Formation of $[M-H]^-$ Ions under Fast-atom Bombardment Conditions: Which is reflected, gas-phase or solution chemistry ?

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The formation of deprotonated molecules $[M-H]^-$ of Trolox having a carboxyl and a phenolic hydroxyl group and the derivatives, under fast-atom bombardment (FAB) conditions, has been examined from the viewpoint of proton-transfer reaction in gas-phase or solution. The negative-ion FAB mass spectra of the derivatives strongly suggested that deprotonation mainly occurs on the carboxyl group through the electrolytic dissociation in matrix solution. The use of higher proton acceptability matrices such as glycerol, penta-methylene glycol, and diethanolamine was favorable for the detection of $[M-H]^-$ ions of a Trolox methyl ester, while the use of lower proton acceptability matrices such as *m*-nitrobenzyl alcohol and dithiothreitol was unfavorable for the $[M-H]^-$ formation. While the result obtained suggested that the formation of $[M-H]^-$ ions reflects the gas-phase basicities of matrices used, the results from the negative-ion FAB mass spectra of the Trolox methyl ester and α -tocopherol suggested that the $[M-H]^-$ formation reflects solvation states such as hydrophobic and hydrophilic interactions between analyte and matrix molecules in matrix solution. The site of deprotonation of the compounds used has been examined by using collision-induced dissociation (CID) technique, and it was shown that the CID characteristics of $[M-H]^-$ ions depend markedly on the site of deprotonation. It was presumed, consequently, that the $[M-H]^-$ ion formation under FAB conditions is governed by gas-phase thermo-chemistry and/or solution chemistry according to the nature of analyte and matrix used.

1. Introduction

While fast-atom bombardment (FAB) and liquid secondary ion mass spectrometry (LSIMS) are widely applicable to the structure elucidation of non-volatile and thermally labile organic compounds,¹⁾ the ionization events are of interest in connection with the intermolecular proton-transfer reaction to form protonated and deprotonated molecules, $[M+H]^+$ and $[M-H]^-$. It has been actually believed²⁾ that in FAB technique a liquid matrix B such as glycerol plays the roles of a proton donor for $[M+H]^+$ and a proton acceptor for $[M-H]^-$ formation as follows:

Sunner and co-workers³⁾ have described that for the formation of protonated species, $[M+H]^+$ and $[B+H]^+$, the direction of the proton-transfer are determined by the gas-phase basicities (GB) of analyte M and matrix B not the liquid-phase basicities (LB), and that a direct desorption of preformed ions from matrix solution is not supported by the FAB mass spectra.⁴⁾ For anionic compounds containing carboxyl, sulfonic, and phospho

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groups, negative-ion FAB/LSIMS experiments have been often performed to obtain the peaks corresponding to $[M-H]^-$ ions which may come from the electrolytic dissociation of those acidic groups in matrix solution, *i.e.*, $-COO^- \cdots H^+$, $-SO_2O^- \cdots H^+$, and $-OPO(O^-)O \cdots H^+$.⁵⁾ As a matter of fact, the ionization processes under FAB/LSIMS conditions may be governed by both gas-phase and solution chemistry.

The author recently reported⁶⁾ an evidence that the formation of $[M-H]^-$ ion of α -tocopherol which contains a phenolic hydroxyl group occurs by a proton-subtraction reaction between M and B, which may follow the proton-transfer reaction (2) under FAB conditions. The formation mechanism of negative-ion species under FAB/LSIMS conditions has been only studied from the standpoints of a more general strategy called "reverse-derivatization", which is employed to enhance the ion signals by the addition of an acid (proton donor) or a base (proton acceptor) to matrix solution,⁷⁾ and of the proton accepting ability of matrix materials.⁸⁾ Balasanmugam and co-workers⁹⁾ studied the ion-molecule reactions of nitroaromatic compounds under negative-ion FAB conditions, and they described that the odd-electron molecular ions $M^{\cdot -}$ dominate the negative-ion FAB mass spectra of those compounds. Little is reported concerning the mechanism of negative-ion formation under FAB/LSIMS conditions compared with that of the positive-ion formation, while the importance of negative-ions has been pointed out by Sugiura.¹⁰⁾ In the present paper, we will examine the formation of $[M-H]^-$ ions of Trolox (1) and some derivatives, under FAB conditions using various matrix materials, from the standpoints of gas-phase and solution chemistry. Fragmentation characteristics for the $[M-H]^-$ ions differing in the site of deprotonation will be examined by using collision-induced dissociation (CID) technique.

