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COMPARISON OF BARE WIRES AND ACTIVATED EMITTERS FOR FD MS OF OLIGOSACCHARIDES

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Abstract - Ion formation in field desorption (FD) from activated wire emitters covered with field enhancing microneedles has been compared with that from bare wires for some oligosaccharides doped with NaCl. The experiment revealed a close similarity between both types of emitters in the ion formation by electrohydrodynamic disintegration processes at temperatures near the onset of ion emission. In contrast, at higher temperatures above the melting point the sample layers are removed from smooth wires while on activated emitters they are retained in part between the microneedles. In this temperature range surface mobile molecules were found to be ionized not only by FI processes on microneedle tips but also by alkali ion attachment on charged alkali ion donating solid deposits. The latter mechanism has not been considered in FD mass spectrometry yet.

I - INTRODUCTION

Activated wire emitters i.e. 10 μm W-wires covered with field enhancing microneedles are widely applied as field anodes in field desorption mass spectrometry (FD MS) of organic compounds. The ion formation in FD from activated emitters has been attributed to so-called desolvation mechanisms and field ionization mechanisms /1/. In the desolvation mechanisms /2 - 7/ pre-formed ions are extracted and desolvated from condensed layers as a result of electrohydrodynamic disintegration of the charged sample layers, typically at temperatures lower than the melting temperature of the solvent free sample. FI mechanisms denote processes of ion formation by electron transfer reactions which are observed in FI MS i.e. under conditions of a sample supply from the gas phase to the tips of field enhancing microneedles. While desolvation mechanisms have been extensively studied by optical microscopy of FD from smooth wire emitters the role of the microneedles in FD of thermally labile and non-volatile compounds has been left largely unexplored.

This paper reports the results of experiments performed to elucidate the role of the microneedles in FD MS of oligosaccharides such as sucrose, raffinose and stachylose. In these experiments the FD behaviour of samples from activated emitters has been compared with that from bare wires as a function of the emitter temperature.

A double focusing mass spectrometer equipped with a new FD ion source was applied in order to observe the state of sample layers deposited on smooth wires by optical microscopy. The microscope was also used to control the position of the loaded part of the emitter in accordance with the acceptance range of the ion optics of the mass spectrometer. Thus, no ion signal was needed for the positioning of the emitter, and the dependence of ion emission on the temperature of a preselected small part of the emitter could be studied.

II - EXPERIMENTAL

A stereo microscope was attached to the self-built FD ion source of the double focusing mass spectrometer (AEI, MS9). The resolution was about 4 μm due to a working distance of about 45 mm. The wire emitter was set at 4 kV and placed at a distance of 2 mm from the counter electrode which was set at...
The acceptance area was determined by microscopy to be about 250 μm in the direction parallel to the wire and the slits of the ion optics, and 50 μm perpendicular to the wire emitter. The mass range of the instrument was about 2300 u. At a mass resolution of 750, which was normally applied, the energy acceptance of the instrument was about 60 eV. The time needed for recording mass spectra was between 5 and 10 minutes.

The activation of the 10 μm wires was performed with indene /8/. The needle lengths were about 30 μm. For bare wire emitters the temperature in the middle part of the wires as a function of the heating current was determined by resistance measurement and the use of calibration curves /4,7/. A similar method was applied in determining the temperatures of resistively heated activated wires /9/. The inaccuracy in the temperature determination was about 10%.

The samples, oligosaccharides + NaCl (weight ratio 100 : 1), were applied in aqueous solution to the emitter surface with the aid of a syringe and a stereo microscope. The thickness of the layer in the small loaded part of the activated emitters could not be controlled because of the hydrophobic property of the microneedles and the optical invisibility of the layer between the microneedles.

III - RESULTS AND DISCUSSION

In FD MS with bare wire emitters the optimum temperature for recording mass spectra is close to the onset temperature of molecular ion emission. Onset temperatures for the FD of sucrose, raffinose and stachyose mixed with NaI from bare wires have already been reported /7/. For the present mixtures of the saccharides with NaCl (weight ratio 100 : 1) the onset-temperatures of the molecular ions were only slightly lower than those reported before: about 75 °C for sucrose, 105 °C for raffinose and 140 °C for stachyose.

Using activated emitters the onset-temperatures for the same sample mixtures were somewhat higher: about 90 °C for sucrose, 110 °C for raffinose and 155 °C for stachyose. Optimum conditions for recording mass spectra were found again in a temperature range close to the onset-temperatures, typically not more than 30 °C above. The mass spectrum of sucrose (Fig. 1a) was recorded under these conditions. Within the limit of reproducibility the spectra do not differ from those obtained by using bare wires. In addition the abundance of the molecular ions was found to be comparable for both emitters and independent of the density of the microneedles.

