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# Laboratory studies in support of the detection of sesquiterpenes by proton-transfer-reaction-mass-spectrometry

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ABSTRACT

The effects of the ratio of the electric field strength to the buffer gas number density (*E*/*N*) in the drift tube of a proton transfer reaction mass spectrometer on the product ion distributions of the sesquiterpenes β-caryophyllene, α-humulene, α-cedrene and longifolene have been investigated.Chemical ionization of the sesquiterpenes resulted in important fragmentation of the nascent excited ion/molecule complex at the highest *E*/*N* values. The most important fragment ions were common to all sesquiterpenes and therefore cannot be used as fingerprints for specific isomers. The yield of the protonated molecule increased on average by a factor 1.6 by decreasing *E*/*N* from 140 to 80 Td. Taking into account the influence of *E*/*N* on the reaction time and on the reactant ion mobility, it is estimated that this decrease in *E*/*N* may lead to an overall increase in the PTR-MS detection sensitivity of sesquiterpenes (based on the ion signal at *m*/*z* 205) by a factor 3.5.Product ion distributions of α-cedrene and longifolene have also been determined at different water vapour pressures. No substantial influence of the water vapour pressure on the product ion yields was observed, which is an advantage when quantifying sesquiterpenes by PTR-MS in samples of varying relative humidity.

## 1. Introduction

The development of the proton-transfer-reaction-mass-spectrometer (PTR-MS) instrument started in the 1990s [1] and in the course of the last decade it has evolved into a widely used analytical technique for the fast, sensitive and on-line detection of many trace gases. The technique is based on the soft ionization of trace gas molecules contained in the sampled air, which is pumped through the drift tube reactor of the PTR-MS. Ionization proceeds by exothermic proton transfer reactions between these trace gases and hydronium ($H_3O^+$) ions and therefore only molecules with a proton affinity larger than the one of water vapour (691 kJ mol$^{-1}$ [2]) can be detected. In contrast to thermal flow tube techniques, the presence of an electric field in the drift tube reactor of the PTR-MS prevents excessive hydration of the reactant $H_3O^+$ ions by reaction with water vapour present in the sample. It also prevents hydration of the product ions resulting from the proton transfer reactions with the reactant neutral molecules, which greatly facilitates mass spectral analysis. On the other hand, the additional kinetic energy gain of the ions in the drift field results in more energetic ion/molecule collisions and thus more fragmentation of the nascent excited protonated molecules. More details on the PTR-MS technique and its applications can be found in a recent extensive review by de Gouw and Warneke [3].

Although PTR-MS instruments nowadays belong to the standard instrumentation in many atmospheric chemistry field and smog chamber experiments, few systematic studies of the influence of instrumental parameters and environmental conditions on the detection of atmospheric trace species have been performed. In the case of volatile organic compounds of biogenic origin, only for monoterpenes a detailed study of the kinetics and product ion distributions of the reactions with $H_3O^+$ ions has been carried out as a function of the drift field and the relative humidity of the carrier gas flow [4,5]. These studies are, however, very important, since for a reliable and accurate detection of trace gas species by Chemical Ionization Mass Spectrometry (CIMS) techniques it is generally required that the ion chemistry is well characterized.

The present paper focuses on the detection of sesquiterpenes by PTR-MS. Sesquiterpenes are $C_{15}H_{24}$ compounds that consist of three isoprene ($C_5H_8$) units and they can be acyclic, exocyclic or endocyclic. Although minor attention has been devoted to sesquiterpene emissions from terrestrial vegetation compared to other non-methane biogenic volatile organic compounds (e.g., isoprene, monoterpenes, biogenic alcohols, etc.), recent studies

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have shown that for some types of vegetation sesquiterpene emissions can be considerable [6] and that they are often related to plant–herbivore interactions and to stress conditions of plants [7].

Most sesquiterpenes have a very short atmospheric lifetime because of their high reactivity with the main atmospheric oxidant species ($O_3$, OH, and $NO_3$) [8], which results in very low ambient concentrations. Therefore, sesquiterpene emissions from vegetation are mainly obtained by using dynamic branch enclosure systems through which ozone-free air is pumped [9]. The atmospheric oxidation of sesquiterpenes mainly leads to the formation of low-volatility compounds, which may condense on pre-existing particles and contribute to secondary organic aerosol (SOA) formation [10,11].

The PTR-MS technique has already been applied for the detection of sesquiterpenes on several occasions and expected product ions and their relative abundances have been reported for some sesquiterpenes at standard PTR-MS conditions [12,13]. In order to better characterize the PTR-MS for sesquiterpene detection we have undertaken a study in which detailed product ion distributions of four sesquiterpenes have been measured at varying conditions of the electric field in the drift tube reactor. The molecules that were studied are α-cedrene, α-humulene, β-caryophyllene, and longifolene and their structures are shown in Fig. 1.

Moreover, since plants emit large quantities of water vapour, detection of biogenic sesquiterpenes has to be carried out in moist air and therefore we also studied the influence of water vapour pressure on the product ion distributions for two of these sesquiterpenes (α-cedrene and longifolene). The results obtained at different drift field values are compared to $H_3O^+$/sesquiterpene product ion distributions that were recently obtained in our laboratory in a Selected Ion Flow Tube (SIFT) instrument at true thermal conditions [14].

Apart from supplying data that may be of interest for the PTR-MS community in general, this study was also motivated by the observation of an unexpected increase of the ratio of the PTR-MS ion signal levels at $m/z$ 81 ($S_{81}$) to the ion signal levels at $m/z$ 137 ($S_{137}$) from branch enclosure BVOC measurements of *Fagus sylvatica* L. saplings in growth chamber experiments that were carried out in the framework of the IMPECVOC project [15]. Both ion species are generally attributed to monoterpenes but our measurements indicated a correlation between an enhanced $S_{81}/S_{137}$ ratio and emission rates of sesquiterpenes (as measured with GC/MS).

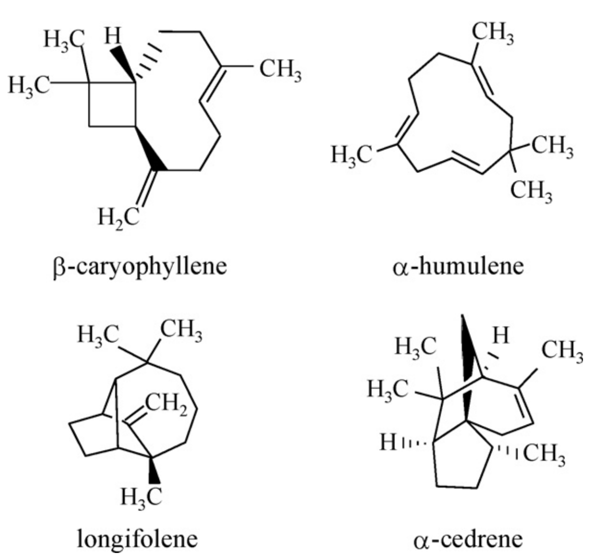

**Fig. 1.** Chemical structures of the sesquiterpenes investigated in this study.

## 2. Experimental

The experiments were carried out with a high-sensitivity (hs) PTR-MS apparatus (Ionicon Analytik GmbH, Austria) at a drift tube pressure of 2.2 hPa and a drift tube temperature of 333 K. The ion source conditions were such that the contribution of $O_2^{\bullet+}$ impurity ions (the major impurity ions) relative to the sum of proton hydrates at standard drift tube voltage (600 V) was limited to 2%. Since recent SIFT measurements that were performed in our laboratory [14] have shown that $O_2^{\bullet+}$ ions react equally fast with sesquiterpenes as do $H_3O^+$ ions, the contribution of product ions originating from $O_2^{\bullet+}$/sesquiterpene reactions to the sum of all sesquiterpene product ions observed in the mass spectra will therefore not exceed 2%.

### 2.1. Dilution of sesquiterpenes in purified, humidity-controlled air

A schematic representation of the experimental set-up for producing diluted sesquiterpene flows is shown in Fig. 2. In order to produce stable sesquiterpene flows a small amount of liquid sesquiterpene was stored in a glass reservoir, which was totally immersed in a thermostatically controlled water bath. By means of a mass flow controller (MKS Instruments) a constant flow of high purity $N_2$ (Air Products, BIP quality), at the same temperature of the water bath, was sent over the liquid sesquiterpene. This $N_2$ flow, enriched with sesquiterpene vapour, was then further diluted in a purified laboratory air flow to obtain sufficiently small sesquiterpene flows to be introduced in the PTR-MS in order to restrict the conversion of the primary ions by reaction with the sesquiterpene to less than one percent. Purification of this air flow was carried out in several steps. After passing a dust filter (Zefluor$^{TM}$ PTFE Membrane Filter, 2 μm pore size) and before entering a diaphragm pump (MVP-055, Pfeiffer Vacuum, Germany), laboratory air was scrubbed for ozone by passing a set of 12 $MnO_2$ coated copper nets (type ETO341FC003, Ansyco, Karlsruhe, Germany) to avoid oxidation of the sesquiterpenes in the inlet line. The ozone- and dust-free air flow exiting the pump, which was restricted by a needle valve at the pump inlet, was subsequently sent through a set of two active coal filters (Airpel 10, Organosorb 10-CO, Desotec, Belgium), the combination of which resulted in an optimal pore size distribution for absorption of volatile organic compounds in the laboratory air. After

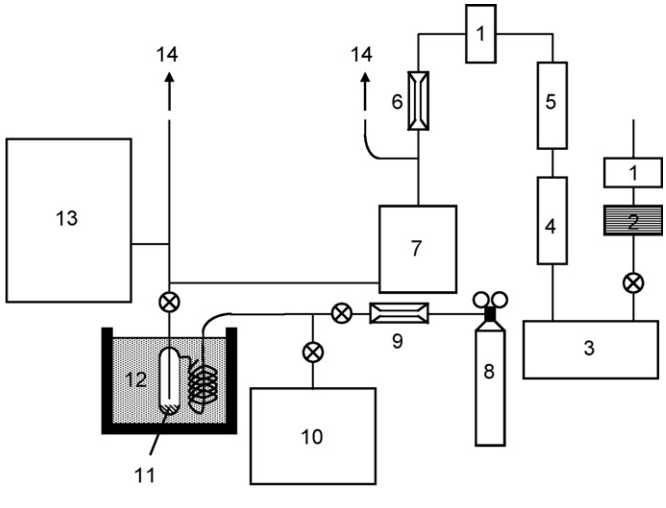

**Fig. 2.** Schematic representation of the experimental set-up: (1) dust filter, (2) ozone scrubber, (3) diaphragm pump, (4)+(5) active coal filters, (6) mass flow meter, (7) dew point generator, (8) $N_2$ bottle, (9) mass flow controller, (10) turbomolecular pumping station, (11) sesquiterpene reservoir, (12) constant temperature bath, (13) PTR-MS, and (14) exhaust.

having passed a second dust filter to remove possible dust from these filters, the air flow was measured by a mass flow meter (MKS Instruments). Part of this flow (1 standard liter per minute) was then pumped by a LI-610 dew point generator (LI-COR) in which it was humidified in a controlled way, and finally mixed with the $N_2$/sesquiterpene flow leaving the reservoir. Part of this mixed flow was then introduced in the PTR-MS by means of a heated capillary PEEK inlet line (60 °C). Apart from this PEEK capillary, all inlet tubing, which was in contact with the sesquiterpenes, was made of stainless steel, kept as short as possible, and heated to 45 °C to prevent condensation of the sesquiterpenes to the tube walls. It should however be noted that possible losses of sesquiterpenes in the inlet lines were not so critical, since our aim was to determine distributions of sesquiterpene product ions and not to determine the absolute sensitivity of the PTR-MS for sesquiterpene detection.

### *2.2. Mass-discrimination measurements of the PTR-MS instrument*

In order to determine sesquiterpene product ion distributions with the PTR-MS, it is important to know the mass discrimination of the PTR-MS instrument. This was accomplished by introducing a commercially obtained dilute mixture of several aromatic compounds R in nitrogen (RESTEK, #34423-PI) of which all but one (ethylbenzene) react with $H_3O^+$ ions by non-dissociative proton transfer, resulting in $RH^+$ product ions. The volume mixing ratio of these compounds, $X_M$, is given by Eq. (1):

$$X_M = \frac{1}{kt}\frac{I(RH^+)}{I(H_3O^+)}\frac{T_d}{T_0}\frac{22,400}{N_A}\frac{p_0}{p_d}\frac{T(H_3O^+)}{T(RH^+)} \qquad (1)$$

In this equation $I(RH^+)$ and $I(H_3O^+)$ are the ion signals of $RH^+$ and $H_3O^+$, respectively, $k$ is the rate constant of the $H_3O^+/R$ reaction, $t$ is the reaction time, $T_d$ and $p_d$ are the temperature of the drift tube and the drift tube pressure respectively, $T_0$ and $p_0$ are standard temperature and pressure (273.15 K and 1013.25 hPa), $N_A$ is Avogadro's number and $T(RH^+)$ and $T(H_3O^+)$ are the overall mass spectrometer transmission coefficients for $RH^+$ and $H_3O^+$ ions, respectively.

The reaction time $t$ in Eq. (1) is given by:

$$t = \frac{L}{v_d} = \frac{L}{\mu E} \qquad (2)$$

In this equation $L$ is the length of the drift tube (9.2 cm), $v_d$ is the ion drift velocity, $\mu$ is the mobility of the $H_3O^+$ ions and $E$ is the electric field in the drift tube.

By comparing the mixing ratios of the individual species, as given by the manufacturer, with the mixing ratios obtained with formula (1) the transmission of the instrument at the $m/z$ values of the product ions can be obtained.

Since mass discrimination depends on several factors, including the voltage settings on electrostatic lenses in the high vacuum region of the mass spectrometer, the quadrupole settings and the voltages on the secondary electron multiplier, it should be determined whenever any of these conditions change.

The transmission of the PTR-MS over the entire useful mass range was obtained by fitting a smooth curve through the transmission data points at the individual $m/z$ values (maximum 10% difference between experimental and fitted data points). A typical transmission curve is shown in Fig. 3. Transmission data were carried out at all days where ion/sesquiterpene product ion distributions were obtained. Although all voltage settings in the mass spectrometer part were kept constant over the entire measurement period, a small decrease in the transmission of the higher masses was observed over time, probably due to ageing of the detector.

Another method to characterize the transmission of the instrument was applied by Steinbacher et al. [16]. In this method controlled amounts of aromatic vapours (and other species) are sequentially added to the PTR-MS inlet flow and the transmission factors are determined by comparing the decrease of the $H_3O^+$ reactant ion signal to the increase in the ion signals of the protonated reactant molecules. Since no uncertainties on rate constants or mixing ratios are involved in this method, the overall error on the transmission curve is smaller. However, we did not use Steinbachers method, since it requires the introduction of large amounts of VOCs, which may contaminate the instrument and therefore interfere with the product ion distribution measurements of the sesquiterpenes.

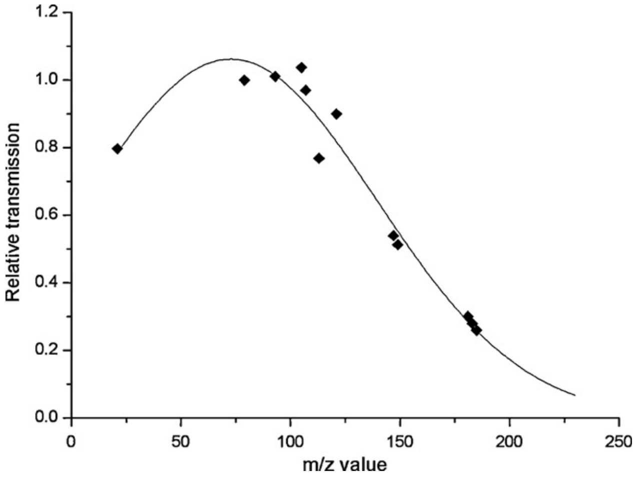

**Fig. 3.** Mass discrimination curve obtained with the procedure described in Section 2.

### *2.3. Procedure for deriving product ion distributions*

For the four sesquiterpenes product ion distributions were obtained at constant water vapour pressure in the inlet line (1.01 kPa) and at 7 different values of $E/N$: 80, 90, 100, 110, 120, 130 and 140 Td (1 Td = $10^{-17}$ V cm$^2$) with $N$ being the buffer gas (air) number density in the drift tube reactor. For α-cedrene and longifolene product ion distributions were also obtained at five other water vapour pressures (0.61, 0.76, 1.32, 1.71 and 2.21 kPa) at all seven $E/N$ values.

Identification of the sesquiterpene product ions was carried out using two complementary approaches.

For each sesquiterpene, mass spectra were obtained at four different sesquiterpene concentrations in the drift tube reactor, which were realized by using four different temperatures (6, 9, 12 and 15 °C) of the water bath ($T_{bath}$), in which the vial containing liquid sesquiterpene was immersed. From these mass spectra sesquiterpene product ions were identified as those ions which, after background correction, varied in a similar way with $T_{bath}$ as the protonated sesquiterpene ion at $m/z$ 205. Secondly the behaviour of the product ion signals as a function of $E/N$ was evaluated. Product ions which showed a continuously decreasing yield with increasing $E/N$, were discarded (except for the protonated sesquiterpene and its hydrate) as they were attributed to protonated impurity molecules (e.g., $m/z$ 59 corresponding to small acetone impurities).

From the remaining set of product ions all those having a count rate higher than one percent of the one of protonated sesquiterpene (not yet corrected for mass discrimination) were then followed in the multiple ion detection mode. In this mode the quadrupole mass filter switches sequentially between a set of predetermined ion masses. After correcting the ion signals for mass discrimination and for the contribution of isotopes of neighbouring ion species, the yields of the individual product ion species (taking into account all their isotopes) were obtained.

### 2.4. Chemicals

α-Humulene (98%), β-caryophyllene (98.5%), longifolene (99%) and α-cedrene (99%) were all obtained commercially from Fluka. Nitrogen used as sesquiterpene dilution gas was obtained from Air Products and is of BIP grade (99.9997%).

## 3. Results and discussion

### 3.1. General comment

Even when adding only one neutral reactant R, the overall ion chemistry taking place in the drift tube of the PTR-MS instrument is rather complex. Because of the presence of water vapour in the reactor, which is contained in the buffer gas flow and also partly originates from the ion source region, the $H_3O^+$ ions exiting the ion source rapidly hydrate to $H_3O^+{\cdot}(H_2O)_n$ ions ($n \geq 1$). The drift field in the reactor, however, promotes collision-induced dissociation of these cluster ions and therefore partly suppresses this hydration. This leads to a steady state proton hydrate distribution in the reactor which, at constant drift tube temperature and pressure, largely depends on the electric field strength and the water vapour concentration in the reactor. The variation of the proton hydrate distribution with $E/N$ can sometimes be exploited to distinguish between isobaric species which have a different reactivity with $H_3O^+$ and $H_3O^+{\cdot}H_2O$ ions, as was recently demonstrated for acrolein and 1-butene [17].

As shown in Fig. 4, the proton hydrate distribution in our experimental conditions was mainly restricted to $H_3O^+$ and $H_3O^+{\cdot}H_2O$ ions and a small contribution of $H_3O^+{\cdot}(H_2O)_2$ at the lowest $E/N$ and the highest water vapour pressure.

Therefore, next to the proton transfer reaction (3) of bare $H_3O^+$ ions with R, reaction (4) may also play an important role, especially at lower values of the reduced electric field $E/N$:

$$H_3O^+ + R \rightarrow HR^+ + H_2O \tag{3}$$

$$H_3O^+{\cdot}(H_2O)_n + R \rightarrow H^+{\cdot}R{\cdot}(H_2O)_m + (n+1-m)H_2O\,(n = 1, 2; m = 0, 1, 2) \tag{4}$$

Reaction (3) will only take place if the proton affinity of R, $PA$(R), is larger than the one of water vapour, $PA(H_2O)$, which equals 691 kJ mol$^{-1}$ [2]. Direct proton transfer from $H_3O^+{\cdot}H_2O$ to R ($n$ = 1, $m$ = 0 in reaction (4)) requires that $PA$(R) is larger than $PA(H_2O) + BE(H_3O^+–H_2O)–BE(H_2O–H_2O)$. Values for the bond energies $BE(H_3O^+–H_2O)$ and $BE(H_2O–H_2O)$ can be found in literature and are 134 [18] and 15 kJ mol$^{-1}$ [19] respectively. Direct proton transfer from $H_3O^+{\cdot}H_2O$ will therefore only take place if $PA(R) > 810$ kJ mol$^{-1}$. Unfortunately proton affinities for sesquiterpenes are not available in the literature. Other possibilities for reaction (4) are ligand switching, where the resulting cluster ion may dissociate due to reaction exoergicity or by energetic collisions with the buffer gas molecules.

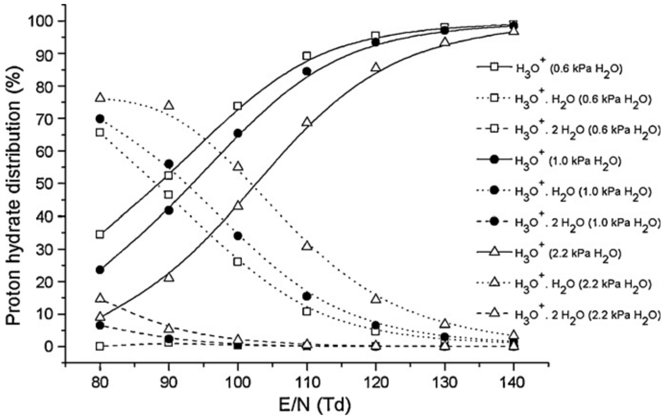

**Fig. 4.** Proton hydrate distribution in the drift tube reactor as a function of the reduced electric field and at three different water vapour pressures in the inlet line.

Furthermore, product ions resulting from reactions (3) and (4) or from further fragmentation of $HR^+$ or $H^+{\cdot}R{\cdot}(H_2O)_m$ may hydrate as well, resulting in an even more complex picture.

Therefore, the product ion distributions which are presented in this paper should be regarded as distributions of product ions originating from this complex ion chemistry and they are only valid at the specific instrument conditions that were used in this set-up. Moreover, ion distributions at the downstream end of the drift tube region can also be distorted to some extent when the ions pass from the reactor exit to the mass spectrometer inlet through the intermediate pressure region of the hs-PTR-MS, and therefore the product ion distributions obtained with the mass spectrometer do not necessarily reflect the real distributions in the drift tube reactor, even when taking into account the overall mass discrimination of the instrument.

Nevertheless, the results presented hereafter remain interesting, since they lead to important conclusions regarding instrumental conditions for optimal sesquiterpene detection. They also nicely complement the truly thermal $H_3O^+$/sesquiterpene reaction studies that were recently obtained in our laboratory with a SIFT reactor, which is much better suited for ion chemistry studies than the PTR-MS, but which lacks sensitivity for efficient detection of sesquiterpenes in ambient air.

### 3.2. E/N dependence of the product ion distributions

In Fig. 5 the product ion distributions of the four sesquiterpenes studied in this work are shown as a function of the $E/N$ parameter. Only product ion species with yields higher than 1.5% at the highest $E/N$ value are shown on these graphs. The ion species include all isotopes and the mass associated with the ion species refers to the mass of the first isotope. The sum of the yields of the product ions with a yield smaller than 1.5% under the different experimental conditions is at most 12% for β-caryophyllene, 10% for α-humulene and 8–9% for α-cedrene and longifolene. For all four sesquiterpenes, the major product ion is the protonated molecule $HR^+$ with yields ranging from 30 to 65% at the highest $E/N$ values.

The $HR^+$ yields of α-cedrene and longifolene are somewhat higher than the one of α-humulene at the same $E/N$ value and are much larger than the one of β-caryophyllene. The $HR^+$ yield on average increases by a factor 1.6 when decreasing the $E/N$ value from 140 Td to 80 Td. The nascent excited complex that is formed upon reaction of the proton hydrates with the sesquiterpenes partly decomposes into a large variety of product ions. Some of these product ions, which are commonly observed for the four sesquiterpenes and which make up the major part of the overall yield of fragment ions, can be classified into two families. Ions belonging to the same family differ by a $CH_2$ unit (14 u), as shown in Table 1.

From Fig. 5 it is clear that the individual yields of the different family members differ among sesquiterpenes. The yield of product ions at $m/z$ 137 is for instance negligible for α-cedrene and longifolene over the complete $E/N$ range, whereas for α-humulene and β-caryophyllene it ranges up to 2.5 and 6%, respectively at the highest $E/N$ value.

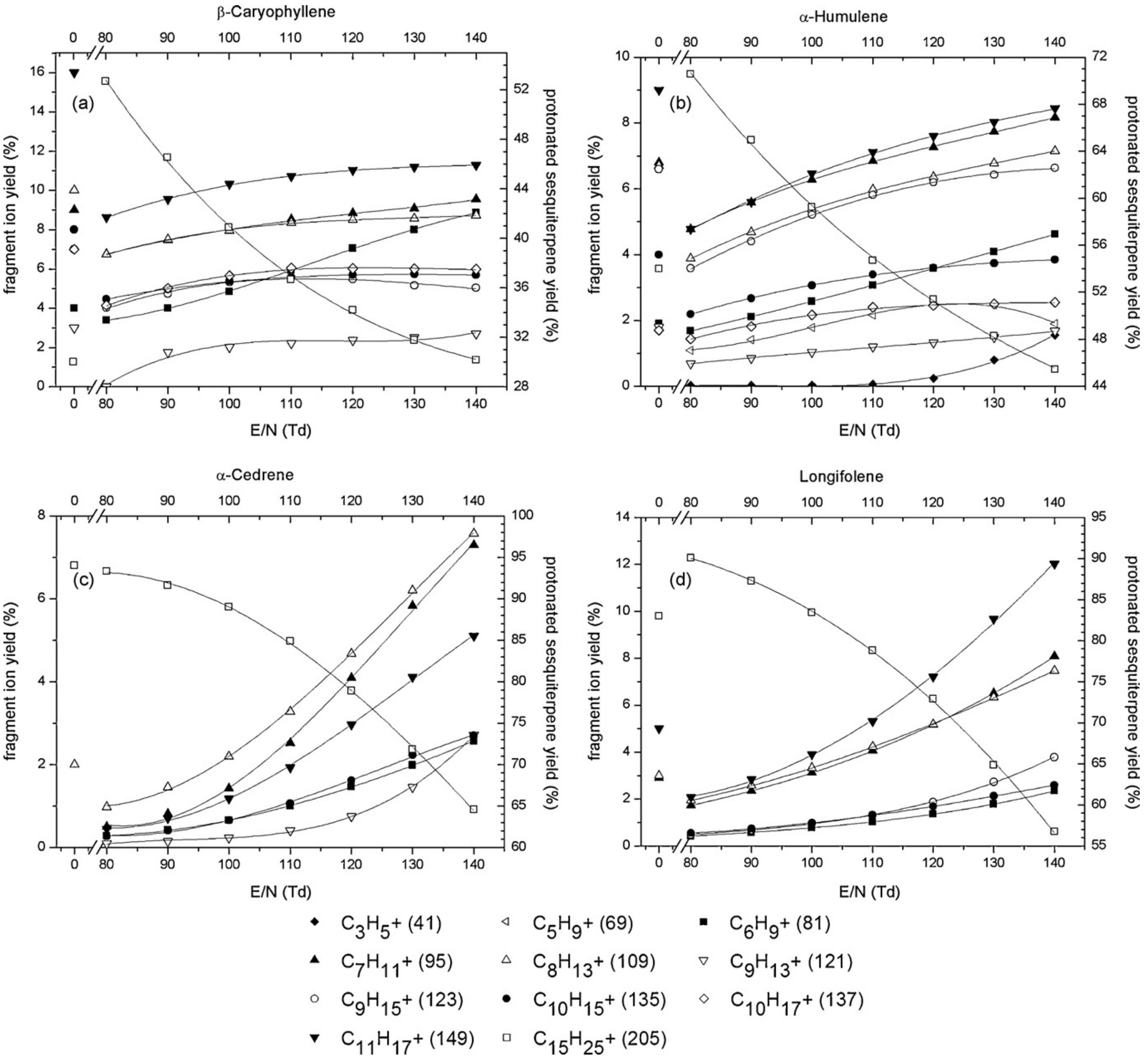

**Fig. 5.** Product ion distributions of the sesquiterpenes as a function of *E*/*N*. Only product ions with a yield > 1.5% at the highest *E*/*N* value (140 Td) are shown. The product ion distributions obtained with the SIFT instrument [14] are also shown on the graphs (at zero *E*/*N*). *m*/*z* values of the first isotope of the ion species are indicated between brackets.

The two families of product ions that were observed in the PTR-MS experiments have also been observed in a recent study of $H_3O^+$/sesquiterpene reactions in a SIFT apparatus in our laboratory [14]. The product ion yields obtained in this SIFT study are also shown in Fig. 5. In the SIFT apparatus ions are truly thermalized by collisions with the helium buffer gas (at a reactor pressure of about 1 hPa), whereas in the PTR-MS instrument the ions gain additional kinetic energy due to the presence of the drift field and one might expect fragmentation of the nascent excited protonated sesquiterpene to be more severe in a drift tube reactor (PTR-MS) than in a thermal flow tube reactor (SIFT). By using Eqs. (1)–(3) in [1] values of 0.081 and 0.102 eV were calculated for the mean relative collision energy between the ions and the buffer gas molecules and for the center-of-mass kinetic energy between $H_3O^+$ and the sesquiterpene, respectively. The mean relative collision energy between ions and neutrals in the SIFT is 0.038 eV.

**Table 1**
Families of fragment ions observed for all four sesquiterpenes. The tabulated *m*/*z* values correspond to the largest isotope of the product ion species.

| Family A | | Family B | |
|---|---|---|---|
| *m*/*z* | Identification | *m*/*z* | Identification |
| 81 | $C_6H_9^+$ | 93 | $C_7H_9^+$ |
| 95 | $C_7H_{11}^+$ | 107 | $C_8H_{11}^+$ |
| 109 | $C_8H_{13}^+$ | 121 | $C_9H_{13}^+$ |
| 123 | $C_9H_{15}^+$ | 135 | $C_{10}H_{15}^+$ |
| 137 | $C_{10}H_{17}^+$ | 149 | $C_{11}H_{17}^+$ |
| | | 163 | $C_{12}H_{19}^+$ |

However, the expected difference in fragmentation between PTR-MS and SIFT results is in contrast with our observations. For β-caryophyllene and α-humulene in particular, the $HR^+$ yields obtained in the PTR-MS experiments at the lowest *E*/*N* value (80 Td) are far higher than the ones obtained in the SIFT experiments. This is in agreement with previous studies on monoterpenes in

PTR-MS [4] and SIFT [20,21] instrumentation. The reaction of $H_3O^+$ with monoterpenes mainly results in the protonated monoterpene, $C_{10}H_{17}{}^+$, at *m/z* 137, and a fragment, $C_6H_9{}^+$, at *m/z* 81. For the monoterpenes, which were studied in common in these studies (α- and β-pinene, limonene and 3-carene), the protonated monoterpene yield in SIFT conditions varied between 55 and 75%, whereas in the PTR-MS study of Tani et al. values around 90% (sum of isotopes at *m/z* 137 and 138) were obtained at the lowest *E/N* value (also 80 Td).

A possible explanation for the higher PTR-MS $HR^+$ yields for mono- and sesquiterpenes at the lowest *E/N* value with respect to SIFT results could be the nature of the buffer gas, which is air in the case of PTR-MS and helium in the SIFT. Air molecules are more efficient in collisionally stabilizing the nascent excited protonated parent molecules. Moreover, the pressure in the PTR-MS reactor is about twice the one in the SIFT reactor. The higher water vapour content of the PTR-MS reactor may also promote collisional stabilization.

At low *E/N* values reaction (4) will become important and the higher PTR-MS $HR^+$ yield might also be expected in case the protonated sesquiterpene molecule would be favoured in the product ion distribution of reaction (4). Measurements at constant *E/N* and different relative humidities, however, show no effect of water vapour concentration on the product ion distributions (see Section 3.3).

### *3.3. Dependence of the product ion distributions on water vapour pressure*

For α-cedrene and longifolene, product ion distribution measurements have been performed at different water vapour pressures in the inlet line. For all *E/N* values no significant variations of the yields of the main product ions have been observed, as is illustrated for α-cedrene in Fig. 6 for an *E/N* value of 140 Td, and in Table 2, showing the functional water vapour pressure dependence of the protonated sesquiterpene yield for α-cedrene and longifolene at seven *E/N* values.

By varying the water vapour pressure of the air flow in which the sesquiterpene is diluted, the proton hydrate distribution is changed, as can be noticed in Fig. 4. Recent SIFT experiments [14] have shown that $H_3O^+{\cdot}H_2O$ ions react equally fast with sesquiterpenes as $H_3O^+$ ions do, i.e., at the collision rate.

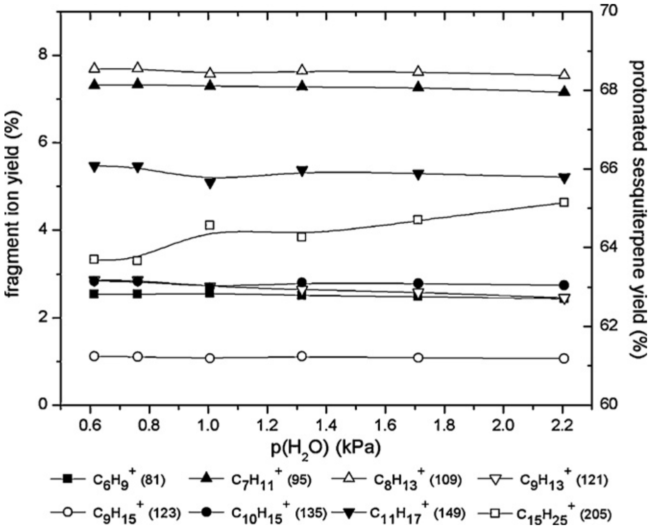

**Fig. 6.** Product ion yields of α-cedrene at the highest *E/N* value versus water vapour pressure in the inlet line. *m/z* values of the first isotope of the ion species are indicated between brackets.

**Table 2**
Dependence of the yield of the protonated sequiterpene on the water vapour pressure in the inlet line for different *E/N* values.

| Sesquiterpene | *E/N* (Td) | Yield (%) for protonated sesquiterpene, *f*(*x*); *x* = water vapour pressure in the inlet line in kPa |
|---|---|---|
| α-Cedrene[a] | 80 | $f(x) = 0.815x + 92.1$ |
| | 90 | $f(x) = 0.957x + 90.2$ |
| | 100 | $f(x) = 1.150x + 87.3$ |
| | 110 | $f(x) = 1.008x + 83.2$ |
| | 120 | $f(x) = 1.106x + 77.2$ |
| | 130 | $f(x) = 1.060x + 70.2$ |
| | 140 | $f(x) = 0.882x + 63.2$ |
| Longifolene[b] | 80 | $f(x) = 2.779x + 87.3$ |
| | 90 | $f(x) = 2.806x + 84.5$ |
| | 100 | $f(x) = 2.264x + 81.2$ |
| | 110 | $f(x) = 2.014x + 76.8$ |
| | 120 | $f(x) = 2.003x + 70.9$ |
| | 130 | $f(x) = 1.707x + 63.1$ |
| | 140 | $f(x) = 2.428x + 54.2$ |

[a] Water vapour pressure in the inlet line, *x*, ranging from 0.61 to 2.21 kPa.
[b] *x* ranging from 0.61 to 1.01 kPa.

