

A selected ion flow tube study of the reactions of H_3O^+ , NO^+ and O_2^{*+} with a series of C_5 , C_6 and C_8 unsaturated biogenic alcohols

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Abstract

The rate constants and product ion distributions of the reactions of H_3O^+ , NO^+ and O_2^{*+} with 1-penten-3-ol, *cis*- and *trans*-2-penten-1-ol, 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 2-methyl-3-buten-2-ol, *cis*- and *trans*-2-hexen-1-ol, *cis*- and *trans*-3-hexen-1-ol, 1-octen-3-ol and 6-methyl-5-hepten-2-ol have been determined at 150 Pa and 295 K using a selected ion flow tube (SIFT).

All reactions were found to proceed at a rate close to the collision rate, calculated with the Su and Chesnavich model, using the polarizability and electric dipole moment of the compounds derived from B3LYP/aug-cc-pVDZ quantum chemical calculations.

All H_3O^+ ion/molecule reactions proceed mainly by elimination of a water molecule after protonation. Therefore, the H_3O^+ precursor ion is not suited to distinguish isomers by the chemical ionization technique in samples, containing several of the C_5 (C_6 or C_8) unsaturated alcohols.

The NO^+ reactions are generally characterized by several reaction pathways, such as hydride and/or hydroxide ion transfer and/or non-dissociative charge transfer and/or three-body association. The SIFT-MS spectra of the ion/molecule reactions of O_2^{*+} with the unsaturated alcohols also show multiple ionic products.

Based upon the measured product ion distributions, it can be concluded that in some particular cases the NO^+ or O_2^{*+} precursor ions are appropriate to identify and quantify isomers in mixtures of the unsaturated alcohols studied. Especially in leaf wounding experiments, during which *cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol are emitted, the chemical ionization technique, based upon the NO^+ or O_2^{*+} precursor ion, may be a valuable diagnostic tool to distinguish and quantify these isomeric forms.

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1. Introduction

During the last decade chemical ionization mass spectrometry (CIMS) and proton transfer reaction mass spectrometry (PTR-MS) in particular, has become a widely applied technique for the fast and sensitive detection of many volatile organic compounds (VOCs) [1]. Within the field of trace gas emission studies, PTR-MS is considered as a very useful instrument to measure fluxes and emission kinetics of biogenic volatile organic compounds (BVOCs), even for some oxygenated BVOCs, for

which detection by traditional sampling methods is not straightforward (e.g. [2]).

Amongst the biogenically emitted oxygenated VOCs are unsaturated C_5 , C_6 and C_8 alcohols. Large quantities of 2-methyl-3-buten-2-ol (MBO), an unsaturated C_5 alcohol, were found to be emitted from certain pine trees in western North America [3]. Both C_5 (1-penten-3-ol) and C_6 (*cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol) unsaturated alcohols are also released from leaves after wounding and have been detected with PTR-MS both in laboratory set-ups [4–6] and in the open atmosphere [6,7]. Some C_8 unsaturated alcohols were found to be emitted by lichens (1-octen-3-ol, also known as mushroom alcohol [8–10]) or have been identified as potential pheromones released by forest insects (6-methyl-5-hepten-2-ol [11]). *cis*-3-Hexen-1-ol and 1-octen-3-ol are also known as volatile flavor compounds [12].

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In contrast to the combination of high sensitivity and small response time, which even makes PTR-MS a suitable analyzer for eddy covariance flux measurements of BVOCs (e.g. [13,14]), the technique suffers from selectivity. PTR-MS is based upon soft ionization in a drift tube reactor of species having a proton affinity larger than that of water vapor (691 kJ/mol [15]) by proton transfer from hydronium ions (H_3O^+). Isomeric species of molecular mass m are frequently detected as protonated molecules at mass $(m + 1)$ and therefore cannot be properly distinguished. Even if the protonated molecules partly decompose in the drift tube reactor, the fragment ions for species with the same chemical functionality are often identical. In the case of alcohols for instance, protonation is often followed by ejection of a water molecule [16]. As an example PTR-MS does not enable distinction between the two C_6 wound compounds *cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol, which are both detected at $m/z = 83$, which is attributed to the dehydrated protonated parent molecule.

One possibility to overcome this problem is to use other chemical ionization reagent ions such as NO^+ , $\text{O}_2^{\bullet+}$ and OH^- [17], all of which are highly reactive with many trace gases, but do not react with the major air constituents. The simultaneous use of H_3O^+ , NO^+ and $\text{O}_2^{\bullet+}$ ions, which may result in different ion chemistries for isomeric VOCs, is frequently applied in the SIFT-MS technique [18].

In the present study we have investigated the ion/molecule reactions of these three precursor ions with a series of biogenic isomeric C_5 (1-penten-3-ol, *cis*- and *trans*-2-penten-1-ol, 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol and 2-methyl-3-buten-2-ol), C_6 (*cis*- and *trans*-2-hexen-1-ol, *cis*- and *trans*-3-hexen-1-ol) and C_8 (1-octen-3-ol and 6-methyl-5-hepten-2-ol) alcohols. Experimental and theoretical rate constants, as well as product ion distributions, will be reported and similarities and/or differences in ion chemistry of the isomeric compounds will be discussed.

2. Experimental

2.1. Instrumental

The SIFT apparatus used in this study is based upon the original design by Smith and Adams [19], and has been described in detail in a previous publication [20]. Therefore, only a short overview will be given here.

A variety of ions are generated by a microwave discharge in a 20 Pa mixture of air and water vapor. The ions, created in the discharge, are extracted into a differentially pumped quadrupole mass filter, where the precursor ions of interest (H_3O^+ , NO^+ or $\text{O}_2^{\bullet+}$) are selected according to their m/z ratio. By means of a venturi inlet, these precursor ions are injected into a 51 cm long flow tube with an internal diameter of 4 cm and convectively transported by a $100 \text{ STP cm}^3 \text{ s}^{-1}$ He buffer gas flow towards the detection part of the instrument. The neutral reactant is introduced into the flow tube by means of a ring shaped inlet, located 23.7 cm downstream from the venturi inlet. After being sampled through a 0.4 mm diameter hole, the precursor and product ions are analyzed according to their m/z ratio by a second quadrupole

mass filter and subsequently detected by a secondary electron multiplier, which is operated in the pulse counting mode.

2.2. Measuring methods

The reaction rate constants of H_3O^+ with the unsaturated alcohols, $k_{\text{exp}}(\text{H}_3\text{O}^+)$, are measured in an absolute way by monitoring the logarithmic decay of the precursor ion signal at different concentrations of the neutral reactant in the flow tube. A volumetric mixture of the neutral reactant in He is prepared in a volume calibrated glass bottle and by adjusting the needle valve (heated to 320 K), which separates the glass bottle from the ring shaped inlet, the flow of the neutral reactant into the flow tube can be varied. This flow is derived from the measured pressure drop of the mixture in the glass bottle as a function of time. From this flow, the carrier gas flow, the pressure in the flow tube and the mixing ratio of the reactant gas, the concentration of the neutral reactant in the flow tube can be derived.

The reaction rate constants of NO^+ and $\text{O}_2^{\bullet+}$ with the unsaturated alcohols are determined relatively with respect to the H_3O^+ reaction rate constant by recording the decay of these three precursor ions simultaneously (SIFT quadrupole in RF-only mode) for different concentrations of the neutral reactant in the flow tube [20,21].

Adding small amounts of water vapor through a finger inlet, located at the same position as the ring shaped neutral reactant inlet, allows us to determine the reaction rate constant of $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ and $\text{NO}^+ \cdot \text{H}_2\text{O}$ relatively with respect to $k_{\text{exp}}(\text{H}_3\text{O}^+)$ and $k_{\text{exp}}(\text{NO}^+)$, respectively, by the method described in Michel et al. [22].

The accuracy of the reaction rate constant measurements is estimated to be 25% with a precision better than 5% for the k_{exp} measurements with H_3O^+ , NO^+ and $\text{O}_2^{\bullet+}$ precursor ions and a precision better than 15% for the $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ and $\text{NO}^+ \cdot \text{H}_2\text{O}$ ion/molecule reactions.

For the determination of the product ion distribution of each H_3O^+ , NO^+ and $\text{O}_2^{\bullet+}$ reaction, the neutral reactant is introduced by means of a finger inlet, located 8 mm in front of the sampling hole of the analyzing mass spectrometer, to eliminate mass dependent diffusion enhancement effects. The conversion of the precursor ions is limited to a few percent to suppress possible secondary ion chemistry. The analyzing quadrupole is used in the multi-ion mode, where the mass spectrometer is sequentially switched at a number of fixed m/z values and the corresponding count rate is measured. Product ion distributions are corrected for mass discrimination of the analyzing mass spectrometer, including possible contamination and aging of the detector. This mass discrimination is on regular basis derived from measurements with calibration gases, as described in [20].

All measurements were carried out at 150 Pa and 295 K.

When SIFT-MS is used for detecting and quantifying trace gases, often humid samples are involved (human breath, ambient air sample, bodily fluid headspace, etc.). As a result the precursor ions will partially associate with water and can on their turn react with the neutral reactants by ligand switching. Product ions formed in the reaction of the neutral reactant with

the primary precursor ions or its hydrates may also partially associate with water. By adding water vapor in the reaction zone of the SIFT apparatus, the outcome for this study is threefold. Firstly, it allows to determine the reaction rate constants of $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and $\text{NO}^+\cdot\text{H}_2\text{O}$ with the neutral reactant (see above). Secondly, spectra clearly show if water clusters of the product ions may be expected when humid samples are used. And thirdly, it is a valuable tool in identifying the product ions of the H_3O^+ , NO^+ and O_2^{*+} reactions. Smith and Španěl observed that carboxy ions have a propensity to associate with water [16], whereas pure hydrocarbon ions show little tendency to hydrate [23]. This diagnostic tool has been used in all further cases, where identification of the product ions was doubtful.

2.3. Chemicals

trans-2-Penten-1-ol, 3-methyl-3-buten-1-ol, *trans*-2-hexen-1-ol, *trans*-3-hexen-1-ol and 1-octen-3-ol are purchased from Sigma Aldrich and have a purity of 95, 97, 96, 98 and 98%, respectively. 1-Penten-3-ol, *cis*-2-penten-1-ol, 3-methyl-2-buten-1-ol, *cis*-2-hexen-1-ol and DL-6-methyl-5-hepten-2-ol are Acros Organics products with a purity of 99, 98, 99, 95 and 99%, respectively. He carrier gas from air products has BIP quality (99.9997%).

3. Results and discussion

3.1. Reaction rate constants

The experimental values, k_{exp} , of the reaction rate constants of H_3O^+ (absolute measurement, see Section 2.2. above) and of NO^+ , O_2^{*+} , $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and $\text{NO}^+\cdot\text{H}_2\text{O}$ (all relative measurements, see Section 2.2.) with the unsaturated alcohols are listed in Table 1.

Also shown in this table are the collision reaction rate constants k_C for these reactions according to the parameterized equation of Su and coworkers [25,26]. k_C calculations require, however, knowledge of the dipole moment μ_D and of the polarizability α of the compounds studied. Since no literature data are available, these parameters were obtained from quantum chemical calculations at the B3LYP-DFT/aug-cc-pVDZ level of theory. The calculations were performed in a distributed computer environment using the Gaussian '03 suite of programs [27]. In order to take into account all possible conformations, the molecules were subjected to a detailed conformational analysis by combining a MMFF [28,29] random search with a MM3/MM4 [30,31] stochastic search [32,33]. The minima found were then optimized at B3LYP/6-31G(d,p) level and the Hessian was calculated to make sure that all located stationary points were real minima. All the B3LYP/6-31G(d,p) minima within an energy window of 4 kcal/mol were then re-optimized with the aug-cc-pVDZ basis set, and the dipole moment and polarizability were calculated for each minimum. Collision rate constant values were then calculated for all individual conformations of a compound using the Su and Chesnavich equation and subsequently Boltzmann averaged using the enthalpy to obtain conformational populations. The enthalpy was calculated at 295.15 K and 150 Pa via DFT using the standard expressions [34]. Vibrational frequencies were scaled by a factor 0.970 [35]. μ_D and α numbers listed in Table 1 are also Boltzmann averaged values.

The agreement between the experimental k_{exp} and theoretical k_C values is generally good. The polarizabilities derived from quantum chemical calculations are in excellent agreement with the polarizabilities obtained by the method proposed by Miller and Savchik [36], based upon the square of a sum of atomic hybrid components. With the latter method a polarizability of 10.4 \AA^3 is found for the C_5 unsaturated alcohols, 12.2 \AA^3 for the C_6 and 15.9 \AA^3 for the C_8 alcohols studied.

Table 1

Experimental rate constants k_{exp} obtained for the reactions of H_3O^+ , $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$, NO^+ , $\text{NO}^+\cdot\text{H}_2\text{O}$ and O_2^{*+} with some unsaturated alcohols at 150 Pa and 295 K

Compound	μ_D (Debye)	α (\AA^3)	k_{exp} [k_C]				
			H_3O^+	$\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$	NO^+	$\text{NO}^+\cdot\text{H}_2\text{O}$	O_2^{*+}
1-Penten-3-ol	1.43	10.6	2.6 [2.7]	2.0 [2.1]	2.4 [2.2]	2.2 [1.9]	2.4 [2.2]
<i>cis</i> -2-Penten-1-ol	1.97	10.7	3.0 [3.2]	2.2 [2.4]	2.7 [2.6]	2.5 [2.2]	2.7 [2.6]
<i>trans</i> -2-Penten-1-ol	1.44	10.8	3.0 [2.7]	2.4 [2.1]	2.7 [2.2]	2.5 [1.9]	2.6 [2.2]
3-Methyl-2-buten-1-ol	2.16	10.8	3.4 [3.4] {2.7} ^a	2.8 [2.6]	3.1 [2.8]	2.9 [2.4]	3.1 [2.7]
3-Methyl-3-buten-1-ol	1.41	10.5	3.2 [2.7]	2.7 [2.1]	2.9 [2.2]	[1.9]	2.9 [2.2]
2-Methyl-3-buten-2-ol ^b	1.51	10.5	2.6 [2.7] {2.2} ^a	2.3 [2.1]	2.3 [2.3]	2.1 [1.9]	2.3 [2.2]
<i>cis</i> -2-Hexen-1-ol	1.97	12.6	2.8 [3.2]	1.9 [2.5]	2.6 [2.7]	2.4 [2.3]	2.6 [2.6]
<i>trans</i> -2-Hexen-1-ol	1.45	12.6	3.3 [2.8] {~3} ^a	2.6 [2.1]	2.9 [2.3]	2.7 [1.9]	2.9 [2.3]
<i>cis</i> -3-Hexen-1-ol ^b	1.65	12.6	3.2 [2.9] {2.8} ^a	2.7 [2.3]	2.9 [2.4]	2.7 [2.1]	2.9 [2.4]
<i>trans</i> -3-Hexen-1-ol	1.50	12.6	3.2 [2.8] {2.5} ^a	2.6 [2.2]	2.8 [2.3]	2.7 [2.0]	2.8 [2.3]
1-Octen-3-ol	1.38	16.2	2.5 [2.9]	1.8 [2.2]	2.3 [2.4]	2.1 [2.0]	2.3 [2.3]
DL-6-Methyl-5-hepten-2-ol	1.59	16.4	2.9 [3.1]	2.3 [2.3]	2.7 [2.5]	2.4 [2.1]	2.6 [2.5]

Collisional reaction rate constants k_C , according to the Su and Chesnavich approach [25,26], are shown in square brackets. These values are averages over the different molecular conformations (see Section 3.1 for details). Polarizabilities α and dipole moments μ_D of the compounds were obtained from B3LYP/aug-cc-pVDZ quantum chemical calculations (see Section 3.1 for details) and are also averaged over the different molecular conformations. Literature values are put between curly braces. Rate constants are expressed in $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^a From Ref. [17].

^b From Ref. [24].

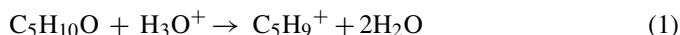
3.2. Product ion distribution

An overview of the product ion distribution of the reactions of H_3O^+ , NO^+ and $\text{O}_2^{+\bullet}$ with the unsaturated alcohols studied is given in Table 2. Only product ions with a branching ratio $\geq 2\%$ are listed and discussed below. For completeness the product ion distribution of 2-methyl-3-buten-2-ol and *cis*-3-hexen-1-ol, obtained in a previous study, are added to Table 2. However, for the discussion of the latter distributions we refer to [24].

In the spectra of the reaction of H_3O^+ with *trans*-2-penten-1-ol and *trans*-2-hexen-1-ol unexpected minor product ion peaks at $m/z = 71$ and 85 , respectively, were observed. Similarly, unexpected minor peaks, located at $m/z = 87$ and 101 , respectively, were observed in the corresponding NO^+ product ion spectra. By comparison with the product ion distributions listed in [16], these peaks could be attributed in a consistent way to 1-pentanol and 1-hexanol impurities. Consequently, the H_3O^+ , NO^+ and $\text{O}_2^{+\bullet}$ product ion distributions for *trans*-2-penten-1-ol and *trans*-2-hexen-1-ol, listed in Table 2, are corrected for these impurities.

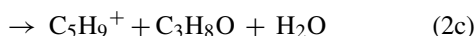
3.2.1. H_3O^+ reactions

The reaction of H_3O^+ with all C_5 , C_6 and C_8 unsaturated alcohols M proceeds mainly by elimination of a water molecule after protonation, resulting in $(\text{M} - \text{OH})^+$ product ions. In the case of *cis*-2-penten-1-ol, for example:



In their SIFT study of the ion/molecule reactions of H_3O^+ with a series of saturated alcohols Španěl and Smith [16] also observed elimination of a water molecule after protonation as the major reaction pathway, except for methanol, ethanol and phenol, where, as a result of non-dissociative proton transfer, only the protonated parent molecules MH^+ are formed. The latter process also occurs in our study for the reaction of H_3O^+ with the unsaturated alcohols 1-penten-3-ol, 3-methyl-3-buten-1-ol, 2-methyl-3-buten-2-ol, *cis*- and *trans*-3-hexen-1-ol, 1-octen-3-ol and 6-methyl-5-hepten-2-ol, however, as a less important reaction channel ($<18\%$).

The reaction of H_3O^+ with the two C_8 unsaturated alcohols shows a third pathway (Eq. (2c) below):



On protonation a fraction of the nascent excited protonated molecules $(\text{MH})^{+\bullet}$ stabilizes (Eq. (2a)), while the remaining fraction dissociates to hydrocarbon ions by ejection of H_2O (Eq. (2b)) or by elimination of $\text{C}_3\text{H}_8\text{O}$ (Eq. (2c)). Elimination of $\text{C}_3\text{H}_8\text{O}$ after protonation also occurs, according to Španěl and Smith [16], in the reaction of H_3O^+ with the saturated C_8 alcohols 1-octanol and 2-octanol.

For the C_5 and C_6 unsaturated alcohols it is also interesting to note that, when the double bond is located in the “2” position, protonated parent molecules are not observed.

Finally, some minor reaction channels are detected: a 3% channel of the reaction of H_3O^+ with *cis*-2-hexen-1-ol results in the formation of $(\text{M} - \text{H})^+$ product ions at $m/z = 99$ and a 4% pathway of the H_3O^+ /1-penten-3-ol reaction gives rise to ions at $m/z = 45$.

In their experiments with the SIFT apparatus of the University of Colorado at Boulder, Custer et al. [17] report major product ions at $m/z = 81$ for 3-methyl-2-buten-1-ol, 2-methyl-3-buten-2-ol and *trans*-2-hexen-1-ol. In our study these product ions are not observed. The minor product ions reported by these authors for 3-methyl-2-buten-1-ol, *trans*-2-hexen-1-ol, *cis*- and *trans*-3-hexen-1-ol have in our experiments a branching ratio $<1\%$, except for protonated *cis*- and *trans*-3-hexen-1-ol ($m/z = 101$), which have both a 6% branching ratio in our study.

In the following paragraph some of the H_3O^+ product ion distributions are compared with PTR-MS experiments. The reader should however keep in mind that SIFT-MS experiments are performed under thermal conditions, while the energy of the ions in PTR-MS instruments is higher, due to the application of an electric field in the drift tube section of such instruments. PTR-MS product ion distributions of 1-penten-3-ol, *cis*- and *trans*-2-penten-1-ol and the three methyl substituted butenols [6] show the same general characteristics as the corresponding SIFT-MS distributions (maximum difference in branching ratio $<11\%$), except for $m/z = 41$ product ions observed in the PTR-MS spectra of the three methyl substituted butenols ($\sim 10\%$ branching ratio for each of these compounds), which are absent in the SIFT-MS spectra. The minor product ion at $m/z = 45$, observed in this study for 1-penten-3-ol, is not detected under PTR-MS conditions.

Buhr et al. [12] observe in their PTR-MS spectrum of the H_3O^+ /1-octen-3-ol reaction major product ions at $m/z = 69$ and 111 with almost equal branching ratio. In our SIFT-MS study the $(\text{M} - \text{OH})^+$ ion at $m/z = 111$ clearly dominates the product ion distribution, while product ions at $m/z = 69$ only represent a minor fraction. The protonated 1-octen-3-ol molecule has a somewhat lower branching ratio in the PTR-MS experiment, while the other minor product ions at $m/z = 41$ and 57 , reported by Buhr et al. with a 4 and 3% branching ratio, respectively, are not observed or are very weak ($<1\%$) in the SIFT-MS spectrum. The PTR-MS spectra of *cis*-3-hexen-1-ol [12] are dominated by $(\text{M} - \text{OH})^+$ ions at $m/z = 83$ (64% branching ratio), resulting from elimination of a water molecule after protonation. This reaction channel is even more pronounced in the SIFT-MS spectra (94% branching ratio). Protonated *cis*-3-hexen-1-ol ($m/z = 101$), observed with a 6% branching ratio in our SIFT study, is not reported by Buhr et al. On the other hand, ions at $m/z = 55$ with a non-negligible 36% branching ratio in the PTR-MS experiment are not detected by SIFT-MS. The difference in carrier gas (air in the case of PTR-MS) and the applied electric field in the PTR-MS instrument clearly favors fragmentation of the nascent excited $(\text{MH})^{+\bullet}$ complex towards smaller product ions in the case of *cis*-3-hexen-1-ol and 1-octen-3-ol.

Table 2

Product ion distribution of the H₃O⁺, NO⁺ and O₂^{•+} reactions with some unsaturated C₅, C₆ and C₈ alcohols at 150 Pa and 295 K