At these lower desorption temperatures the ion formation from activated emitters can be attributed to the same desolvation mechanisms as have been extensively studied for FD from bare wires. This conclusion is supported by the observation of a delayed onset of ion emission from the activated emitters of several minutes after setting the emitter temperature above the threshold of ion emission. This provides evidence of the dependence of ion formation on electrohydrodynamic disintegration of the sample layers. Although protuberances formed between the microneedles are not visible the intensity fluctuations were indicative of the same processes as those studied with bare wires.

For all samples and FD from bare wires the ion emission ceased in a temperature range of about 30 to 50 °C above the onset temperature due to a more or less complete loss of the sample layer by the field stress. In contrast the ion emission from activated emitters continued up to much higher temperatures even significantly beyond the melting temperature of the solvent free samples. The retention of sample material at elevated temperatures by activated emitters can be explained by a lower field stress and a better adhesion of the layer between the microneedles. Accordingly, sample material can be volatized by thermal heating and ionized by FI processes on the tip of field enhancing microneedles.

The mass spectrum of sucrose obtained at 200 °C (melting point ≈ 185 °C) is shown in Fig. 1b. In addition to abundant fragment ions, (M+H)+ and (M+Na)+ molecular ions are present in the spectrum. The main fragment ions (m/z 163
Fig. 1: FD mass spectra of sucrose + NaCl (weight ratio 100:1) obtained by using an activated wire emitter for two emitter heating currents: a) 16.5 mA (90 °C), and b) 25 mA (200 °C)

and 311) and the (M+H)+ ion can be attributed to FI of sucrose molecules by electron removal (m/z 311/10/) and protonation. However, at this high temperature the (M+Na)+ ions can hardly be formed by an electrohydrodynamic mechanism of desolvation. This conclusion is based on the following observation: Above the melting temperature sample layers under field stress are removed within a few seconds by a burst of ion emission in which cluster ions are formed at high abundance. In contrast the (M+Na)+ ion signal of Fig. 3, although weak, lasts for minutes with intensity fluctuations smaller than those observed for (M+Na)+ ions at lower temperature. Furthermore no cluster ions are formed at these high temperatures.

Since the (M+Na)+ ions cannot be attributed to an FI process the experiments point to a mechanism of ion formation which has not yet been considered to contribute to the ion emission in FD MS. In view of the fact that the (M+Na)+ ions are formed under conditions of volatilization of sucrose molecules but not of the salt, it is very reasonable to assume that the sodium ion attachment occurs by interaction of mobile surface molecules with charged precipitated salt particles:

\[(\text{NaCl})_n (\text{Na}^+) + M \rightarrow (\text{NaCl})_n (\text{Na}^+)_{n-1} + (\text{M+Na})^+\]
The alkali ion donating solid deposit may also be composed of a mixture of NaCl with more strongly bound sucrose molecules facilitating the removal of alkali ions.

This mechanism of cationization has been observed and investigated for molecules supplied from the gas phase onto the surface of salt layers (and of electrolytic solutions) charged by a high electric field /11 - 13/. Accordingly in FD experiments with sucrose + LiCl (weight ratio 100 : 1) and acetone supplied from the gas phase (M+Li)^+ ions were formed from sucrose and acetone at temperatures above about 160 °C. The lithium salt was chosen because the affinity of acetone to Na" was not sufficient for cationization of acetone under these conditions.

The supply of sucrose molecules to the alkali ion donating surface areas should be due mainly to surface diffusion. (M+Na)^+ ions could be observed up to about 270 °C for sucrose samples with higher NaCl concentrations.

(M+Na)^+ ions of the more thermally labile raffinose and stachyose have been observed only near the onset of ion emission but not at higher temperatures (> 200 °C). However, abundant fragment ions were formed from these compounds at higher temperatures in a broad temperature range.

IV - CONCLUSIONS

The present study shows that in FD MS of thermally labile compounds from activated emitters, the following temperature regimes can basically be distinguished: at lower temperatures, near the onset of ion emission, ions are formed by the same mechanism and with the same emission characteristics as observed in FD from bare wire emitters, while at higher temperatures, above the melting point, sample layers are removed from bare wires due to the field stress while sample material is retained between the microneedles of activated emitters. Under these conditions surface mobile and thermally stable molecules can be ionized on the tip of the microneedles by FI processes and, under appropriate conditions, also by alkali ion attachment on charged alkali ion-donating solid precipitates. At still higher temperatures surface diffusion should be of minor importance as a supply mechanism to ionization centers, and the direct evaporation of thermal degradation products should dominate.

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