

Application of Chemical Ionization by H₃O⁺ or NO⁺ and subsequent Collision Induced Dissociation of major product ions to selective on-line detection of sesquiterpenes and monoterpenes

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Abstract

Selective detection of Biogenic Volatile Organic Compounds (BVOC) is important due to the fact that individual BVOCs can affect atmospheric chemistry in different ways. However, existing on-line Chemical Ionization Mass Spectrometry (CIMS) techniques for BVOC quantification suffer from the difficulty to discriminate isomeric compounds.

Therefore, the feasibility of selective detection of a series of seven sesquiterpenes (SQT) and six monoterpenes (MT) using collision-induced dissociation (CID) of major product ions of their reactions with H₃O⁺ and/or NO⁺ has been investigated in a Flowing Afterglow Tandem Mass Spectrometer (FA-TMS). These BVOCs were chemically ionized by H₃O⁺ or NO⁺ reagent ions in the FA, resulting in major product ions at m/z 205 (SQT + H₃O⁺), m/z 204 (SQT + NO⁺) and m/z 136 (MT + NO⁺). These ions were subsequently subjected to CID with Ar atoms in the TMS collision cell

Although the fragmentation of protonated SQT (m/z 205) resulted in fragment ions at the same m/z values for all SQT investigated, differences in fragment ion intensities have been found between SQT. This enables SQT distinction based on intensity ratios at certain defined collision energies. The fragmentation of SQT molecular ions (m/z 204) resulted in the identification of tracer-fragment ions for α -cedrene, δ -neoclovene, isolongifolene and α -humulene. Finally, fragmentation of MT molecular ions (m/z 136) has also revealed some tracer-fragment ions for individual compounds or groups of compounds. Consequently, chemical ionization by NO⁺, followed by MS/MS seems to open a way for selective quantification of BVOCs in mixtures.

Introduction

A considerable quantity of global non-methane biogenic volatile organic compound emissions can be attributed to isoprenoids. Of these isoprenoids, isoprene is globally emitted in largest quantities but, dependent on the vegetation species and biotic and abiotic factors, monoterpene (MT, C₁₀H₁₆) and sesquiterpene (SQT, C₁₅H₂₄) emissions can be considerable as well. Within the class of isoprenoids, large differences have been observed between individual compounds regarding oxidation mechanisms, oxidation products formed and secondary organic aerosol (SOA) formation. Consequently, compound-specific concentration and flux measurements are necessary for accurate modeling of isoprenoid atmospheric chemistry and their impact on air quality and global climate.

Gas Chromatography Mass Spectrometric (GC-MS) and Chemical Ionization Mass Spectrometric (CIMS) techniques are commonly used to detect and quantify isoprenoids. CIMS techniques, such as Proton Transfer Reaction Mass Spectrometry (PTR-MS), have a high sensitivity and allow fast on-line measurements of reactive BVOCs such as SQT. However, an important disadvantage to CIMS techniques using H_3O^+ reactant ions is their impossibility to distinguish isomeric compounds. Improvements to selectivity can possibly be made by using other CI reagent ions such as NO^+ (e.g. [1], [2]) and/or the application of MS/MS techniques for the search for compound-specific fragmentation schemes obtained under controlled conditions ([3], [4]).

Recent collision induced dissociation (CID) experiments on a series of protonated MT (m/z 137) and two protonated SQT (m/z 205) by Müller *et al.* [4] have shown promising results concerning differentiation between isomeric protonated species. For further verification of the applicability of this approach to SQT differentiation, CID of a larger selection of SQT must be evaluated.

Therefore, in this study, the proton transfer product (m/z 205) from the reaction of H_3O^+ of seven different SQT and the charge transfer products of the reactions of NO^+ with six MT (m/z 136) and seven SQT (m/z 204) have been subjected to CID in a FA-TMS in view of their respective selective detection with H_3O^+ and NO^+ .

Experimental Methods

The isoprenoids investigated in this research are the MT α -pinene, β -pinene, Δ^3 -carene, γ -terpinene, limonene and myrcene, the SQT aromadendrene, β -caryophyllene, α -cedrene, α -humulene, isolongifolene, longifolene and δ -neoclovene.