2. Experimental

The experiments were performed on a JEOL JMS-DX303 double-focusing mass spectrometer equipped with a JMA-DA5100 data system (JEOL Ltd., Tokyo, Japan). The fast-atom argon beam used was generated from Ar^{+} ions which were accelerated to 5 kV. The FAB gun emission current was 10 mA. The liquid matrices used were a 1 : 2 (v/v) mixture of dithiothreitol (DTT) and thioglycerol (TG) (referred to as DTT/TG12),¹¹⁾ *m*-nitrobenzyl alcohol (NBA), glycerol (G), pentamethylene glycol (PMG), and diethanolamine (DEA). The matrices DTT, NBA, G, PMG, and DEA were purchased from Tokyo Kasei Ltd. (Tokyo, Japan), and TG was purchased from Fluka AG, (Buchs, Switzerland). Sample was dissolved in the matrices at a concentration of ca. $8 \mu g/\mu L$ by using a micropipet of $10 \mu L$ (Drummond Sci. Co., Pennsylvania, U.S.A.). Trolox was purchased from Aldrich Chemical Company, Inc. (Wisconsin, U.S.A.). The derivatives, methyl esters and acetates, derived from Trolox were purified by a preparative thin-layer chromatography (TLC) system.¹²⁾ The structures of Trolox (1) and the derivatives are shown in Chart 1. To obtain CID spectra of $[M-H]^-$ ions, B/E-constant linked scan experiments were performed by collision with helium ($\sim 50\%$ beam reduction).

3. Results and Discussion

According to the latest study,¹³⁾ it is considered that ion formation under FAB conditions occurs in both steps of the collision cascade occurring immediately before

Chart 1.

cavity formation and the ion-molecule reactions due to frequent collisions between neutrals and/or ionic species in a cavity. The cavity which means a dense gas-like phase consisting of matrix and analyte molecules having high-translational energy, B_{fast} and M^{fast} , may be formed by the processes of collision cascade caused by the collision between a matrix molecule in the liquid surface layer, B_{surf} , and a fast atom A_{fast} , as a most early FAB event. It could be considered that the ionization events in the collision cascade and in the cavity may be governed by solution (or solvation) and gas-phase chemistry, respectively. Although the dynamic processes of the collision cascade and the frequent collisions in the cavity cannot be described by the equilibrium thermodynamics, it seems to be convenience for the understanding of FAB/LSIMS ion formation to write down the thermodynamic descriptions for the ionic dissociation in matrix solution and gas-phase (see Appendix).

3.1 Effects of derivation and matrix on the formation of $[M-H]^-$ ions

When the DTT/TG12 matrix is used, a Trolox methyl ester (2) only slightly showed or did not show a peak corresponding to deprotonated molecule $[M-H]^-$ in the negative-ion FAB mass spectrum, while the FAB mass spectra of Trolox (1) and an acetate (3) showed the intense peak corresponding to $[M-H]^-$ ions, as shown in Fig. 1. An asterisk indicates the peaks originating from the matrix. The negative-ion FAB mass spectra of other derivatives 4 and 5, of which carboxyl groups were protected by methylation, did not show the peak corresponding to $[M-H]^-$ ions, though the spectra are not shown. These results strongly suggest that the site of deprotonation in 1 and the acetate 3 is not phenolic hydroxyl but carboxyl group. This will be confirmed later by using CID technique.

