ENHANCED FORMATION OF MULTIPLY CHARGED IONS IN NEGATIVE ION FIELD DESORPTION MASS SPECTROMETRY OF ORGANIC COMPOUNDS
E. Bramer-Weger, S. Thiebes, F. Röllgen

To cite this version:
E. Bramer-Weger, S. Thiebes, F. Röllgen. ENHANCED FORMATION OF MULTIPLY CHARGED IONS IN NEGATIVE ION FIELD DESORPTION MASS SPECTROMETRY OF ORGANIC COMPOUNDS. Journal de Physique Colloques, 1989, 50 (C8), pp.C8-159-C8-162. <10.1051/jphyscol:1989828>. <jpa-00229926>

HAL Id: jpa-00229926
https://hal.archives-ouvertes.fr/jpa-00229926
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ENHANCED FORMATION OF MULTIPLY CHARGED IONS IN NEGATIVE ION FIELD DESORPTION MASS SPECTROMETRY OF ORGANIC COMPOUNDS

E. Bramer-Weger, S. Thiebes and F.W. Röllgen

Institut für Physikalische Chemie, Universität Bonn, Wegelerstrasse 12, D-5300 Bonn 1, F.R.G.

Abstract - Enhanced formation of doubly and triply charged negative ions has been obtained in negative ion field desorption mass spectrometry (NFD MS) of acids and salts by applying a matrix mixture of polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG). Abundant doubly charged ions of disaccharides could be obtained from a mixture with a quaternary ammonium salt and sodium chloride. The matrix properties leading to the formation of multiply charged ions are discussed.

1 - INTRODUCTION

In negative ion field desorption mass spectrometry (NFD MS) ions are extracted from viscous electrolytic layers at field strengths below the threshold of electron emission [1, 2]. In order to facilitate the desolvation of ions at low field strength the samples are dissolved in a matrix. Typically an aqueous solution of polyethylene glycol (PEG), i.e. HO(CH₂CH₂O)ₓH of a mean molecular weight of about 4000 u is applied. Mass spectra are obtained by loading untreated 10 µm tungsten wire cathodes with the sample/matrix mixture and heating the wire resistively at an applied potential of about -8 kV with respect to the 3 mm distant counter electrode. The NFD method is useful for the analysis of salts and acids forming solvated ions in solution. Very polar compounds can also be ionized by proton abstraction and/or anion attachment. The principles of the mechanism of desolvation of ions by field desorption [3, 4] and of some matrix and additive effects in NFD MS have been described [5-7].

While the sensitivity of NFD MS for acids with one acidic group is normally high, detection problems exist for acids with two or more acidic groups. Frequently weak (M-H)- ion signals, occasionally also (M-2H)²⁻ ions [2] and sometimes no molecular ions at all were found in the spectra of dicarboxylic or disulfonic acids and their salts. The low sensitivity of NFD MS for such compounds prompted us to search for matrix compounds and mixtures to overcome this limitation. The results of this study are new matrix mixtures which strongly raise the detection sensitivity for such acids and salts. Surprisingly it turned out that the increase in sensitivity is in part due to the enhanced formation of multiply charged ions. This effect is reported and discussed in the following.

2 - RESULTS

A limiting property of PEG for its use in NFD MS is the low viscosity and weak adhesion to the emitter surface at higher temperature (> 100 °C). Accordingly the search for new matrices facilitating the formation of molecular ions of compounds with higher cohesive energies such as acids with several acidic groups was directed to those which improve the adhesion and increase the viscosity of sample matrix mixture at elevated temperatures. A mixture of polyvinyl pyrrolidone (Fig. 1) of a mean molecular weight of about 10000 u (PVP) with PEG (weight ratio typically 1:5) and water as solvent was found to have very promising properties in raising the NFD sensitivity for such compounds. In addition this matrix mixture led to the appearance of abundant doubly and triply charged ions in the mass spectra of acids and salts.
The enhanced formation of multiply charged ions was observed for a variety of di- and trisulfonic acids and of dicarboxylic acids and their salts. The ions are typically formed at higher temperatures compared to conventional NFD conditions applying only PEG as matrix. Under favourable conditions mass spectra exhibiting exclusively the multiply charged ion can be obtained. This is shown for a doubly charged molecular ion of naphthalene disulfonic acid and for a triply charged molecular ion of naphthalene trisulfonic acid in Fig. 2 and 3 respectively. So far no quadruply charged ion could be observed yet in the spectra of acids with more than three acidic groups and also not in the spectra of the corresponding salts.

Doubly charged ions were also found to be formed from a disaccharide by applying a mixture of a quaternary ammonium salt, such as hexadecyltrimethyl ammonium chloride, and sodium chloride to the aqueous solution. This effect is shown in Fig. 4 for sucrose. The formation of doubly charged negative ions from a non-acid compound has not been observed before.

3 - DISCUSSION

Properties of the matrix/sample solution which affect the ion formation in NFD MS are the adhesion of the layer under field stress to the substrate, the viscosity, the solubility of the sample molecule in the matrix and the ion chemistry between the sample, matrix and additives such as salts. We believe that the enhanced formation of multiply charged ions depends on favourable conditions regarding all the four properties.

The multiply charged ions in the Fig. 2-4 are formed by deprotonation reactions either already in solution or during the extraction of singly charged ions by ion molecule reactions in the desolvation region. Evidence for double ionization of neutral molecules by ion molecule reactions in the solvent free matrix is provided by the (M-2H)\(^2^-\) ion of sucrose in the spectrum of Fig. 4 because sucrose does not form solvated ions. It is very probable that both the mono- and deprotonated sucrose molecules are formed by reactions with Cl\(^-\) giving HCl and the (M-H)\(^-\) and (M-2H)\(^2^-\) ions, respectively. This kind of ion chemistry in the desolvation region of an ion emitting surface layer has been discussed in Ref. [5].

Since under the conditions of Fig. 2 and 3 only doubly and triply charged ions, respectively, of the naphthalene sulfonic acids are desorbed it is reasonable to assume that these ions are preformed in solution and are desolvated and extracted by preservation of the charge state. This mechanism implies that the loss of water at elevated temperatures does not lead to charge recombination and a precipitation of the acids but to a retention of the ions in the matrix. Probably basic properties of PVP cause a stabilization of the ions in the matrix with respect to charge removal reactions.

Optical microscopy of the macroscopic behaviour of PVP containing sample layers under NFD conditions revealed an adhesion and a higher viscosity of the layer up to about 300 °C. The higher temperatures at which ion emission is observed do not only reflect the viscous property of PVP but also the
Fig. 2: NFD MS of naphthalene-1,5-disulfonic acid obtained from a mixture of PVP and PEG (weight ratio 1:5). Emitter heating current 19 mA.

Fig. 3: NFD mass spectrum of naphthalene-1,3,5-trisulfonic acid obtained from a mixture of PVP and PEG (weight ratio 1:5). Emitter heating current 28 mA.
Fig. 4: NFD mass spectrum of sucrose obtained from a mixture of hexadecyltrimethyl ammonium chloride and sodium chloride (weight ratio 50:1). Emitter heating current 16 mA.

thermal activation needed to desorb the ions from the polymer matrix via a cooperative mechanism described in Ref. [4]. This is indicated by the higher emitter heating current required for desorption of triply charged compared to doubly charged ions (see Fig. 2 and 3).

These considerations do not sufficiently explain the enhanced formation of multiply charged ions but might provide a guideline for further mechanistic studies.

ACKNOWLEDGEMENTS

The authors thank the Wissenschaftsministerium des Landes Nordrhein-Westfalen and the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES