fragments associated with CO elimination from glycolates in MS^2. All labeled *m/z* 47-like fragments showed formation of *m/z* 35 and *m/z* 49 ions similar to ions observed in the MS^3 spectrum (Fig. 5A) of the *m/z* 47 fragment generated from the unlabeled glycolate (*m/z* 75). Dissociation products at *m/z* 35 and *m/z* 49 have been identified as a hydroxyl ion solvated by a water molecule and a hydroxyl ion solvated by a methanol molecule, respectively. Fig. 6 illustrates the fragmentation of *m/z* 47 hydroxylmethanolate through redistribution of charge from an oxygen of geminal diolate which leads to elimination of formaldehyde and formation of a hydroxyl ion. In turn, the hydroxyl ion then becomes solvated by either a water or methanol molecule. The dissociation products (*m/z* 35, *m/z* 36) of hydroxylmethanolate (Fig. 5B), associated with fragmentation of the deuterium labeled glycolate, provide a supporting evidence for the proposed mechanisms of formation of hydrox-

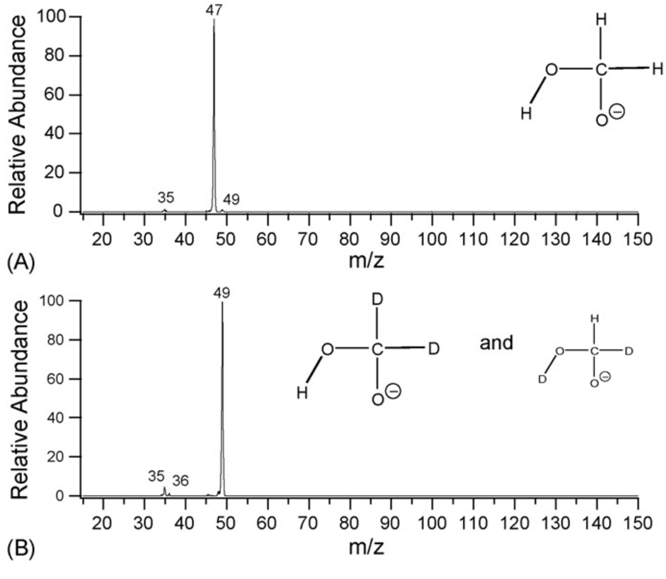

Fig. 5. Ion trap MS^3 spectra of fragment ions generated by CO elimination from: (A) glycolic acid, (B) 2,2-D_2 labeled glycolic acid.

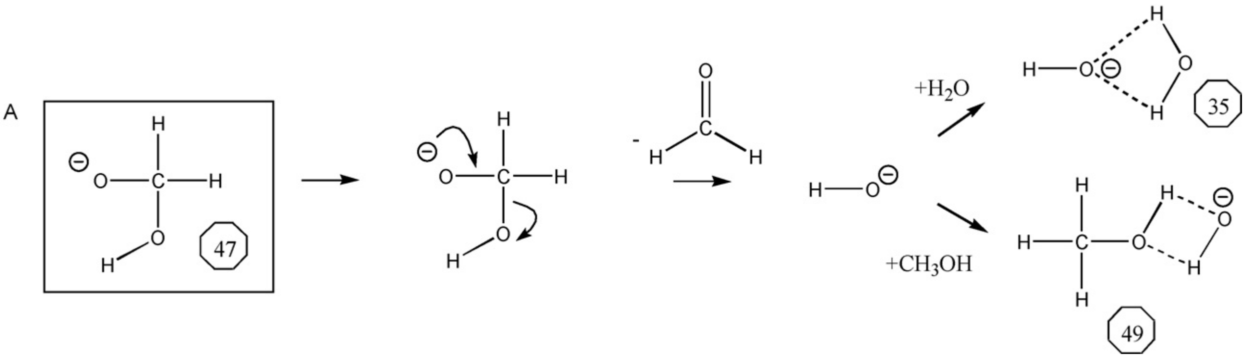

Fig. 6. Proposed dissociation patterns of *m*/*z* 47 hydroxymethanolate.

ylmethanolate (Fig. 2B and C). According to these mechanisms, a hydroxyl group of hydroxylmethanolate should contain, in a major part, the initial hydroxylic hydrogen, and to a smaller extent, a hydrogen from the α-carbon. The relative intensity of the *m*/*z* 35 and the *m*/*z* 36 fragments from dissociation of the *m*/*z* 49 hydroxylmethanolate (Fig. 5B), incorporating one deuterium atom in its structure, indicates in fact that the initial hydroxyl hydrogen is accommodated mainly on a hydroxyl group of hydroxylmethanolate. The mass spectrum of hydroxylmethanolate on the other hand, demonstrates the fate of hydroxyl ions in mass spectrometry. As can be seen in the spectra in Fig. 5, the *m*/*z* 17 OH^- ion has not been detected directly. The preferential formation of a solvated hydroxyl ion is dictated by a partial dislocation of a negative charge in the structure of a complex ion.

4. Conclusion

The goal of the authors was to establish a mechanism for the fragmentation of glycolic acid in negative mode using electrospray ionization in combination with ion trap mass analysis and Q-TOF mass spectrometry. The isotopically labeled standards of glycolic acid provided extremely useful tandem mass spectrometry information which allowed establishing the detailed fragmentation patterns of glycolate. The dissociation of glycolate proceeds through two general pathways. The major patterns are initiated by nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon. Subsequent elimination of H_2 produces glyoxalate whereas a loss of CO and formaldehyde results in formation of hydroxymethanolate and formate, respectively. The nucleophilic attack on the α-carbon also generates a hydroxyl anion, which was detected as a species solvated by a molecule of water or methanol. The minor dissociation patterns originate from a proton transfer from the α-carbon to a negatively charged carboxylic oxygen and lead to formation of hydroxymethanolate and a hydrated hydroxyl ion. The fragmentation of glyoxalate was found to proceed through dissociation pathways very similar to those observed for glycolate. The dissociation of hydroxymethanolate is an interesting example of the fragmentation of an extremely fragile negative ion of a geminal diol, which results in formation of solvated hydroxyl anions. The information obtained from dissociation of glycolate demonstrates a lack of fragmentation pathways which would involve the proton transfer from the α-hydroxyl group to a negatively charged carboxylic oxygen. Such an initial step would result in nucleophilic attack of the hydroxylic oxygen on the carboxylic carbon and elimination of H_2O from glycolate to form a β-hydroxyketene ion. The reaction of H_2O elimination from glycolate was not observed in our study. The initial step of the proton transfer from the α-hydroxyl group to a carboxylic oxygen results in the major fragmentation pathways of lactate [9], however, this is not observed at all in dissociation of glycolate. The nucleophilic attack of a negatively charged carboxylic oxygen on the α-carbon, on the other hand, initiates the major fragmentation pathways of glycolate, but has not been observed in dissociation of lactate. Consequently, the significant differences observed in CID of glycolate and lactate are related to completely different fragmentation pathways of these two structurally similar species.

The fragmentation of glycolic acid in negative mode has shown a number of interesting features such as unique structures of small negative ions and novel mechanisms of their formation. A critical concept for understanding fragmentation of glycolate is formation of an α-lactone intermediate ion following nucleophilic attack of the carboxylic oxygen on the α-carbon. A similar concept for the gas phase reactions of neutral glycolic acid has been postulated before based on theoretical studies on the mechanisms of the decomposition of α-hydroxycarboxylic and alkoxyacetic acids [11,12]. We believe that our experimental observations provide a support for α-lactone as an intermediate in dissociation reactions of negative ions of glycolic acid.

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