From the relations (A4) and (A6) in Appendix, one can expect that the use of higher basicity matrix will be favorable for the proton-transfer reaction to form $[M-H]^-$ ions. In order to confirm this expectation, the negative-ion FAB mass spectra of 1 and 2 were obtained by using some different matrices NBA, PMG (or G), and DEA which differ from to each other in the GB. The FAB mass spectra of 1 gave the peaks corresponding to deprotonated ion, $[M-H]^-$, at m/z 249 and to fragment ions at m/z 205, 189, 163, and/or 85 whichever matrix was used, as shown in Fig. 2. On the other hand, the FAB mass spectra of 2 obtained with PMG and DEA systems showed the peaks corresponding to deprotonated ion, $[M-H]^-$, at m/z 263 and a fragment ion at m/z 163, while the FAB spectrum with NBA only slightly showed the $[M-H]^-$ ion peak (Fig. 3). Since the carboxyl group in 2 has been protected by methylation, the site of deprotonation for 2 should be on the phenolic hydroxyl group. The result obtained for 2 is understandable

Fig. 1. Negative-ion FAB mass spectra of (a) Trolox (1), (b) a methyl ester (2), and (c) an acetate (3) obtained with DTT/TG12 matrix.

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Fig. 2. Negative-ion FAB mass spectra of Trolox (1) obtained with (a) NBA, (b) PMG, and (c) DEA matrices.

Fig. 3. Negative-ion FAB mass spectra of a methyl ester (2) obtained with (a) NBA, (b) PMG, and (c) DEA matrices.

from the facts that NBA is relatively weak in the GB^{3a)} or in a proton acceptability,⁶⁾ and that the LA of organic carboxylic acids are larger than that of phenols in solution. The proton acceptability of some matrices has been evaluated by measuring the positive-ion FAB mass spectra of 1 : 1 (v/v) mixtures of matrices B₁ and B₂, and the order evaluated was DEA > PMG > G > DTT > NBA. The absolute intensities of $[M-H]^-$ ions for **2** as printed in the FAB mass spectral data obtained from an experiment were 9.00 for NBA, 32.8 for DTT/TG12, 125 for PMG, and 298 for DEA, while those for **1** were 44.0 for NBA, 283 for DTT/TG12, 62 for PMG, and 68 for DEA. In another experiment, the absolute intensities of $[M-H]^-$ ions for **2** were no detection for NBA and DTT/TG12, 18.6 for PMG, 24.9 for G, 138 for DEA, while those for **1** were 4.45 for NBA, 7.87 for DTT/TG12, 24.9 for PMG, 42.7 for G, and 81.9 for DEA. Although the appearance and absolute intensities of $[M-H]^-$ ions remarkably fluctuated each time experiments were performed, the results obtained were consistent with the fact that the proton acceptabilities of NBA and DTT are weaker than those of G, PMG, and DEA. Further, the absolute intensities of $[M-H]^-$ ions roughly reflect the GBs (kcal mol⁻¹) which are 186 for NBA, 196 for G, and 220 for DEA,^{3a)} though the rate of ion formation under FAB conditions is governed by physicochemical factors such as surface activity (SA) and hydrophobicity^{7a, 14-16)} as well as thermochemical properties such as GB, proton affinity (PA), and LB.

Although the results obtained above indicate that deprotonation on the phenolic hydroxyl group of **2** is hard to occur under FAB conditions with DTT/TG12 and NBA matrices, this is inconsistent with the negative-ion FAB-MS study of α -tocopherol (**6**) having a 6-hydroxy-2,5,7,8-tetramethylchroman (HTMC) moiety which is a common structure with Trolox (**1**) and the methyl ester (**2**). The negative-ion FAB mass spectra of **6** gave peaks corresponding to deprotonated molecule $[M-H]^-$ and a characteristic fragment ion at m/z 163, whichever matrix was used.⁶⁾ The distinctions between **1** and **6** are that the compound **6** has a hydrophobic phytyl side chain and is oily in nature, while **1** has a hydrophilic carboxyl group and is a solid state. Furthermore, the compound **6** was insoluble in hydrophilic matrices and formed a micelle state in all matrices used, while **1** and the derivatives (**2**~**5**) were soluble in the matrices. The phenolic hydroxyl groups in the HTMC moiety on the surface of a micelle of **6** could interact with the proton accepting site(s) such as amine nitrogen and alcohol oxygen in matrix molecules, though such a hydrogen bonding or hydrophilic interaction might be often inhibited by the methyl groups on either side of the hydroxyl group. The schematic illustration for the interaction between **6** and NBA molecules are shown in Scheme 1. Since the HTMC moiety in **1** and **2** is rather hydrophobic in nature owing to the methyl groups, on the other hand, it seems likely that the HTMC moiety in these compounds mainly interact with the fatsoluble or hydrophobic sites of matrix molecules, not with the basic sites (Scheme 2). This means that for **1** and **2** the equilibrium constant K_H to form an ion-pair, $(M-H)^- \cdots H^+ \cdots B$ (see A1 and A2.1 in Appendix), between the phenolic hydroxyl group of analyte and the basic site of matrix molecules in matrix solution is small because of a steric hinderance originating from the hydrophobic and bulky methyl groups. The steric hinderance will affect not enthalpy change ΔH_H° but entropy change ΔS_H° to form the ion-pair, in the ΔG_H of eq. (A2.1). Consequent-