In case the reactions of the different proton hydrates with the sesquiterpenes would lead to different product ion distributions, this would result in an “overall” product ion distribution which is humidity dependent. This is in contrast with our observations and with earlier SIFT experiments, where addition of small amounts of water vapour to the SIFT reactor had no influence on the overall sesquiterpene product ion distribution as well. Addition of $H_2O$ vapour to the reactor also does not result in the formation of water clusters of the hydrocarbon fragment ions, which is in agreement with the common observation in SIFT-MS studies that pure hydrocarbon ions have no propensity to hydrate [22].

### *3.4. Considerations about the sensitivity of the PTR-MS instrument for sesquiterpene detection and about interferences with the detection of other terpenes*

In order to be able to quantify trace gases with very low mixing ratios with CIMS, it is important that these species give rise to a clear fingerprint ion, which is not produced in reactions with other trace gases and which has a relatively high yield. For sesquiterpenes this is the case for the protonated molecule at *m/z* 205. A decrease of the *E/N* value in the drift tube reactor not only results in an increase of the yield of the protonated molecule (as explained in Section 3.2), but also in an increase of the reaction time *t* as given by Eq. (2). Apart from the fact that the reaction time is inversely proportional to *E* (and therefore also to *E/N* at constant pressure and temperature in the drift tube), it is also affected by the variation of the ion mobility $\mu$ of the reagent proton hydrate ions, which depends on the proton hydrate distribution in the drift tube reactor. A detailed study from Warneke et al. [23] shows that in typical PTR-MS conditions $\mu$ can decrease by 20% when decreasing *E/N* from 140 Td to 80 Td (the upper and lower values in our study).

Taking into account the *E/N* dependence of the yield of the protonated molecule and of the reaction time (including variations of the ion mobility), we estimated the overall sensitivity for sesquiterpene detection to increase by a factor 3.5 when decreasing *E/N* from 140 to 80 Td.

Absolute PTR-MS sensitivities for sesquiterpene detection have not been obtained in this work. This requires the introduction of dilute sesquiterpene flows in the PTR-MS with a stable and accurately known mixing ratio. Given the lack of sesquiterpene vapour pressure data at the temperature of the bath in which the sesquiterpene reservoir was immersed, this could not be realized in the present experimental set-up.

Finally it should be noted that in many applications sesquiterpenes and monoterpenes are simultaneously present in the sampled air. As shown in Table 1 and Fig. 5, the presence of sesquiterpenes also leads to product ions at *m*/*z* 81 and *m*/*z* 137, which are typical fingerprints ions for monoterpenes. For the four sesquiterpenes studied here the contribution to the ion signal at *m*/*z* 137 is at high *E*/*N* values clearly smaller than to the ion signal at *m*/*z* 81 (especially for α-cedrene and longifolene). This is in line with our observation of increased ratios of the PTR-MS ion signal levels at *m*/*z* 81 to the ion signal levels at *m*/*z* 137 during branch enclosure BVOC measurements of *Fagus sylvatica* L. saplings in growth chamber experiments as mentioned in Section 1. In conditions where sesquiterpene emissions have been observed (by GC/MS), the ion signal at *m*/*z* 81 is most probably due to monoterpenes and sesquiterpenes.

Therefore, in order to avoid interferences the results from the present study indicate that the protonated monoterpene is a better fingerprint for monoterpene detection than the fragment at *m*/*z* 81.

## 4. Conclusion

The work presented here demonstrates that the introduction of sesquiterpenes in a PTR-MS instrument results in a large number of product ions, the distribution of which is strongly dependent on the *E*/*N* value of the drift tube region. Interestingly, these distributions are not affected by changing relative humidities, and therefore the sensitivity of the PTR-MS for sesquiterpene detection based on specific fingerprint ions (e.g., at *m*/*z* 205 or *m*/*z* 149) is not expected to be humidity-dependent either.

Our results also indicate that in PTR-MS studies, which focus on sesquiterpene detection, it might be interesting to reduce the *E*/*N* value, since this will result in a non-negligible increase in detection sensitivity.

The sesquiterpene product ion distributions also show that one should be careful when quantifying monoterpenes if sesquiterpenes are simultaneously present in the sampled air, and that, in studies which focus on monoterpene emissions, it is often wise to follow the ion signal at the mass of the protonated sesquiterpene as well.

Finally, we realize that only a limited number of sesquiterpenes have been studied here and that, given the large interest that is currently devoted to this family of biogenic volatile organic compounds, it might be interesting to verify whether the general conclusions are also valid for other commonly observed sesquiterpenes.

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