Introduction

Ion transformation processes, in particular ion molecule reactions, as subsequent steps upon directing generated ions to the analyzer region may significantly change the outcome of a mass spectrum. Once the ionization process instantaneously transfers the neutral sample out of its equilibrium state the ion population relaxes into a new equilibrium. Usually the thermodynamically most favorable dissociation that includes ions significantly differs from its neutral counterpart. The extent of microinstability with increasing complexity of the sample and increasing number of total collisions occurring after the ionization process. To keep the initial ionization, which does reflect the neutral sample composition the number of ion molecules after initial ion formation needs to be minimized. This type of process control is termed "kinetic control" within the present framework.

Approach:
- Application of one of the strongest known gas phase acid, H₃O⁺ as the main primary charge carrier. 
  - Generation of H₃O⁺ either by a high pressure DC plasma or a low pressure RF discharge. 
  - Subsequent quantitative transformation of H₂O into reactive ions [H₂O]+ and [H₃O]+ for less exothermic analyte protonation. Direct exposure of the analytes to the plasma afterglow is largely avoided. 
  - Maintaining the protonation reactions of the analyte under kinetic control.

Methods

**MS**
- High pressure DC plasma source, custom low pressure RF discharge source
- Helium 3.0 and Nitrogen 5.0, Messer Group, Kleinfelden, Germany

**Inlet Source**
- Custom high pressure DC plasma source

**Case Studies**
- Benzene, toluene, o-xylene in nitrogen (1 ppm)
- Benzene, toluene, o-xylene in nitrogen (10 ppm)
- All gases were used without further purification.

**Gas Flows**
- All gas flows are controlled by mass flow controllers, MS Instruments Deutschland GmbH, Berlin, Germany

Experimental setup

The gas phase sample is introduced into the transfer quadrupole at variable axial positions, determining the ionization time and the time for subsequent ion-molecule reactions ("transformation processes") to occur.

A steady flow of primary reactive ions ([H₂O]+ or [H₃O]+) expends covalently into the quadrupole within the first differentially pumped pressure region.

**Ions Sources**

Two alternative ion sources are mounted on a custom Time-of-Flight mass spectrometer: A high pressure DC plasma (i) and a low pressure RF discharge (ii). A steady flow of primary reactive ions ([H₂O]+ or [H₃O]+) expends covalently into the quadrupole within the first differentially pumped pressure region (i – 3 mbar), which corresponds to a 100 mbar collisions with background particles per second, estimated from simple gas kinetic theory. A sample introduction stage allows to add the neutral sample at precisely determined positions into the quadrupole, which is in turn determined the total number of collisions. The extent of kinetic control with respect to the detection limits is assessed as a function of mixing ratio, amount of primary reactive ions and sample introduction position. Furthermore, the ability of the chemical system to dissipate excess energy from the protonation step is evaluated by the observed degree of fragmentation.

**High pressure DC plasma (i)**

The DC plasma is operated with helium at elevated pressure, which leads to the production of metastable helium atoms (1). In reaction cascade H₂O is formed by Penning ionization of H₂O and subsequent reaction steps with neutral hydrogen (2).

**Low pressure RF discharge (ii)**

The RF discharge source is operated directly with hydrogen at low pressure. The discharge source includes a helical coil reactor (HCR) providing sufficient RF energy to sustain the discharge. The RF plasma leads to the direct production of H₂O (for more details of Foster TP 422).

The figure above displays the prototyped BTEX signal distribution for three different sample positions in dependence of the transfer quadrupole background pressure for a 10 ppm BTEX mixture.

- The observed signal distributions are not sensitive to the quadrupole pressure and sample position.
- The upper figure on the left shows the total signal intensities and the lower figure on the left the signal distributions for a BTEX mixture introduced at three different positions into the quadrupole at the same pressure.
- The analyte signal intensities increase with the distance of the sample introduction position to the quadrupole exit.
- All observations strongly suggest, that the analyte-protonation step is under kinetic control with regard to all three sample introduction positions.

Conclusions

- Both ion sources, the high pressure DC plasma and the low pressure RF discharge source lead to comparable mass spectra when employed nitrogen as bulk gas.
- Subsequent quantitative transformation of H₂O into the reactive ions [H₂O]+ and [H₃O]+ for less exothermic protonation is demonstrated.
- Degree of protonation for the used analytes is > 95 %.
- Exclusion of formation of [M+H]+ ions observed.
- Protonation of an BTEX mixture under full kinetic control is demonstrated with LODs reaching low ppt levels.

Outlook

- Evaluation of a spark discharge plasma as a further alternative ion source for the formation of H₃O⁺ as primary charge carrier.
- A more detailed investigation of the extent of kinetic control with respect to ionization limits, mixing ratio, amount of primary reactive ions and sample introduction positions.
- Comparisons of the proton capacities of the different ion sources and determination of the total primary and analyte ion currents.
- Temporarily repeated experiments with pulsed ion sources (laser ionization) to determine the absolute reaction times in the quadrupole.
- Numerical simulations of reaction kinetics and ion trajectories in the quadrupole.
- Search for suitable reactive ions for a "reagent cascade" to further lower the excess energy upon protonation.

Literature


Acknowledgement

Generous financial support TOFwerk AG, Thun, Switzerland is greatly acknowledged.