



Laboratory studies in support of the detection of biogenic unsaturated alcohols by proton transfer reaction-mass spectrometry

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ABSTRACT

The effect of the ratio of the electric field to the buffer gas number density (E/N) in the drift tube reactor of a proton transfer reaction-mass spectrometer (PTR-MS) on the product ion distributions of seven common biogenic unsaturated alcohols (2-methyl-3-buten-2-ol, 1-penten-3-ol, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol, 6-methyl-5-hepten-2-ol and linalool) has been investigated. At low E/N values, the dominant product ion is the dehydrated protonated alcohol. Increasing E/N results in more extensive fragmentation for all compounds. For cis-3-hexenol and 6-methyl-5-hepten-2-ol the contribution of the protonated molecule can be enhanced by reducing E/N with respect to commonly used PTR-MS E/N values (120–130 Td). Significant differences have been found between some of the isomeric species studied, opening a way for selective detection. The C_{10} alcohol linalool mainly results in product ions at m/z 137 and 81, which are also PTR-MS fingerprints of monoterpenes. This may complicate monoterpene quantification when linalool and monoterpenes are simultaneously present in sampled air.

Furthermore the influence of the water vapour pressure in the PTR-MS inlet line on the product ion distributions has been determined. Some major fingerprint ions of the unsaturated alcohols were found to depend significantly on the water vapour pressure in the inlet line and this should be taken into account for accurate quantification of these species by PTR-MS.

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1. Introduction

Biogenic non-methane volatile organic compounds (BVOCs) are known to be of high significance to atmospheric chemistry because of their high reactivity with the main atmospheric oxidants (OH^\bullet , O_3 , NO_3^\bullet) [1] and the huge rates at which they are emitted globally by terrestrial vegetation ($\sim 1150 \text{ Tg C year}^{-1}$) [2]. An important fraction of these BVOCs consists of unsaturated compounds which, following reactions with OH^\bullet (during the day) or NO_3 radicals (at night), can form peroxy radicals which react with NO to NO_2 . Since photolysis of NO_2 is the first step in the formation of tropospheric O_3 , oxidation of biogenic VOCs directly results in net ozone formation in polluted environments [3]. Accurate quantification of BVOC fluxes from terrestrial ecosystems, leading to improved emission inventories, is expected to result in better estimations of tropospheric oxidant levels using regional chemistry and transport models.

Oxidation of BVOCs can also result in secondary organic aerosol formation (SOA) through condensation of less-volatile oxidation products on existing aerosols or possibly through formation of new aerosol nuclei [4]. Aerosols as well as elevated tropospheric oxidant levels are known to have a negative impact on air quality and on human health in particular.

Proton transfer reaction-mass spectrometry (PTR-MS) is a frequently used technique for the measurement of BVOC concentrations. It was originally developed about 15 years ago at the University of Innsbruck by Lindinger et al. and has been described in many extensive review papers [5–7]. Basically it is a soft ionization technique based on exothermic proton transfer reactions between H_3O^+ ions and compounds with a higher proton affinity than water. These ion/molecule reactions take place in a drift tube reactor through which the sampled air flow is pumped continuously. At the downstream end of the drift tube, reagent and product ions are sampled into a quadrupole mass spectrometer, and the product ion signal of the trace compound to be measured is proportional to the mixing ratio of that compound in the air flow. PTR-MS allows the monitoring of several VOCs of interest with a high sensitivity (10–100 pptv) and rapid response time (100–200 μs) [6,7]. In addition, the technique does not require any

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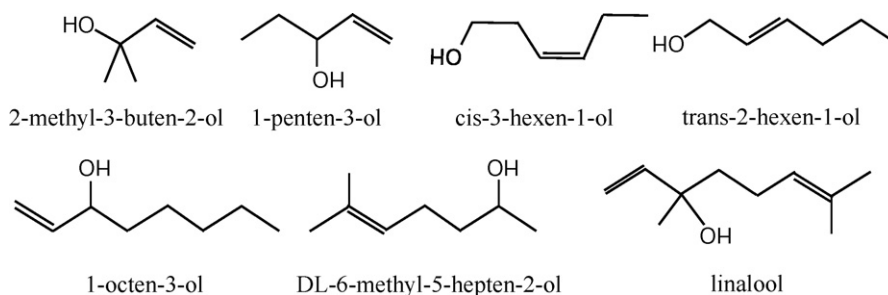


Fig. 1. Structures of the biogenic unsaturated alcohols studied.

sample treatment such as drying or pre-concentration. Due to these advantages it is nowadays frequently applied in diverse fields such as atmospheric/environmental chemistry and monitoring, breath analysis and food chemistry [7] and it complements the highly sensitive and chemically detailed snapshots obtained by the rather time-consuming GC techniques.

A major disadvantage of PTR-MS, however, is that identification is only based on the mass of the product ions, which is a valuable but certainly not a unique indicator of the identity of trace gases. It is clear that different isomers in most cases cannot be separated in this manner. In order to overcome this inconvenience, substantial efforts have recently been put into the development of fast and sensitive on-line techniques combining chemical ionization with MS/MS capabilities (e.g. [8,9]), enabling in this way selective detection of isomers by multiple reaction monitoring-mass spectrometry (MRM-MS).

Interpretation of PTR-MS mass spectra can also be complicated by the fragmentation of product ions, which may lead to mass overlap. By decreasing the drift tube voltage this fragmentation can be reduced, resulting in a higher contribution of the protonated molecule or of a typical fragment with a mass close to the one of the protonated molecule. This voltage decrease, however, also results in increased hydration of reactant and product ions, which in turn can also lead to more complex mass spectra.

Some authors [10–12] pointed out that, in order to increase detection sensitivity or to differentiate between isobaric or isomeric compounds in standard PTR-MS instruments, it might be useful to change the PTR-MS settings (in essence the E/N parameter with E the drift field and N the air number density in the reactor) as a function of the VOC to be monitored. In this respect, there is a clear need for systematic studies of PTR-MS product ion distributions of various classes of VOCs as a function of instrumental parameters (E/N) and environmental conditions (relative humidity–RH).

First systematic studies of this kind for biogenic VOCs were initiated by Tani et al. [13,14] who studied the influence of E/N and RH on PTR-MS product ion distributions of monoterpenes. More recently, Demarcke et al. [10] and Kim et al. [15] reported similar studies involving sesquiterpenes. These studies revealed that a decrease of E/N from 140 to 80 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2 \text{ molecule}^{-1}$) could lead to an increase in sesquiterpene detection sensitivity (based on the protonated sesquiterpene ion signal at m/z 205) by a factor 3.5. Moreover, the product ion distributions were found to be independent of relative humidity, which simplifies calibration, and the data indicate that PTR-MS detection of monoterpenes can be hampered by the simultaneous presence of sesquiterpenes since the latter are known to produce fragment ions at the m/z values (81 and 137) of the fingerprint ions of the former.

The present systematic study focuses on unsaturated alcohols of biogenic origin. PTR-MS product ion distributions of two C₅ alcohols (2-methyl-3-buten-2-ol and 1-penten-3-ol, $M = 86 \text{ g mol}^{-1}$), two C₆ alcohols (cis-3-hexen-1-ol and trans-2-hexen-1-ol, $M = 100 \text{ g mol}^{-1}$), two C₈ alcohols (1-octen-3-ol and

DL-6-methyl-5-hepten-2-ol, $M = 126 \text{ g mol}^{-1}$) and the C₁₀ alcohol linalool ($M = 154 \text{ g mol}^{-1}$) at different E/N values and relative humidities will be reported. The chemical structure of these compounds is shown in Fig. 1.

The choice for these compounds was motivated by the fact that they have all been reported to be emitted by plants, fungi or insects. High emission rates of 2-methyl-3-buten-2-ol were measured from needles of several pine species in Western North America [16–18]. The C₅ alcohols 1-penten-3-ol and 2-methyl-3-buten-2-ol and the C₆ alcohols cis-3-hexen-1-ol and trans-2-hexen-1-ol were found to be emitted by plants which were exposed to physical damage such as cutting and/or drying [19–21]. The high sensitivity and fast response of the PTR-MS instrument made it possible to establish the transient nature of the emissions of these compounds. The C₈ alcohol 1-octen-3-ol was found to be emitted by mushrooms, exhibiting the typical fungal odour note [22]. 6-Methyl-5-hepten-2-ol, also known as sulcatol, is a pheromone which is released by forest insects [23,24]. Finally, next to being an important fragrance compound [25], the terpenoid C₁₀ alcohol linalool has been reported to be emitted by some Mediterranean Pine (*Pinus pinea* [26] and *Pinus halepensis* [27]) and *Quercus* species [28] and orange blossoms of some citrus varieties [29]. Recent branch enclosure studies in the framework of the IMPECVOC project (www.impecvoc.ugent.be) have revealed significant emissions of linalool from *Fagus sylvatica* L. trees in controlled growth chamber conditions as well as from adult trees in a natural environment [30]. PTR-MS measurements of monoterpenes (by monitoring product ions at m/z 137) in some of these experiments were clearly hampered by the presence of linalool. Studying the variation of the linalool product ion distribution at different instrumental conditions can be considered as a first step in trying to solve this interference.

Furthermore, all seven reactants have previously been introduced in a Selected Ion Flow Tube-Mass Spectrometer (SIFT-MS) in our laboratory [31–33], which enables qualitative comparison of PTR-MS and SIFT-MS product ion distributions.

2. Experimental

In the present study, a high sensitivity (hs) PTR-MS apparatus (Ionicon Analytik GmbH, Austria) was used at a drift tube pressure of 2.2 hPa and a drift temperature of 333 K. The experimental setup for introducing the alcohols in the PTR-MS is a modified version of the one used previously to introduce sesquiterpenes [10].

2.1. Dilution of alcohols in purified and humidity-controlled air

A schematic representation of the experimental setup for diluting the reactant alcohols in humidity-controlled, dust- and VOC-free laboratory air is shown in Fig. 2.

Laboratory air is pumped by a diaphragm pump (MVP-055, Pfeiffer Vacuum, Germany) and sent through a dust filter (Zefluor™ PTFE Membrane Filter, 2 μm pore size) (#1 in Fig. 2) and a set

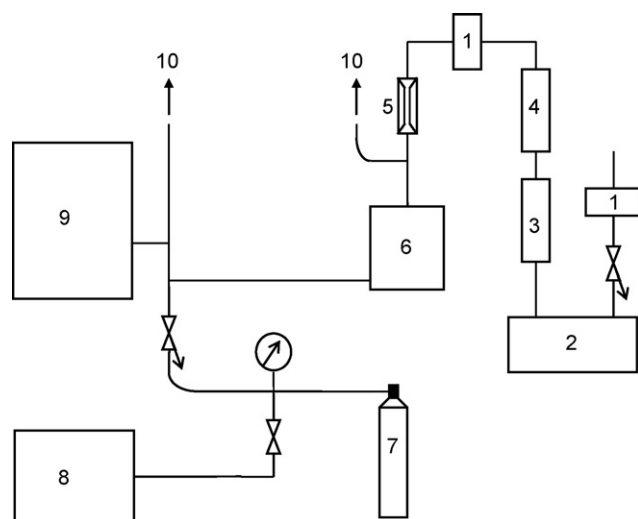


Fig. 2. Schematic representation of the experimental setup for introducing dilute mixtures of the reactant compounds in dust- and VOC-free air in the PTR-MS: (1) dust filter (2) diaphragm pump, (3) and (4) active coal filters, (5) flowmeter, (6) dew point generator, (7) gas bottle with diluted alcohol, (8) vacuum pump, (9) PTR-MS and (10) exhaust.

of active coal filters (Airpel 10, Organosorb 10-CO, Desotec, Belgium) (#3 and 4), resulting in the efficient removal of volatile organic compounds in the air flow. A second dust filter (#1) was used to remove possible dust particles originating from the active coal filters. Subsequently, part of this dust- and VOC-free air flow (1 L min^{-1}) was introduced in a LI-610 dew point generator (LICOR) (#6) for controlling the humidity. A small flow of a dilute mixture of the unsaturated alcohol in helium was then added to the purified and humidity-controlled air flow by means of a needle valve. The dilute alcohol/He mixture was prepared in a 5 L glass bottle (#7) at a total initial He pressure of about 1100 hPa. The alcohol mixing ratio in the bottle varied from 1.1×10^{-3} for the C_5 alcohols to 1.2×10^{-4} for linalool.

Part of the purified humidity-controlled air flow containing traces of the reactant alcohol was then introduced in the PTR-MS through a heated PEEK capillary inlet line (60°C). Apart from this PEEK line, all inlet tubing, which was in contact with the alcohols and which was made of stainless steel, was kept as short as possible, and heated to 60°C to prevent condensation on the tube walls. It should however be noted that possible losses of alcohols in the inlet lines were not very important for the present study, since the aim was to determine PTR-MS product ion distributions of biogenic unsaturated alcohols and not to determine the absolute sensitivity of the PTR-MS for detection of these compounds.

2.2. Mass discrimination measurements

The overall ion transmission of the PTR-MS is mass-dependent and must be known in order to determine accurate product ion distributions. Therefore, mass discrimination measurements were performed regularly according to the procedure described in a previous publication [10].

2.3. Chemicals used

2-Methyl-3-buten-2-ol, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol and linalool were purchased from Sigma Aldrich and have a purity of 98, 98, 96, 98 and 97%, respectively. 1-Penten-3-ol and DL-6-methyl-5-hepten-2-ol are Acros Organics products with a purity of 99% for both compounds. Helium was obtained from Air Products and has a purity of 99.9997%.

3. Results and discussion

3.1. General comment

Because of the high water vapour content of ambient air, hydronium reagent ions (H_3O^+) rapidly hydrolyse to form higher order proton hydrates (mainly $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 1$ and 2). The presence of the drift field, however, counteracts this cluster ion formation and at the E/N values that are commonly used in PTR-MS (120–130 Td), the contribution of bare hydronium ions to the proton hydrate distribution is about 95%. Hydronium ions react with all seven unsaturated alcohols M studied at the collision limit, as reported in earlier SIFT studies [31,32]. The main reaction mechanism that was observed for reactions between H_3O^+ ions and unsaturated alcohols in these SIFT studies was proton transfer followed by ejection of a water molecule, resulting in the $(M-\text{OH})^+$ ion. Only a limited fraction of the nascent excited complex MH^{**} is stabilized through collisions with the buffer gas molecules, resulting in the protonated molecular ion MH^+ . It should be noted, however, that in these SIFT studies, reactant and product ions are in thermal equilibrium with helium buffer gas molecules, whereas in the present PTR-MS experiments the ions are subjected to the drift field, which results in an increased collision energy and consequently in more extensive fragmentation.

Since variation of the drift field strength implies changes in the distribution of reactant proton hydrates as well as changes in the collision energy of the reactant ion/alcohol system, it will have a profound influence on the overall PTR-MS product ion distribution of individual compounds. In what follows the influence of this drift field, expressed in terms of the E/N ratio, on the product ion distributions of the different compounds will be shown and discussed. It should be stressed that in this work distributions of ion species (taking into account all isotopes) are presented instead of relative ion signal contributions to the different m/z ratios, as is frequently observed in PTR-MS related literature. The m/z values in the figures refer to the first isotope of the ion species.

3.2. Procedure for deriving PTR-MS product ion distributions of the reactant alcohols

Full mass scans were used to identify the product ions at two water vapour pressures at the PTR-MS inlet (0.61 and 1.71 kPa), controlled by the dew point generator, and at two E/N values (80 and 140 Td). At each condition, scans were normalized with respect to the most abundant product ion of the total scan. All product ions with a normalized count rate higher than 0.5% in at least one of the conditions were then followed in the multiple ion detection (MID) mode, for five water vapour pressures (0.61, 0.76, 1.32, 1.71 and 2.21 kPa) and three different values of E/N (80, 110 and 140 Td). At a water vapour pressure of 0.61 kPa measurements were performed at four additional values of E/N (90, 100, 120 and 130 Td). Corrections for background signals, mass discrimination and isotopic abundance were subsequently applied to the averaged count rates of the product ions that were monitored in the MID mode.

For some of the unsaturated biogenic alcohols of interest in the present study, fragment ions were observed at m/z 39 and m/z 55, which can be assigned to the main isotope of C_3H_3^+ and C_4H_7^+ ion species, respectively. Since the second most abundant isotope of $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and the main isotope of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ (two reactant ions which become important at lower E/N values) also have m/z values of 39 and 55, respectively, special care had to be taken to determine what fraction of the ion signals resulted from the product ions and what fraction from the reactant ions.

At the highest E/N values the ratio of the ion signal intensity at m/z 56 to the one at m/z 55 (all signals corrected for background and mass discrimination) is very close to the expected isotopic abun-

dance of 0.044 for the second isotope of the $C_4H_7^+$ fragment (m/z 56). Therefore the ion signal at m/z 55 could almost entirely be attributed to this hydrocarbon fragment. At intermediate E/N values, however, the $H_3O^+ \cdot (H_2O)_2$ signal intensity at m/z 55 becomes rather high. Consequently, determination of the contribution of $C_4H_7^+$ to m/z 55 by subtracting the ion signal intensities with and without reactant gas may become inaccurate. Since the isotopic abundance of $H_3O^+ \cdot (H_2O)_2$ at m/z 56 is about 20 times lower than the one of $C_4H_7^+$ at m/z 56, it is more appropriate to obtain the $C_4H_7^+$ ion intensity at m/z 55 by dividing the difference in ion signal intensity with and without reactant gas at m/z 56 by a factor 0.044. At low E/N values, at which the abundance of the reactant $H_3O^+ \cdot (H_2O)_2$ ion to the proton hydrate distribution becomes important, the contribution of the $C_4H_7^+$ ion species to the product ion distribution could already be neglected, as could be derived from its decreasing trend with decreasing E/N .

Determination of the contribution of the $C_3H_3^+$ fragment to the ion signal at m/z 39 could be limited to the two highest E/N values at which the relative difference of the ion signal with and without reactant alcohol was still sufficiently high for reliable quantification. Because the contribution of the $C_3H_3^+$ fragment to the product ion distributions was found to strongly decrease with decreasing E/N values and since this contribution at the second highest E/N value (130 Td) was never higher than 2%, the product ion signal at m/z 39 could be neglected at E/N values below 130 Td.

3.3. E/N dependence of the product ion distributions of the investigated unsaturated biogenic alcohols

3.3.1. C_5 alcohols

The E/N dependence of the product ion distributions of 2-methyl-3-buten-2-ol and 1-penten-3-ol is shown in Fig. 3. Only product ions contributing more than 1% for at least one E/N value are plotted. For reasons of comparison, product ion distributions of the reactions of H_3O^+ , $H_3O^+ \cdot H_2O$ and $H_3O^+ \cdot (H_2O)_2$ ions with these molecules, recently obtained in a SIFT apparatus equipped with a Flowing Afterglow ion source (FA-SIFT) [33], are also shown.

PTR-MS product ions that are common for both C_5 unsaturated alcohols were found at m/z values of 87, 69, 41 and 39. These ion species can be assigned to the protonated molecule $C_5H_{11}O^+$, $C_5H_9^+$ (the product ion resulting from elimination of a water molecule following proton transfer), $C_3H_5^+$ and $C_3H_3^+$, respectively. The contribution of the protonated molecule (m/z 87) at high E/N values (>120 Td) is in rather good agreement with what was obtained in SIFT measurements involving bare hydronium ions. For the entire range of E/N values the dehydrated protonated molecule (m/z 69) is the major product ion with a contribution from 95% at 80 Td to 40% at 140 Td for both species. At increasing E/N values the abundance of this ion decreases and the fragment ions $C_3H_5^+$ (m/z 41) and $C_3H_3^+$ (m/z 39) start to emerge. These two ion species were also observed as CID fragments of $C_5H_9^+$ in a recent Flowing Afterglow-Tandem Mass Spectrometry (FA-TMS) study of biogenic C_5 compounds [8]. As expected from their small contributions at low E/N values, the fragments at m/z 39 and 41 were not observed in the SIFT studies.

For 1-penten-3-ol a product ion species was also observed at m/z 45 and was attributed to the oxygenated hydrocarbon $C_2H_5O^+$. This ion species was also present in the SIFT-MS H_3O^+ product ion distribution and the FA-TMS study clearly demonstrated it to be a Collision-Induced-Dissociation fragment of protonated 1-penten-3-ol [8].

The product ion distributions for 2-methyl-3-buten-2-ol are in fair agreement with the ones which were reported recently by Herdinger et al. [34] for the same compound over a more limited E/N range (100–130 Td). However, in contrast to their study in which the contribution of the protonated molecule (m/z 87) remains almost constant over the entire E/N range, a clear varia-

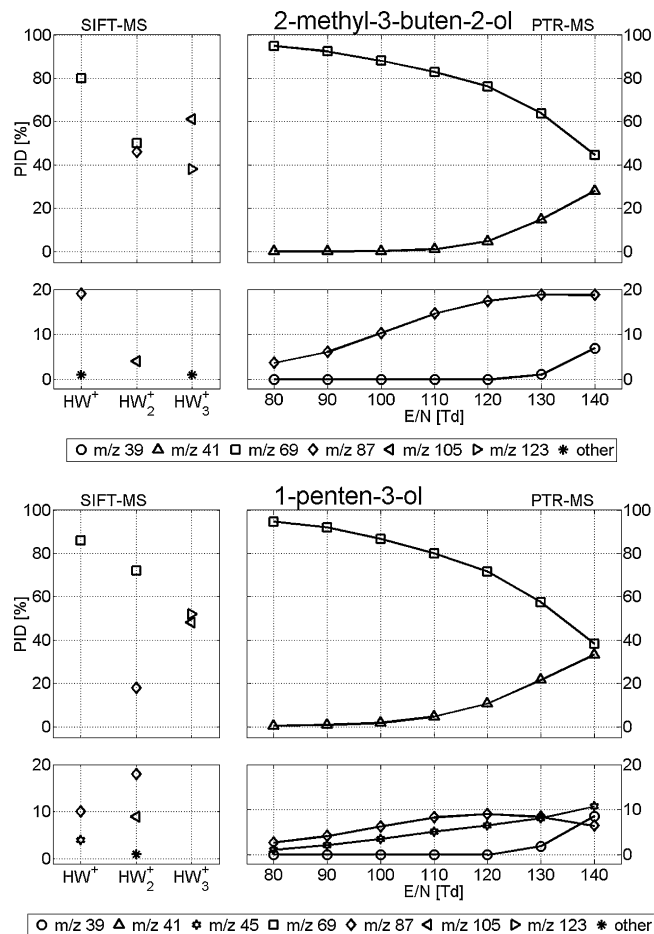


Fig. 3. Product ion distributions (PID [%]) of 2-methyl-3-buten-2-ol (up) and 1-penten-3-ol (down) as a function of E/N at a water vapour pressure of 0.61 kPa obtained by PTR-MS (right) and compared to SIFT-MS product ion distributions of reactions of individual proton hydrate reactants with the neutral compounds [33] ($W = H_2O$) (left). Only those product ions with an abundance of more than 1% for at least one of the E/N settings are shown.

tion of the contribution of the protonated molecule was noticed as a function of E/N in our study. This was also the case for 1-penten-3-ol. The lowest contribution of m/z 87 was observed at the lowest E/N values, which is somewhat surprising. Higher contributions of $H_3O^+ \cdot H_2O$ and $H_3O^+ \cdot (H_2O)_2$ at low E/N values cannot be invoked to explain this behaviour. Indeed, the FA-SIFT product ion distributions of these higher order proton hydrates suggest that the contribution of the protonated molecule should increase with decreasing E/N , rather than decrease.

Ions at m/z 105 and 123, which have been observed as ligand switching products of the reactions of $H_3O^+ \cdot H_2O$ and $H_3O^+ \cdot (H_2O)_2$ with the C_5 alcohols in the FA-SIFT study, were absent in the PTR-MS spectra, even at the lowest E/N value.

3.3.2. C_6 alcohols

PTR-MS product ions contributing more than 1% for at least one E/N value for *cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol are shown in Fig. 4. In this figure, recent data on product ion distributions of H_3O^+ , $H_3O^+ \cdot H_2O$ and $H_3O^+ \cdot (H_2O)_2$ ions with these C_6 alcohols, obtained in a FA-SIFT instrument [33], can also be found.

As can be noticed in this figure, at high E/N values the ion chemistry is dominated by dissociative proton transfer and the product ion distributions are very similar for both compounds. Whereas for *trans*-2-hexen-1-ol the protonated molecular ion $C_6H_{13}O^+$ at m/z 101 was not observed over the entire E/N range, its contribution

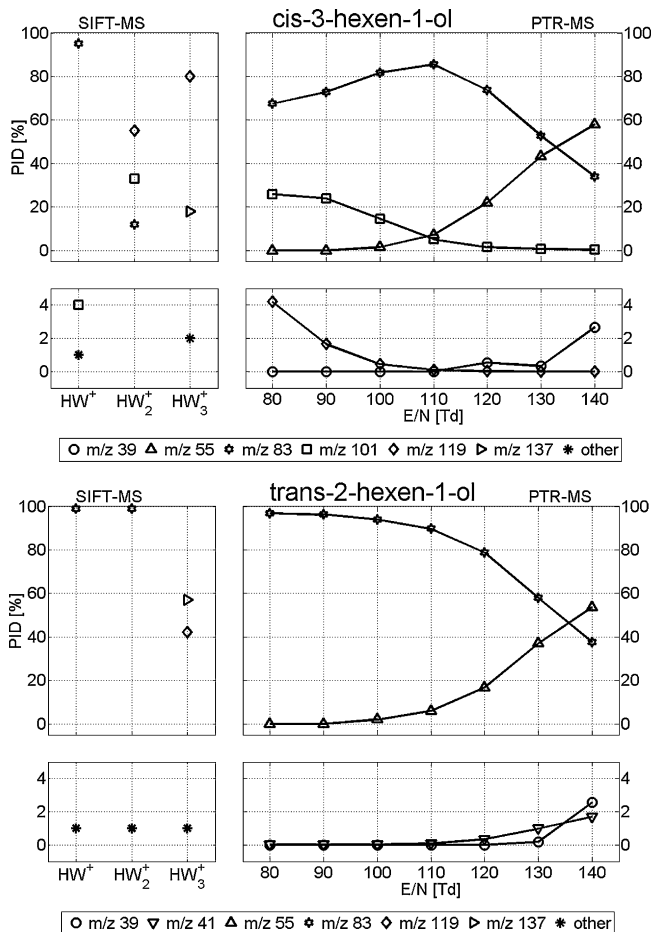


Fig. 4. Product ion distributions (PID [%]) of *cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol as a function of E/N at a water vapour pressure of 0.61 kPa. Only those product ions with an abundance of more than 1% for at least one of the E/N settings are shown. SIFT-MS product ion distributions of reactions of individual proton hydrate reactants with the neutral compounds are also shown [33] ($W = H_2O$).

gradually increased from 0% at 140 Td to about 30% at 80 Td for *cis*-3-hexen-1-ol.

For both C_6 alcohols high contributions were obtained for the dehydrated protonated molecule at m/z 83, especially at low E/N values. At higher E/N , i.e. higher collision energies, fragments appeared at m/z 55, 41 and 39, which are assigned to $C_4H_7^+$, $C_3H_5^+$ and $C_3H_3^+$, respectively. At 140 Td $C_4H_7^+$ even became the dominant ion species for both compounds.

The absence of the protonated molecule in the case of *trans*-2-hexen-1-ol (m/z 101) is in agreement with previous SIFT studies [32] and is supported mechanistically by more efficient formation of the dehydrated protonated molecule because of resonance stabilisation of this allyl cation. Its contribution in the SIFT product ion distribution of the H_3O^+/cis -3-hexen-1-ol reaction (4%), however, is much smaller than the contribution in PTR-MS at the lowest E/N value (26%). This time the ion chemistry of higher order proton hydrates with the C_6 alcohols, which has also been elucidated in the recent FA-SIFT study [33], can help to clarify this difference. At an E/N value of 80 Td $H_3O^+ \cdot H_2O$ is the predominant proton hydrate in the PTR-MS drift tube reactor. Consequently, one would expect an increase of protonated *cis*-3-hexen-1-ol as is the case in the FA-SIFT $H_3O^+ \cdot H_2O/\text{cis}$ -3-hexen-1-ol product ion distribution. Further comparison of the PTR-MS and SIFT-MS product ion distributions show that the lower molecular weight PTR-MS fragments at m/z 55, 41 and 39 do not appear in the SIFT data. On the other hand, a non-negligible contribution (4%) of the hydrated pro-

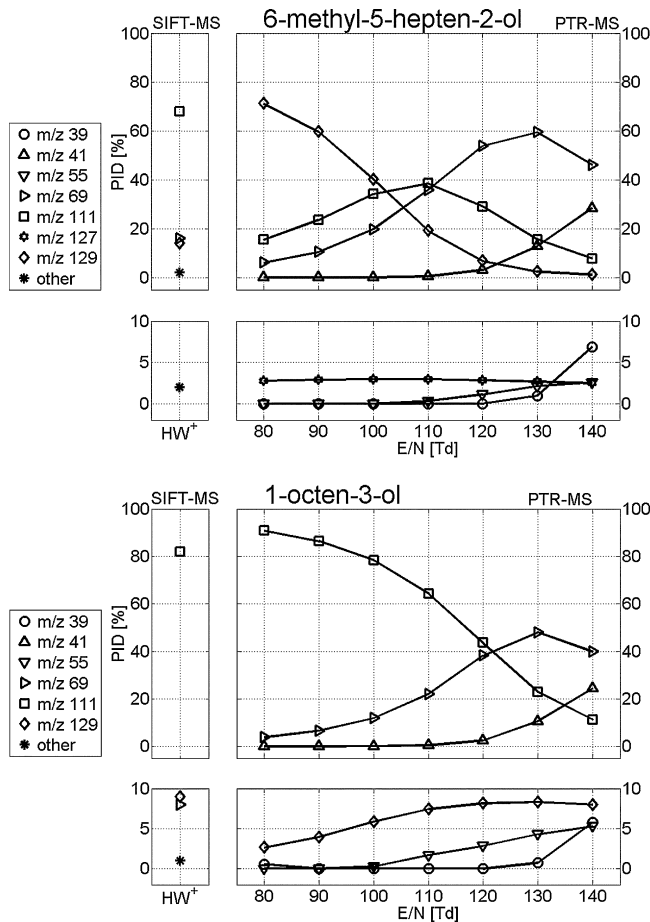


Fig. 5. Product ion distributions (PID [%]) of 6-methyl-5-hepten-2-ol and 1-octen-3-ol as a function of E/N at a water vapour pressure of 0.61 kPa. Only those product ions with an abundance of more than 1% for at least one of the E/N settings are shown. Also shown are SIFT-MS product ion distributions of H_3O^+ with these compounds [32].

nated molecule ($H_3O^+ \cdot C_6H_{12}O$ at m/z 119) for *cis*-3-hexen-1-ol at 80 Td, may be explained by ligand switching reactions of $H_3O^+ \cdot H_2O$ and $H_3O^+ \cdot (H_2O)_2$ (followed by ejection of a H_2O molecule), since considerable branching ratios were found for these ligand switching channels in the FA-SIFT experiments. However, direct hydration of protonated *cis*-3-hexen-1-ol as a source of the ion species at m/z 119 is also an option since this ion species does not appear in the case of *trans*-2-hexen-1-ol, which is consistent with the absence of the protonated molecule.

3.3.3. C_8 alcohols

PTR-MS product ion distributions of the two unsaturated biogenic C_8 alcohols 6-methyl-5-hepten-2-ol and 1-octen-3-ol are shown as a function of E/N and at a water vapour pressure of 0.61 kPa in Fig. 5. Again the SIFT product ion distribution of the reactions of H_3O^+ ions with the two compounds are shown as well [32].

As can be noticed in this figure, these compounds show more fragmentation than the C_5 and C_6 alcohols and it is worth pointing out that some product ions have identical m/z ratios as those formed when introducing C_5 alcohols in the PTR-MS. This is probably due to a similar chemical structure, more specifically of 1-octen-3-ol and 1-penten-3-ol.

Important differences can be noticed in the product ion distribution of the two compounds. Whereas the contribution of the protonated molecular ion $C_8H_{17}O^+$ at m/z 129 for 6-methyl-5-hepten-2-ol is negligible at 140 Td and increases with decreasing

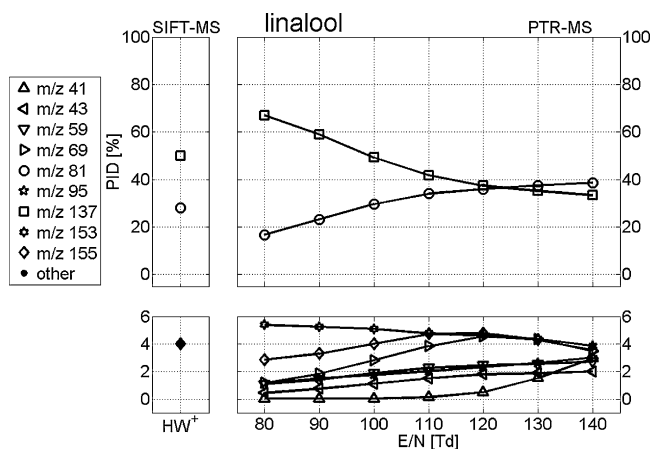


Fig. 6. Product ion distribution of linalool as a function of E/N at a water vapour pressure of 0.61 kPa. Only those product ions with an abundance of more than 1% for at least one of the E/N settings are shown. Also shown is the SIFT-MS product ion distribution of the H_3O^+ /linalool reaction [31].

