

Instrument Modification for Inducing Parent Ion Fragmentation by Electron Beam Excitation

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Overview

Purpose

To perform induced parent ion fragmentation by electron beam excitation on a modified a triple quadrupole mass-spectrometer.

Method

- ESI was used to introduce sample solution to the mass-spectrometer;
- An electron excitation chamber was put in between two quadrupole;
- The chamber contains an entrance lens and an exit lens for ion focusing;
- The electron beam pass is perpendicular to the ion beam pass;
- The relative ion/electron energy can be tuned from 0 eV to 200 eV;
- The second quadrupole was used as a mass analyzer;

Result

Excitation of ions by interaction with electrons was successfully used to induce dissociation of reserpine molecular ions. The fragments corresponding to CH_3 radical and CH_2OH moieties elimination were observed.

Acknowledgement

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Introduction

The physical chemical methods employed to induce fragmentation of precursor ions in MS/MS experiments vary. Forcing precursor ions to collide with inert gas atoms is the most common means used to induce fragmentation. This technique, which is known as collisionally induced (or activated) dissociation (CID or CAD), is a powerful tool for acquiring amino acid sequence data from peptides that can be used to identify proteins and sites of modification on proteins. It is a feature of CID experiments that excitation energy is difficult to control and even more difficult to measure. Compared to CID, the use of an electron beam has the advantage that the excitation energy is better defined [1-3]. In addition, the internal energy of a precursor ion may be varied so that the product ion profile can be evaluated as a function of that energy. No commercial instruments are available in which ions can be excited by electrons. In the present work, we described the modification of a triple quadrupole instrument so that this kind of experiment can be performed.

Method

A triple quadrupole mass-spectrometer (Finnigan TSQ 700) was modified. The collision chamber (originally located between the first and the second quadrupoles) was replaced with a custom-made electron collision chamber. The electron collision chamber has an entrance focusing lens and an exit focusing lens for ions; electrons are introduced into the chamber perpendicular to the ion beam (Figure 1). A Thoriated Iridium disc cathode from Kimball Physics Inc. (ES-509) was used to produce the electron beam. A grid was placed in front of the cathode to extract the electrons, and another grid was placed at the entrance of the excitation chamber to establish a uniform accelerating field. Reserpine ions were formed by using a syringe pump (Harvard Apparatus, South Natick, MA) to infuse solution at a flow rate of 0.06mL/hr into an electrospray ionization source (ESI). The electron energy could be tuned from 0 eV to 200 eV; the relative ion/electron energy was set to 70 eV in this study. The ions produced by the excitation were analyzed by the second quadrupole.

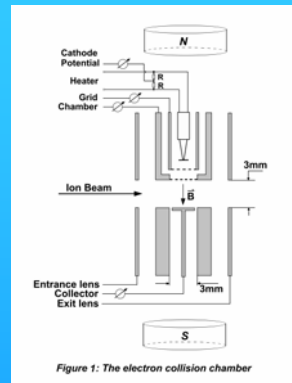


Figure 1: The electron collision chamber

Results

The intensity of the total ion signal increased about 120% when singly charged protonated molecular ions of reserpine were crossed with a 50 μA beam of electrons (Figure 2). This increase could be due to both the electron impact ionization (EI) of the M (608) molecules and the excitation of MH^+ (609) ions which are contained in the electrosprayed beam that passes through Q1 and enters the electron excitation chamber. The intensities of the fragment peaks at m/z 594 and 577, which are observed in the spectrum without electrons as a result of metastable decomposition, increased relative to the molecular ion intensity by about ten fold (Figure 3). These two fragment ions correspond to the neutral losses of CH_3 radical and CH_2OH respectively. Some smaller mass peaks in the range $m/z = 100\text{--}300$ originate from chemical background and are conditioned by the direct EI ionization of neutrals.

Conclusion

Ions can be excited by interaction with energetic electrons to induce dissociation. This was demonstrated through the observation of significantly enhanced neutral losses of CH_3 radical and CH_2OH moieties from molecular ions of reserpine produced by electron excitation.

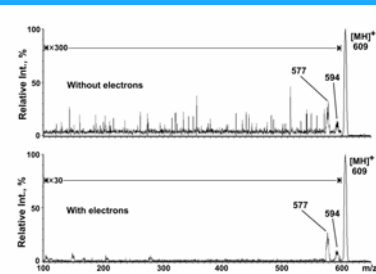


Figure 3: Mass spectra of reserpine with and without applying electrons

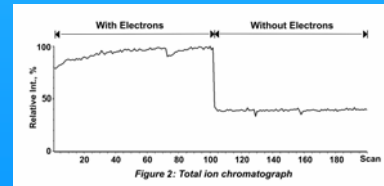


Figure 2: Total ion chromatograph

Reference

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3. M. D. Fedor, R. B. Cody, D. J. Burlinsky, B. S. Freiser, R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, **39**, 55 (1981).