Compound	<i>m</i>	H ₃ O ⁺			NO ⁺			O ₂ ^{•+}			
		<i>m/z</i>	Ion	%	<i>m/z</i>	Ion	%	<i>m/z</i>	Ion	%	
1-Penten-3-ol IE = 9.4–9.6 eV ^b	86	45	C ₂ H ₅ O ⁺	4	57	C ₃ H ₅ O ^{+,a}	5	57	C ₃ H ₅ O ⁺	75	
		69	C ₅ H ₉ ⁺	85	69	C ₅ H ₉ ⁺	37	71	C ₄ H ₇ O ⁺	2	
		87	C ₅ H ₁₁ O ⁺	11	85	C ₅ H ₉ O ⁺	56	86	C ₅ H ₁₀ O ^{•+}	13	
						2		Others	10		
<i>cis</i> -2-Penten-1-ol	86	69	C ₅ H ₉ ⁺	99	68	C ₅ H ₈ ^{•+,a}	4	44	C ₂ H ₄ O ^{•+}	7	
			Others	1	69	C ₅ H ₉ ⁺	24	56	C ₃ H ₄ O ^{•+,a}	3	
					85	C ₅ H ₉ O ⁺	68	57	C ₃ H ₅ O ⁺	56	
					86	C ₅ H ₁₀ O ^{•+}	4	68	C ₅ H ₈ ^{•+}	15	
								71	C ₄ H ₇ O ⁺	4	
						86	C ₅ H ₁₀ O ^{•+}	9			
							Others	6			
<i>trans</i> -2-Penten-1-ol	86	69	C ₅ H ₉ ⁺	99	69	C ₅ H ₉ ⁺	31	44	C ₂ H ₄ O ^{•+}	7	
			Others	1	85	C ₅ H ₉ O ⁺	58	56	C ₃ H ₄ O ^{•+,a}	5	
					86	C ₅ H ₁₀ O ^{•+}	8	57	C ₃ H ₅ O ⁺	62	
						Others	3	68	C ₅ H ₈ ^{•+}	5	
								71	C ₄ H ₇ O ⁺	3	
						86	C ₅ H ₁₀ O ^{•+}	13			
							Others	5			
3-Methyl-2-buten-1-ol	86	69	C ₅ H ₉ ⁺	98	69	C ₅ H ₉ ⁺	40	68	C ₅ H ₈ ^{•+}	7	
			Others	2	71	C ₄ H ₇ O ^{+,a}	2	71	C ₄ H ₇ O ⁺	80	
					85	C ₅ H ₉ O ⁺	22	86	C ₅ H ₁₀ O ^{•+}	9	
					86	C ₅ H ₁₀ O ^{•+}	35		Others	4	
						Others	1				
3-Methyl-3-buten-1-ol	86	69	C ₅ H ₉ ⁺	89	60	C ₃ H ₈ O ^{•+,a}	13	56	C ₄ H ₈ ^{•+,a}	31	
			87	C ₅ H ₁₁ O ⁺	9	68	C ₅ H ₈ ^{•+,a}	3	67	C ₅ H ₇ ⁺	8
			Others	2	85	C ₅ H ₉ O ⁺	7	68	C ₅ H ₈ ^{•+}	44	
					86	C ₅ H ₁₀ O ^{•+}	66	71	C ₄ H ₇ O ⁺	6	
					98	(NO·C ₅ H ₈) ⁺	7	86	C ₅ H ₁₀ O ^{•+}	7	
						Others	4		Others	4	
2-Methyl-3-buten-2-ol ^c IE = 9.90 eV ^d	86	69	C ₅ H ₉ ⁺	80	69	C ₅ H ₉ ⁺	96	43		4	
			87	C ₅ H ₁₁ O ⁺	18		Others	4	58		4
				Others	2				59	C ₃ H ₇ O ^{+,a}	10
									69	C ₅ H ₉ ⁺	2
									71	C ₄ H ₇ O ⁺	71
									86	C ₅ H ₁₀ O ^{•+}	8
										Others	1
<i>cis</i> -2-Hexen-1-ol	100	83	C ₆ H ₁₁ ⁺	96	82	C ₆ H ₁₀ ^{•+,a}	7	44	C ₂ H ₄ O ^{•+}	5	
			99	C ₆ H ₁₁ O ⁺	3	83	C ₆ H ₁₁ ⁺	23	56	C ₃ H ₄ O ^{•+,a}	5
			Others	1	99	C ₆ H ₁₁ O ⁺	61	57	C ₃ H ₅ O ⁺	36	
					100	C ₆ H ₁₂ O ^{•+}	4	67	C ₅ H ₇ ⁺	8	
						Others	5	71	C ₄ H ₇ O ⁺	5	
								72	C ₄ H ₈ O ^{•+}	3	
								82	C ₆ H ₁₀ ^{•+}	23	
								100	C ₆ H ₁₂ O ^{•+}	3	
									Others	12	
<i>trans</i> -2-Hexen-1-ol	100	83	C ₆ H ₁₁ ⁺	99	83	C ₆ H ₁₁ ⁺	31	44	C ₂ H ₄ O ^{•+}	6	
			Others	1	99	C ₆ H ₁₁ O ⁺	55	56	C ₃ H ₄ O ^{•+,a}	5	
					100	C ₆ H ₁₂ O ^{•+}	10	57	C ₃ H ₅ O ⁺	44	
						Others	4	67	C ₅ H ₇ ⁺	5	
								71	C ₄ H ₇ O ⁺	7	
								72	C ₄ H ₈ O ^{•+}	4	
								82	C ₆ H ₁₀ ^{•+}	15	
								100	C ₆ H ₁₂ O ^{•+}	5	
									Others	9	
<i>cis</i> -3-Hexen-1-ol ^c	100	83	C ₆ H ₁₁ ⁺	94	72	C ₄ H ₈ O ^{•+,a}	9	57		3	
			101	C ₆ H ₁₃ O ⁺	6	82	C ₆ H ₁₀ ^{•+}	25	67	C ₅ H ₇ ^{+,a}	25
						99	C ₆ H ₁₁ O ⁺	22	69	C ₅ H ₉ ^{+,a}	6
						100	C ₆ H ₁₂ O ^{•+}	34	70	C ₅ H ₁₀ ^{•+,a}	9

Table 2 (Continued)

Compound	<i>m</i>	H ₃ O ⁺			NO ⁺			O ₂ ^{•+}		
		<i>m/z</i>	Ion	%	<i>m/z</i>	Ion	%	<i>m/z</i>	Ion	%
<i>trans</i> -3-Hexen-1-ol	100				112	(NO·C ₆ H ₁₀) ⁺	4	81		2
					130	(NO·C ₆ H ₁₂ O) ⁺	3	82	C ₆ H ₁₀ ^{•+}	43
						Others	3		Others	12
		83	C ₆ H ₁₁ ⁺	93	72	C ₄ H ₈ O ^{•+,a}	4	57	C ₃ H ₅ O ⁺	3
		101	C ₆ H ₁₃ O ⁺	6	82	C ₆ H ₁₀ ^{•+,a}	25	67	C ₅ H ₇ ⁺	19
			Others	1	99	C ₆ H ₁₁ O ⁺	31	69	C ₅ H ₉ ⁺	12
					100	C ₆ H ₁₂ O ^{•+}	34	70	C ₅ H ₁₀ ^{•+}	12
				Others	6	82	C ₆ H ₁₀ ^{•+}	38		
							Others	16		
1-Octen-3-ol	128	69	C ₅ H ₉ ⁺	8	69	C ₄ H ₅ O ^{+,a}	2	57	C ₃ H ₅ O ⁺	28
		111	C ₈ H ₁₅ ⁺	82	99	C ₆ H ₁₁ O ^{+,a}	7	68	C ₅ H ₈ ^{•+}	4
		129	C ₈ H ₁₇ O ⁺	9	111	C ₈ H ₁₅ ⁺	29	71	C ₄ H ₇ O ⁺	3
			Others	1	127	C ₈ H ₁₅ O ⁺	57	72	C ₄ H ₈ O ^{•+}	24
						Others	5	81	C ₆ H ₉ ⁺	3
								82	C ₆ H ₁₀ ^{•+}	4
								85	C ₅ H ₉ O ⁺	7
						99	C ₆ H ₁₁ O ⁺	6		
						110	C ₈ H ₁₄ ^{•+}	4		
							Others	17		
DL-6-Methyl-5-hepten-2-ol	128	69	C ₅ H ₉ ⁺	16	85	C ₆ H ₁₃ ^{+,a}	2	58	C ₃ H ₆ O ^{•+}	3
		111	C ₈ H ₁₅ ⁺	68	110	C ₈ H ₁₄ ^{•+,a}	12	68	C ₅ H ₈ ^{•+}	4
		129	C ₈ H ₁₇ O ⁺	14	127	C ₈ H ₁₅ O ⁺	2	69	C ₅ H ₉ ⁺	2
			Others	2	128	C ₈ H ₁₆ O ^{•+}	77	71	C ₄ H ₇ O ⁺	7
						Others	7	85	C ₅ H ₉ O ⁺	2
								95	C ₇ H ₁₁ ⁺	34
								110	C ₈ H ₁₄ ^{•+}	35
							Others	13		

Only product ions with a branching ratio $\geq 2\%$ are listed. Product ions with smaller branching ratio are gathered in "others". *m*: mass of the compounds in u; IE: ionization energy; %: branching ratio of the product ion, taking into account all its isotopes, *m/z* value refers to the first isotope of the product ion.

^a Tentative product identification.

^b Ref. [37].

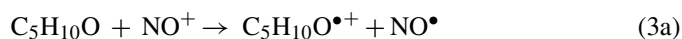
^c Ref. [24].

^d Ref. [38].

3.2.2. NO⁺ reactions

3.2.2.1. C₅ alcohols. The following reaction mechanisms have been observed in the reactions of NO⁺ with the unsaturated C₅ alcohols. Firstly, hydride ion transfer takes place in all reactions and is the dominant process for 1-penten-3-ol, *cis*- and *trans*-2-penten-1-ol. Secondly, hydroxide ion transfer is a major reaction pathway, except for 3-methyl-3-buten-1-ol, where it is not observed. The OH⁻ ion transfer process is the dominant channel for 3-methyl-2-buten-1-ol and the only reaction channel observed in the NO⁺/2-methyl-3-buten-2-ol reaction. Hydride and/or hydroxide ion transfer are, according to Španěl and Smith [16], also major mechanisms in the reaction of NO⁺ with most saturated alcohols. Thirdly, ionized parent molecules M^{•+} have been detected in all reactions, except for 1-penten-3-ol and 2-methyl-3-buten-2-ol (ionization energy IE of these compounds (see Table 2) > IE(NO[•]) = 9.26 eV [39]). C₅H₁₀O^{•+} parent cations are the main product ion species for the NO⁺/3-methyl-3-buten-1-ol ion/molecule reaction.

Above mentioned reaction pathways are illustrated below by the NO⁺/*trans*-2-penten-1-ol reaction:



Eq. (3a) corresponds to non-dissociative charge transfer, Eqs. (3b) and (3c) to hydride and hydroxide ion transfer, respectively.

A few minor product ions have also been detected, such as ions at *m/z* = 68, tentatively identified as (M – H₂O)^{•+}, for *cis*-2-penten-1-ol and 3-methyl-3-buten-1-ol. The minor product ion (NO·C₅H₈)⁺ at *m/z* = 98 for 3-methyl-3-buten-1-ol can be attributed to fragmentation of the nascent excited association complex (NO·C₅H₁₀O)^{•+}, in which NO[•] remains incorporated. Since this minor product results from an association reaction, its branching ratio (and therefore also the branching ratio of the other NO⁺/3-methyl-3-buten-1-ol reaction channels) will be pressure- and temperature dependent. The same reaction also shows a 13% branching ratio for product ions at *m/z* = 60, most likely formed by fragmentation of the nascent excited parent cation (C₅H₁₀O)^{•+*}.

3.2.2.2. C₆ alcohols. Hydride ion transfer and non-dissociative charge transfer occur for all four C₆ unsaturated alcohols listed in Table 2: H⁻ ion transfer is the dominant reaction pathway for *cis*- and *trans*-2-hexen-1-ol, but competes closely with non-dissociative charge transfer for *cis*- and *trans*-3-hexen-1-ol. The latter process is only a minor reaction channel for *cis*- and *trans*-2-hexen-1-ol.

Hydroxide ion transfer is not observed for *cis*- and *trans*-3-hexen-1-ol, but is a major reaction process for the other two alcohols. Ions at *m/z* = 82, tentatively identified as (M - H₂O)^{•+}, are major product ions for the NO⁺/*cis*- and *trans*-3-hexen-1-ol reactions. These ions are also formed in the case of *cis*-2-hexen-1-ol, although with a smaller branching ratio.

Minor product ions at *m/z* = 72 are detected for *cis*- and *trans*-3-hexen-1-ol, probably due to fragmentation of the nascent excited parent ions (C₆H₁₂O)^{•+*}. Finally, as reported in [24], (NO·C₆H₁₂O)⁺ ions at *m/z* = 130, resulting from three-body association, and (NO·C₆H₁₀)⁺ fragments of the association complex at *m/z* = 112 are also observed in the NO⁺/*cis*-3-hexen-1-ol reaction as minor ionic products.

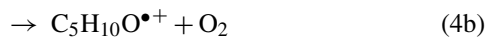
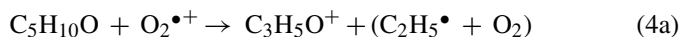
3.2.2.3. C₈ alcohols. The major reaction mechanisms for 1-octen-3-ol and 6-methyl-5-hepten-2-ol are clearly different. The reaction of NO⁺ with 1-octen-3-ol proceeds mainly by hydride and hydroxide ion transfer, while the reaction with 6-methyl-5-hepten-2-ol is mainly characterized by non-dissociative charge transfer. For the latter reaction, ions at *m/z* = 110, probably (M - H₂O)^{•+} ions, are also observed. Again the spectra show a few minor product ions as listed in Table 2.

3.2.3. O₂^{•+} reactions

All O₂^{•+} reactions can be described as exothermic charge transfer processes followed by fragmentation, although in some cases other mechanisms cannot be excluded a priori (for example, methide ion transfer, see reaction (6) below; ethide ion transfer in reactions (4a) and (5a), etc.). This fragmentation results in most cases in multiple product ions, so only the major ones (branching ratio > 10%) will be discussed below.

The reader, who is interested in a detailed description of the competitive character of collisional stabilization versus unimolecular dissociation in similar charge transfer reactions and in modeling of the underlying processes, is referred to the work of Viggiano, Troe and co-workers [40–42].

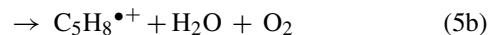
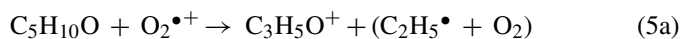
3.2.3.1. C₅ alcohols. The O₂^{•+} reaction with 1-penten-3-ol and *trans*-2-penten-1-ol is mainly determined by the C₃H₅O⁺ product ion at *m/z* = 57 and the unfragmented charge transfer parent ion C₅H₁₀O^{•+} at *m/z* = 86:



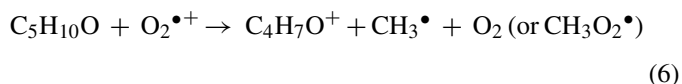
The neutral products in reaction (4a) are placed between brackets, since other combinations of neutral products may be

possible. As thermodynamic data are missing to trace the energetics of these reactions, some neutral products or combinations cannot be ruled out a priori. This notation will be used further on, whenever the neutral reaction products are uncertain.

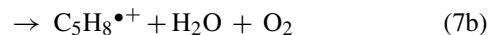
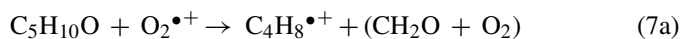
C₃H₅O⁺ ions (*m/z* = 57) are also the major product ions for the O₂^{•+}/*cis*-2-penten-1-ol reaction, next to (M - H₂O)^{•+} ions at *m/z* = 68:



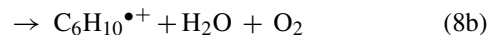
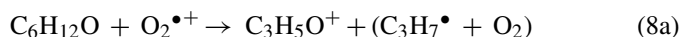
Ejection of CH₃[•] (or methide ion transfer) dominates the reaction of O₂^{•+} with the branched alcohols 3-methyl-2-buten-1-ol and 2-methyl-3-buten-2-ol:



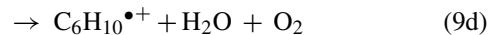
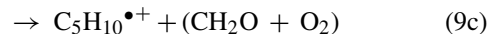
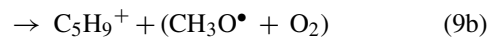
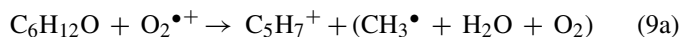
The O₂^{•+}/3-methyl-3-buten-1-ol reaction results mainly in the formation of the hydrocarbon ions C₄H₈^{•+} (*m/z* = 56) and C₅H₈^{•+} (*m/z* = 68):



3.2.3.2. C₆ alcohols. Ions at *m/z* = 57 and (M - H₂O)^{•+} ions at *m/z* = 82 are mainly observed in the reaction of O₂^{•+} with the *cis* and *trans* isomer of 2-hexen-1-ol:

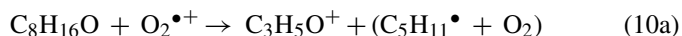


The reaction with the C₆ alcohol *trans*-3-hexen-1-ol shows four major reaction pathways, which give rise to hydrocarbon ions at *m/z* = 67, 69, 70 and 82:

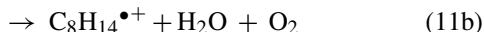
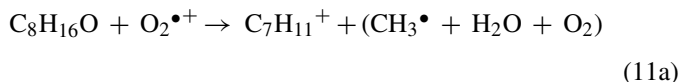


These hydrocarbon ions are also detected in the O₂^{•+}/*cis*-3-hexen-1-ol reaction, but only reactions (9a) and (9d) are major pathways (>10%).

3.2.3.3. C₈ alcohols. The reaction of O₂^{•+} with the two C₈ alcohols results in multiple ionic products. However, their major reaction channels are quite different. Carboxy ions, located at *m/z* = 57 and 72, are preferentially formed in the reaction with 1-octen-3-ol:



whereas hydrocarbon ions at $m/z=95$ and 110 dominate the product ion spectra of the $O_2^{\bullet+}$ /6-methyl-5-hepten-2-ol reaction:



4. Conclusion

A glance at Table 2 already reveals that, in the case of a mixture of some of the C_5 (C_6 or C_8) unsaturated alcohols we have studied, the H_3O^+ precursor ion is neither suited to identify these isomers, nor to quantify them by the chemical ionization technique, since all H_3O^+ ion/molecule reactions mainly proceed by the same mechanism, i.e. elimination of a water molecule after protonation.

NO^+ precursor ions are generally not appropriate to distinguish between the C_5 isomers, since all C_5 compounds have one or more major processes in common with each other in their reaction with NO^+ , as is visualized in Fig. 1.

However, in some particular cases the NO^+ SIFT-MS spectra are useful to identify some of the C_5 isomers in mixtures of these alcohols: if no product ions are observed at $m/z=86$ (non-dissociative charge transfer), the mixture consists only of 1-penten-3-ol and/or 2-methyl-3-buten-2-ol. In this case the product ion signals at $m/z=69$ (hydroxide ion transfer) and 85 (hydride ion transfer) can be used to quantify 1-penten-3-ol and 2-methyl-3-buten-2-ol separately. On the other hand, if the product ion signal at $m/z=69$ is missing, the sample contains only 3-methyl-3-buten-1-ol, which can be quantified on the basis of the strength of the ion signal at $m/z=86$.

As is shown in Fig. 2, the $O_2^{\bullet+}$ reactions with the C_5 unsaturated alcohols have several reaction channels in common.

However, the product ions at $m/z=57$ are only due to the three non-branched C_5 alcohols 1-penten-3-ol, *cis*- and *trans*-2-penten-1-ol. Therefore, the absence of this ion signal in the $O_2^{\bullet+}$ spectrum of a mixture already indicates that these alcohols are

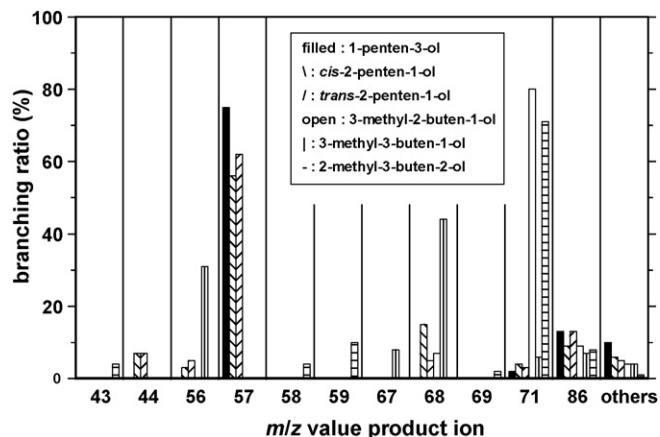


Fig. 2. Histogram of the product ion distributions of the reactions of $O_2^{\bullet+}$ precursor ions with six unsaturated C_5 alcohols.

not present in the mixture. Similarly, the absence of the ion signal at $m/z=68$ excludes *cis*- and *trans*-2-penten-1-ol, 3-methyl-2-buten-1-ol and 3-methyl-3-buten-1-ol. In this case 1-penten-3-ol and 2-methyl-3-buten-2-ol can be quantified based upon the ion signal strengths at $m/z=57$ and 71 .

Figs. 3 and 4 clearly show that the product ion distributions of the reactions of NO^+ ($O_2^{\bullet+}$ respectively) with *cis*- and *trans*-2-hexen-1-ol are nearly identical. Therefore, NO^+ and $O_2^{\bullet+}$ cannot be used to make distinction between these *cis* and *trans* compounds. The same conclusion can be drawn for the *cis* and *trans* configurations of 2-penten-1-ol (Figs. 1 and 2) and of 3-hexen-1-ol and (Figs. 3 and 4).

During leaf wounding many BVOCs are released, among which *trans*-2-hexen-1-ol and *cis*-3-hexen-1-ol [4–7]. In PTR-MS experiments both compounds give mainly $(M-OH)^+$ product ions at $m/z=83$ and can therefore not be separated by this detection technique. In this particular case the use of NO^+ precursor ions is appropriate. Indeed, as is shown in Fig. 3, product ions at $m/z=83$, resulting from hydroxide ion transfer, can only be attributed to *trans*-2-hexen-1-ol, while $(M-H_2O)^{\bullet+}$ ions at $m/z=82$ (and minor product ions at $m/z=72$, 112 and 130) only originate from *cis*-3-hexen-1-ol. As the sample from leaf

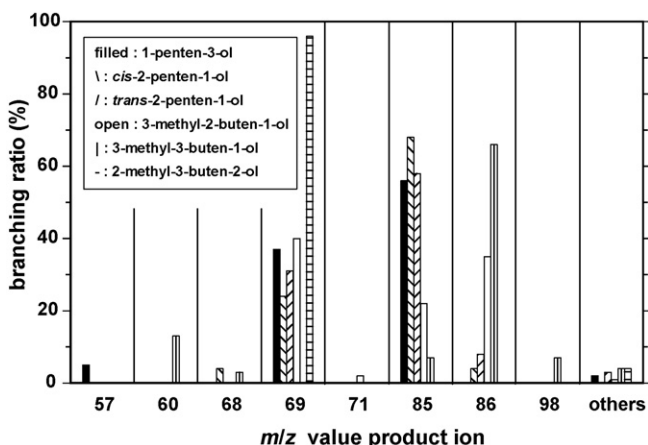


Fig. 1. Histogram of the product ion distributions of the reactions of NO^+ precursor ions with six unsaturated C_5 alcohols.

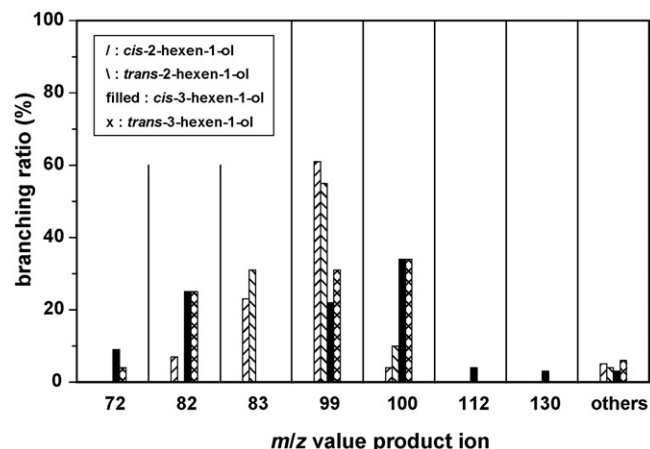


Fig. 3. Histogram of the product ion distributions of the reactions of NO^+ precursor ions with four unsaturated C_6 alcohols.

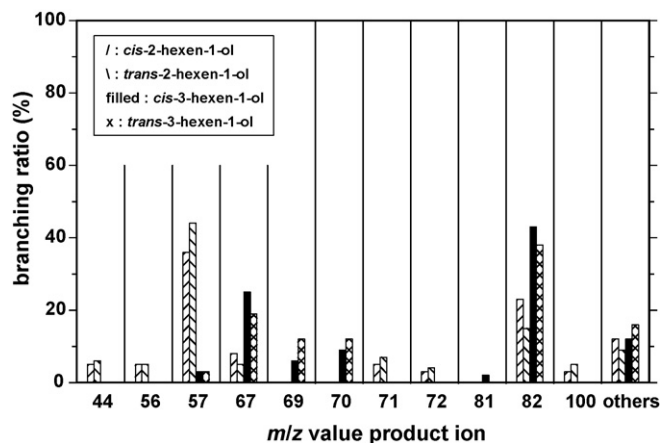


Fig. 4. Histogram of the product ion distributions of the reactions of $O_2^{+\bullet}$ precursor ions with four unsaturated C_6 alcohols.

wounding experiments is humid, product ions may hydrate. This hydration will be minor for the $(M - H_2O)^{+\bullet}$ and $(M - OH)^{+\bullet}$ product ions at $m/z = 82$ and 83 , respectively, since hydrocarbon ions show little tendency to hydrate [23]. Some interference may be expected from the hydration of the NO^+ precursor ions, since the resulting hydrated NO^+ ions may act on their turn as precursor ions for which the product ion distribution is unknown. However this interference is expected to be minor, since the association rate of NO^+ with water is relatively small (association rate of NO^+ with water in He [43] is more than one order smaller than the association rate of H_3O^+ with water in He at 298 K [44]). Although promising, comparison with other analytical techniques, such as GC-MS, is appropriate to validate NO^+ as CIMS precursor ion for the selective detection of the isomeric leaf wounding compounds *trans*-2-hexen-1-ol and *cis*-3-hexen-1-ol. The use of $O_2^{+\bullet}$ precursor ions is for these leaf wounding compounds also a valuable diagnostic tool (Fig. 4): ionic products at $m/z = 44, 56, 71, 72$ and 100 are only due to *trans*-2-hexen-1-ol, while $m/z = 69, 70$ and 81 ions are representative for *cis*-3-hexen-1-ol only.

Finally, although we have only studied two specific C_8 unsaturated alcohols, it is already clear that quite different NO^+ ($O_2^{+\bullet}$) product ion distributions can be obtained for this class of compounds. The use of NO^+ and/or $O_2^{+\bullet}$ precursor ions may be useful for the detection of C_8 unsaturated alcohols.

Acknowledgements

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