ly, it could be presumed that the intermolecular proton-transfer to form deprotonated molecules $[M-H]^-$ under FAB conditions here is governed by solution chemistry which relates to hydrophilic and/or hydrophobic interactions between analyte and matrix molecules, as well as gas-phase thermochemistry.

3.2 CID characteristics of $[M-H]^-$ ions

As described above, the results obtained suggested that the deprotonation of Trolox (**1**) and the acetate (**3**) takes place on the carboxyl group, while that of the methyl ester (**2**) takes place on the phenolic hydroxyl group. In order to see the fragmentation characteristics for the deprotonated molecule as a phenolate anion, the CID spectrum of $[M-H]^-$ ion of **2** was obtained (Fig. 4). The CID characteristic of the phenolate anion for **2**, giving an intense fragment at m/z 163, was the same as that of a phenolate anion for α -tocopherol (**6**), as shown in the CID spectrum of $[M-H]^-$ ion of **6** (Fig. 5). The fragmentation to form the m/z 163 ion could be explained by a retro-Diels-Alder (RDA) cleavage of the $[M-H]^-$ ions, as shown in Scheme 3.

On the other hand, the CID spectrum of $[M-H]^-$ ion of **1** gave peaks corresponding to the fragments at m/z 205, 189, 163, and 85, as shown in Fig. 6. The CID characteristic of **1**, which is of a carboxylate anion, quite differs from that of **2**. It was confirmed, furthermore, by using the CID technique that the m/z 189 and 163 ions in the CID spectrum (Fig. 6) are originating from the m/z 205 ion as shown in Fig. 7. Proposed

Scheme 1.

||||| hydrophobic interaction

Scheme 2.

Fig. 4. Collision-induced dissociation spectrum of deprotonated molecule $[M-H]^-$ at m/z 263 of a methyl ester (2), produced under FAB conditions with DEA matrix.

Fig. 5. Collision-induced dissociation spectrum of deprotonated molecule $[M-H]^-$ at m/z 429 of α -tocopherol (6), produced under FAB conditions with DEA matrix.

fragmentation pathways and ion structures for the carboxylate anion for **1** are shown in Scheme 4.

4. Conclusion

Either gas-phase or solution chemistry seems to be essential for the ionization events under FAB/LSIMS conditions. It is probably real that certain compounds lie as ions previously in matrix solution, while other compounds will be ionized in gas-phase. In particular, the former could be measured and characterized by a dissociation or association constant for a given ionic-solution equilibrium system. It is important to recognize, however, that the ionic equilibria in matrix solution may be highly distorted

by FAB-induced dynamic processes such as collision cascade and phase-explosion³⁾ as a vaporization phenomenon, and the ion formation as a sputtering due to FAB-induced vaporization would not necessarily reflect the ionic equilibria in matrix solution because the ion formation generally quite differs from the vaporization phenomenon. A most important factor for ion yields detectable is volatility or desolvation ability of analyte molecules from matrix surface, which relates to SA and hydrophobicity,^{7a, 14-16)} rather than ionic dissociation or association as the "preformed state" in matrix solution.

The favorable formation of deprotonated molecules $[M-H]^-$ of Trolox (1) and the acetate (3), which have a carboxyl group, may come from a cooperative effect of ionic dissociation and volatility of these compounds under FAB conditions. For these compounds, the formation of gas-phase ionic species would occur in the step of collision cascade as a relatively high-energy process which brings about rupture of intermolecular interactions, so that in this case the ion formation and vaporization may take

Fig. 6. Collision-induced dissociation spectrum of deprotonated molecule $[M-H]^-$ at m/z 249 of Trolox (1), produced under FAB conditions with NBA matrix.