E/N towards 70% at 80 Td, an opposite trend is noticed for 1-octen-3-ol. Indeed, the contribution of $\text{C}_8\text{H}_{17}\text{O}^+$ for the latter species is about 8% at 140 Td, in fair agreement with the SIFT-MS branching ratio of this product ion for the reaction of bare H_3O^+ with 1-octen-3-ol, but gradually decreases with decreasing E/N .

Quite different trends were also found for the dehydrated protonated molecule $\text{C}_8\text{H}_{15}^+$ at m/z 111. Whereas the contribution of this ion species goes through a maximum at 110 Td for 6-methyl-5-hepten-2-ol, it decreases from 91% at 80 Td to 11% at 140 Td for 1-octen-3-ol. A fragment at m/z 127 was only observed for 6-methyl-5-hepten-2-ol and its contribution was not found to vary with E/N . Since no FA-SIFT product ion distributions of $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ are available for the C_8 compounds, ion chemistry cannot be taken into account to explain the observed differences. The lower molecular weight fragments at m/z 69, 55, 41 and 39, however, show quite similar behaviour as a function of E/N for both compounds.

A PTR-MS product ion distribution of 1-octen-3-ol has been reported previously by Buhr et al. [35] who introduced the headspace of an aqueous solution of this compound in a PTR-MS at a drift voltage of 600 V. The results that were obtained by these authors are in agreement with the product ion distribution found in the present study at similar instrumental conditions.

3.3.4. C_{10} alcohol linalool

PTR-MS product ion distributions of linalool are shown as a function of E/N and at a water vapour pressure of 0.61 kPa in Fig. 6. The SIFT product ion distribution of the reaction of H_3O^+ ions with the linalool is shown as well [32].

As can be noticed in Fig. 6, two major product ions dominate the PTR-MS product ion distribution of linalool, more particularly the dehydrated protonated molecule $\text{C}_{10}\text{H}_{17}^+$ at m/z 137, and a C_6H_9^+ fragment at m/z 81.

The increased contribution of $\text{C}_{10}\text{H}_{17}^+$ at low E/N can again be explained by the larger contribution of this ion species in the product ion distribution of $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ ions with linalool, as determined by FA-SIFT experiments [36].

The contribution of the protonated molecular ion $\text{C}_{10}\text{H}_{19}\text{O}^+$ at m/z 155 varies between 3 and 5% over the entire E/N range and is in agreement with the SIFT branching ratio of the non-dissociative proton transfer channel (4%) and with Maleknia et al. [11], who also concluded that reduced drift tube voltages do not increase the abundance of protonated linalool.

Table 1

Relative variation (in %) of the product ion branching ratios (BR) of the different compounds between the highest (2.21 kPa) and lowest (0.61 kPa) water vapour pressure at the PTR-MS inlet, i.e. $(\text{BR}_{2.21\text{ kPa}} - \text{BR}_{0.61\text{ kPa}})/\text{BR}_{0.61\text{ kPa}}$, for three different E/N values. Relative variations of product ions with a branching ratio below 2% have not been considered and are marked by "X".

m/z	2-Methyl-3-buten-2-ol			1-Penten-3-ol		
	80 Td	110 Td	140 Td	80 Td	110 Td	140 Td
39	X	X	-60	X	X	-42
41	X	X	-16	X	-30	-12
45	X	X	X	X	-25	-13
69	2	5	19	2	4	18
87	-47	-23	0	-43	-20	15
m/z	cis-3-Hexen-1-ol			trans-2-Hexen-1-ol		
	80 Td	110 Td	140 Td	80 Td	110 Td	140 Td
39	X	X	-44	X	X	-43
41	X	X	X	X	X	-20
55	X	-38	-4	X	-26	-9
83	1	0	20	1	2	17
101	-5	88	X	X	X	X
119	64	X	X	X	X	X
m/z	6-Methyl-5-hepten-2-ol			1-Octen-3-ol		
	80 Td	110 Td	140 Td	80 Td	110 Td	140 Td
39	X	X	-58	X	X	-58
41	X	-56	-21	X	X	-23
55	X	X	4	X	X	9
69	-46	-26	22	-30	-20	13
111	-45	-9	38	3	12	31
127	X	X	X	X	X	X
129	7	72	66	-46	-18	0
m/z	Linalool					
	80 Td	110 Td	140 Td	80 Td	110 Td	140 Td
41	X	X	X	X	X	-26
43	X	X	X	X	X	X
59	X	X	-17	X	X	-4
69	X	X	-21	X	X	9
81	-36	-7	-7	X	X	-2
95	-31	-7	-7	X	X	-2
137	-5	6	6	X	X	1
153	-6	3	3	X	X	0
155	-29	-15	-15	X	X	5

Apart from the above reported ion species, fragments were also observed at m/z 153 ($\text{C}_{10}\text{H}_{17}\text{O}^+$), 95, 59, 69, 43 and 41, but their abundances never exceeded 6% within the entire E/N range.

3.4. Influence of the relative humidity on the product ion distributions

The influence of air humidity on the product ion distributions of the compounds studied has been investigated at three different E/N values (80, 110 and 140 Td) and at seven values of the water vapour partial pressure (0.61, 0.76, 1.32, 1.71, 2.21 kPa) at the inlet of the PTR-MS. All product ion contributions were found either to be independent of water vapour pressure or to vary with water vapour pressure in a linear way.

The humidity dependence of the contributions of the individual product ions to the product ion distribution of the various compounds is shown in Table 1.

In this table only product ions with a contribution higher than 2% are considered and the numbers in the table refer to the percentage variation of the contribution at the highest water vapour pressure (2.21 kPa) with respect to the contribution at the lowest water vapour pressure (0.61 kPa). A typical example of the humid-

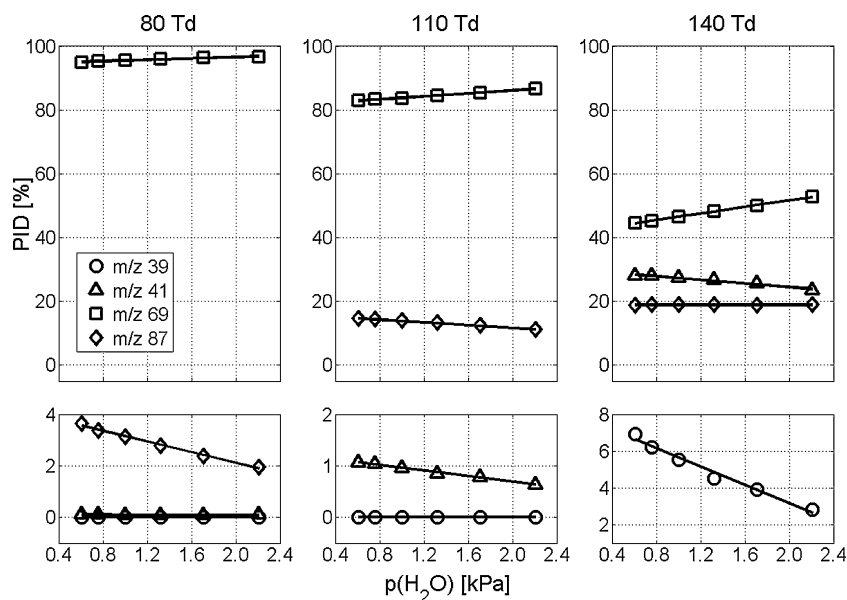


Fig. 7. Water vapour pressure dependence of the PTR-MS product ion distribution of 2-methyl-3-butene-2-ol at three E/N values (80, 110 and 140 Td).

ity dependence of the product ion distribution is shown in Fig. 7 for the case of 2-methyl-3-buten-2-ol.

As pointed out in Section 3.3.1 and shown in Fig. 3, the contribution of the protonated molecule at m/z 87 shows a decrease with decreasing E/N , i.e. with increased contribution of higher order proton hydrates. The data from Fig. 3 were obtained at the lowest water vapour pressure (0.61 kPa), but from Fig. 7 it can be noticed that this decreasing trend continues when keeping E/N at 80 Td and adding additional water vapour to the inlet flow. The same behaviour, resulting in a large negative value in Table 1, was also observed for the contribution of the protonated 1-penten-3-ol (−43%) and protonated 1-octen-3-ol (−46%), as well as for protonated linalool (−39%).

Other important information that can be derived from Table 1 is that at high E/N values the contribution of the dehydrated protonated molecule, which is often considered as the PTR-MS fingerprint ion species for the compounds studied, generally increases significantly (between 17 and 38% for all compounds studied, except for linalool) when varying the water vapour pressure from 0.61 to 2.21 kPa.

4. Conclusion

The results obtained in the present study indicate that it is useful to explore the variation of the product ion distributions of this class of compounds as a function of E/N and humidity. Indeed, for the C_6 alcohols, for instance, it becomes clear that a reduction of E/N with respect to traditionally used PTR-MS voltages (120–130 Td) results in a significant contribution of the protonated molecule for *cis*-3-hexen-1-ol. Since no contribution of the protonated molecule was observed for *trans*-2-hexen-1-ol over the entire E/N range, product ions at m/z 101 can be used to discriminate between these two isomers. Variation of E/N may also aid in discriminating C_3 isomers as it was found that the E/N dependence of the protonated and dehydrated protonated molecule at m/z 129 and 111, respectively, was highly different for 6-methyl-5-hepten-2-ol and 1-octen-3-ol.

The PTR-MS product ion distribution versus E/N for the C_{10} alcohol linalool shows the same trend as what has been reported by Tani et al. [13] for monoterpenes, i.e. increased contribution of m/z 137 at lower E/N values, and the contribution of the protonated molecule at m/z 155 remains below 5% at all E/N values that were consid-

ered. Consequently, variation of E/N is not an option for selective detection of monoterpenes and linalool in cases where the linalool signal at m/z 155 is too small for proper quantification at conditions in which fast measurements are required (e.g. eddy covariance flux measurements).

The results obtained in this work confirm that the reactions between H_3O^+ and unsaturated biogenic alcohols mainly proceed by dissociative proton transfer with elimination of a water molecule after protonation as the dominant reaction mechanism, as was previously observed in several SIFT and PTR-MS studies. As could be expected, more fragmentation was observed in PTR-MS than in SIFT-MS, giving rise to specific fragment ions. Despite the differences in the nature of the buffer gas, the collision energy and the buffer gas pressure and temperature between the (FA-)SIFT-MS and PTR-MS techniques, FA-SIFT product ion distributions of individual reactions of $H_3O^+ \cdot (H_2O)_n$ ($n=0-2$) with unsaturated alcohols are often useful to qualitatively explain the variation of the PTR-MS product ion distributions with E/N .

Finally it is worthy of notice that at the E/N values which are commonly used in PTR-MS, the contribution of the MH^+ and $(M-OH)^+$ ions, which are most often monitored as the fingerprint ions of the unsaturated alcohols, have a significant dependence on the water vapour pressure in the inlet line. For accurate quantification of unsaturated biogenic alcohols by PTR-MS, calibrations of these compounds should therefore best be carried out at different relative humidities.

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