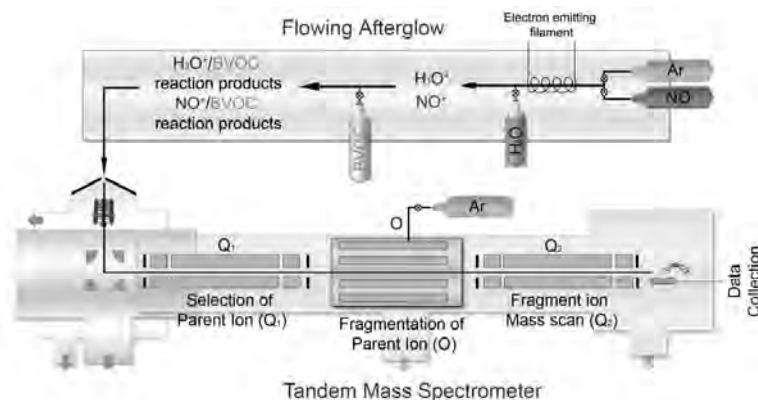


Figure 1: Schematic representation of the FA-TMS instrument

The instrument used in this experiment is a FA-TMS (see figure 1), consisting of a home-made Flowing Afterglow reactor coupled to a custom-designed Tandem Mass Spectrometer [3]. A controlled quantity of the isoprenoid neutral reactant is introduced in the FA and the reaction between the H_3O^+ or NO^+ reagent ion and the neutral takes place in the FA in Ar buffer gas at thermal conditions (295 K). After reaction, all product ions are sampled into the TMS. The CI product ion of interest is selected by a first quadrupole and subsequently enters the octupole collision cell where it can undergo CID. The collision cell is filled with Ar collision gas at a pressure of 0.11 Pa and depending on the collision energy in the center-of-mass frame (E_{CM}).

determined by the pole bias of the octupole and the stopping potential (determined by retardation potential analysis [3]), one or more fragments can be produced. The second quadrupole is used as a mass analyzer and after detection with a secondary electron multiplier, a fragmentation spectrum is obtained. When repeating this process for several E_{CM} values, fragmentation yields as a function of E_{CM} are obtained.

Results and discussion

CID of protonated SQT at m/z 205

A lot (30+) of different fragment ions were obtained from the CID of protonated SQT. To classify these fragments, fragment families were created of which each family gathered fragment ions separated by a CH_2 unit. This resulted in the identification of five separate families. Fragment ions found at an $E_{CM} < 2$ eV were found to correspond well to major fragments ions found for other techniques such as SIFT-MS and PTR-MS when introducing pure SQT.

Although our results were not corrected for mass discrimination, fragmentation fractions for protonated α -humulene at a m/z value of 0.68 eV are remarkably similar to the fragmentation fractions of α -humulene obtained by Müller *et al.* [4] in a PTR-LIT and a QqQ-MS at 12 V collision cell offset (U_{CC}). In comparison to the findings of Müller *et al.*, no tracer fragment ions were found for the SQT studied and only differences in selected intensity ratios, such as I_{69}/I_{123} , I_{121}/I_{123} and I_{83}/I_{135} , allow to respectively discriminate isolongifolene, α -cedrene and aromadendrene from the other SQT.

CID of the NO^+ /SQT charge transfer product at m/z 204

The fragmentation patterns of SQT molecular ions provide powerful information for the selective detection of SQTs.

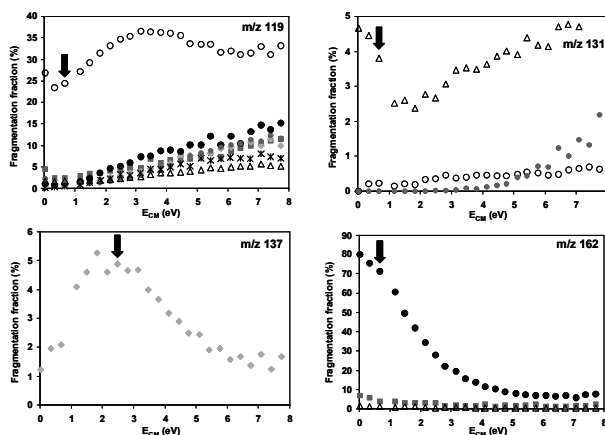


Figure 2: Fragmentation fractions (%) of ions at m/z 119, m/z 131, m/z 137 and m/z 162 as a function of ECM for break-up of protonated α -cedrene (\circ), δ -neoclovene (\bullet), aromadendrene (\blacksquare), longifolene (\blacklozenge), isolongifolene (\bullet), β -caryophyllene (\ast) and α -humulene (\triangle). Arrows indicate ECM values at which selective detection of α -cedrene (m/z 119), α -humulene (m/z 131), isolongifolene (m/z 137) and d -neoclovene (m/z 162)

At well-chosen collision energies, some tracers can be found. A fragment ion is considered as a tracer of a specific SQT if its fragmentation fraction is at least ten times higher than for the other SQTs studied. This is the case for ions at 0.7 eV (m/z 119) for α -cedrene, 0.7 (m/z 162) and 6.1 eV (m/z 83) for δ -neoclovene, 2.5 eV (m/z 137) for longifolene and 0.7 eV (m/z 131) for α -humulene. The fragmentation fractions as a function of ECM for the ions at m/z 119, 131, 137 and 162 are given in figure 2. Due to the often low fragmentation fractions of the tracer ions, the sensitivity of the instrument is a limiting factor.

CID of the NO⁺/MT charge transfer product at m/z 136

In comparison with the SQT, some tracers for individual MT were found at well-chosen collision energies for fragmentation of the MT charge transfer product at m/z 136. Tracers of limonene were found at 5.0 eV (m/z 68) and 4.6 eV (m/z 95).

Other tracer ions could be found under particular conditions. As an example, at 2.7 eV, ions at m/z 92 can only be used as sensitive tracer ions for α -pinene if Δ^3 -carene and limonene are not present in the mixture. Similarly, Δ^3 -carene can only be sensitively monitored at 0.9 eV via the ions at m/z 121 when the only other MT in the mixture is α -pinene.

Acknowledgements

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