Fig. 7. Collision-induced dissociation spectrum of a fragment at m/z 205 originating from the deprotonated molecule $[M-H]^-$ of Trolox (1).

Scheme 4.

place simultaneously. On the other hand, the reason why the methyl ester (2) hardly gave the deprotonated ion peak in the FAB mass spectra with NBA and DTT/TG12 matrices may be due to a non-dissociation state (the absence of preformed ions) and/or the use of lower proton accepting ability matrices, not to volatility. The formation of deprotonated molecule of 2 by using G, PMG, and DEA matrices, which are relatively high in the proton acceptability and the GB, may occur through the proton-transfer reaction (2) in the dense gas-like phase. Therefore, the ion formation of non-ionic compounds under FAB/LSIMS conditions would be governed by gas-phase thermochemistry and/or ion-molecule reactions like a chemical ionization process. It is exactly dependent on the nature of analyte and matrix used where ion formation occurs.

Appendix: Thermodynamics for deprotonation in matrix solution and gas-phase

The equilibria for ionization and dissociation of analyte M as a Brönsted acid in liquid matrix B as a Brönsted base are represented as follows¹⁷⁾;

where $(M-H)^- \cdots H^+ \cdots B$ represents an ion-pair solvated and it corresponds to a "quasi-preformed state" named by the author.¹⁸⁾ In this equilibrium, the equilibrium constants for first (ionization), second (dissociation), and overall steps can be written as follows;

$$K_{il} = [(M-H)^- \cdots H^+ \cdots B] / [B][M] \quad (A2.1)$$

$$K_{dl} = [(M-H)^-][B+H]^+ / [(M-H)^- \cdots H^+ \cdots B] \quad (A2.2)$$

$$K_{dl} = K_{il} K_{dl} = [(M-H)^-][B+H]^+ / [B][M] \quad (A2.3)$$

Ionic dissociation constant K_{dl} is measurable either by optical or electrical means, and a substantial "precharged or preformed state"⁷⁾ of the analyte could be quantitatively defined by the constant K_{dl} . Furthermore, the standard Gibbs free energy changes that correspond to K_{il} , K_{dl} , and K_{dl} can be given as follows;

$$\Delta G_{il}^\circ = -RT \ln K_{il} \quad (A3.1)$$

$$\Delta G_{dl}^\circ = -RT \ln K_{dl} \quad (A3.2)$$

$$\Delta G_{dl}^\circ = \Delta G_{il}^\circ + \Delta G_{dl}^\circ = -RT \ln K_{dl} \quad (A3.3)$$

here R and T are gas constant and absolute temperature, respectively. The overall change $-\Delta G_{dl}^\circ$ equals to the sum of liquid phase acidity of M, $LA(M)$, and $LB(B)$,

$$-\Delta G_{dl}^\circ = LA(M) + LB(B) \quad (A4)$$

On the other hand, the proton-transfer reaction (2) in gas-phase can be divided into two processes as follows;

By the definition,¹⁹⁾ the Gibbs free energy changes for dissociation (A5.1), $-\Delta G_{dg}^\circ$, and protonation (A5.2), $-\Delta G_{ag}^\circ$ equal to the gas-phase acidity of M, $GA(M)$, and the GB of B, $GB(B)$, respectively. Therefore, the free energy change for the reaction (2), $-\Delta G_{dg}^\circ$ can be represented by

$$-\Delta G_{dg}^\circ = GA(M) + GB(B) \quad (A6)$$

The fact that the formation of $[M+H]^+$ ions under FAB/LSIMS conditions is often governed by the gas-phase equilibrium thermochemistry^{3, 20)} substantiates an assumption for the cavity model,¹³⁾ *i.e.*, the frequent collisions between matrix and analyte molecules having high-translational energy (t) in the cavity. The proposed frequent collisions might be insufficient to cause thermal equilibration (energy conversion from t into vibrational and/or rotational energy), but sufficient to allow proton-transfer equilibration. The proton-transfer reaction to form $[M-H]^+$ ions will be favorable for larger values of $-\Delta G_{dl}^\circ$ and $-\Delta G_{dg}^\circ$.

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