

Ion/molecule reaction studies in support of the detection of sesquiterpenes by CIMS

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Abstract

The ion/molecule reactions of H_3O^+ ions with a series of sesquiterpenes have been studied in view of their detection by CIMS. For all sesquiterpenes multiple product ions have been observed, but the protonated molecular parent ion is always the major ion species with yields ranging from 30 to 94 %. All reactions proceed at the collision rate, which is calculated to be close to $3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Preliminary studies indicate that NO^+ may also be a potential reagent ion for sesquiterpene detection.

Introduction

It is well-established that large amounts of volatile organic compounds (VOC) are emitted by terrestrial vegetation. Isoprene (C_5H_8) and the monoterpenes ($\text{C}_{10}\text{H}_{16}$) are generally found to be the biogenic VOCs (BVOCs) with the highest emission rates, but oxygenated BVOCs and sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) are also known to be emitted directly by vegetation. Quantification of sesquiterpene emissions is an experimental challenge because of their low vapor pressure and their ability to react very rapidly with atmospheric oxidants (mainly O_3), resulting in atmospheric lifetimes of only a few tens of seconds for some compounds. Important efforts have been carried out lately to develop and improve analytical techniques for sesquiterpene detection and quantification [1]. PTR-MS instrumentation has also been used recently to measure sesquiterpene concentrations, e.g. in smog chamber studies of sesquiterpene ozonolysis [2] and in VOC emission studies from herbivore infested branches [3]. In principle a PTR-MS instrument can be used to derive sesquiterpene concentrations from ion/molecule reaction rate constants, reaction time and product ion distributions, provided these are accurately known. In this paper we report preliminary results from a selected ion flow tube (SIFT) study of H_3O^+ /sesquiterpene reactions, as well as calculated collision rate constants for these reactions. The latter are based upon density functional theory calculations of polarizabilities and electric dipole moments.

Methods

Selected ion flow tube studies

The ion/molecule reactions were studied in a selected ion flow tube reactor at room temperature and at 150 Pa. A schematic representation of the instrument is given in Figure 1. H_3O^+ precursor ions (and others) are produced in a microwave discharge in a mixture of air and water vapor, mass selected in a first quadrupole filter and injected in a flow tube reactor. The ions in the flow tube are convectively transported by a helium buffer gas flow towards the mass spectrometer inlet,

where they are sampled, mass-analyzed by a second quadrupole filter and detected by a secondary electron multiplier which is operated in the pulse counting mode. More detailed information about the instrument can be found in [4]. To avoid differential diffusion of the product ions when performing product ion distributions, sesquiterpenes were introduced right in front of the mass spectrometer inlet. Introduction of stable sesquiterpene flows was accomplished by sending a helium flow over a reservoir containing liquid sesquiterpene which was kept at a constant temperature (usually 298 K). The tubing between the reservoir and the flow tube was made of stainless steel and kept at 373 K. Mass discrimination measurements of the spectrometer were carried out regularly to account for detector deteriorations.

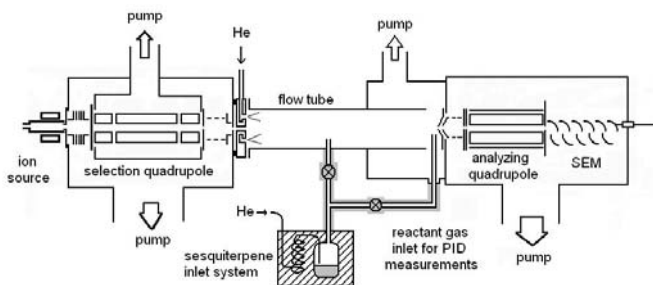


Fig. 1: schematic representation of the SIFT apparatus

Density functional theory calculations

Collision rate constants k_C of the H_3O^+ /sesquiterpene reactions were obtained with the parameterized equation of Su and Chesnavich [5,6]. Polarizabilities and electric dipole moments were calculated using density functional theory (DFT). The hybrid B3LYP functional was employed, which has a good performance in combination with the aug-cc-pVDZ basis set. The sesquiterpenes were subjected to a thorough conformational analysis (MMFF random search in combination with an MM3/MM4 stochastic search) to find all possible conformations within an energy barrier of 4 kcal/mol from the lowest energy configuration. All these conformations were taken into account when calculating an average collision rate constant. All DFT calculations were carried out with the Gaussian'03 software [7] in a distributed computer environment.

Results and discussion

An overview of the product distribution of the reactions of H_3O^+ precursor ions with β -caryophyllene, α -humulene, longifolene and α -cedrene, obtained at thermal conditions with the SIFT instrument is given in Table 1. The reactions of H_3O^+ with α -cedrene and longifolene mainly result in the protonated parent molecule (>80 %). Non-dissociative proton transfer is less efficient for the reactions with β -caryophyllene and α -humulene. Multiple fragment ions are observed and these can be divided in 2 groups of which all elements are separated by a CH_2 unit (14 u). One group contains ions with masses 81, 95, 109, 123 and 137 u. The other group contains

ions with masses 121, 135 and 149 u. It should be noted that the ions with mass 81 and 137 u from the first group are also characteristic for the reactions of H_3O^+ with monoterpenes.

β-caryophyllene			α-humulene		
<i>m/z</i>	<i>Product ion</i>	%	<i>m/z</i>	<i>Product ion</i>	%
81	C_6H_9^+	4	81	C_6H_9^+	2
95	$\text{C}_7\text{H}_{11}^+$	9	95	$\text{C}_7\text{H}_{11}^+$	7
109	$\text{C}_8\text{H}_{13}^+$	10	109	$\text{C}_8\text{H}_{13}^+$	7
121	$\text{C}_9\text{H}_{13}^+$	3	121	$\text{C}_9\text{H}_{13}^+$	2
123	$\text{C}_9\text{H}_{15}^+$	7	123	$\text{C}_9\text{H}_{15}^+$	7
135	$\text{C}_{10}\text{H}_{15}^+$	8	135	$\text{C}_{10}\text{H}_{15}^+$	4
137	$\text{C}_{10}\text{H}_{17}^+$	7	137	$\text{C}_{10}\text{H}_{17}^+$	2
149	$\text{C}_{11}\text{H}_{17}^+$	16	149	$\text{C}_{11}\text{H}_{17}^+$	9
205	$\text{C}_{15}\text{H}_{25}^+$	30	205	$\text{C}_{15}\text{H}_{25}^+$	54
others		6	others		6
longifolene			α-cedrene		
<i>m/z</i>	<i>Product ion</i>	%	<i>m/z</i>	<i>Product ion</i>	%
95	$\text{C}_7\text{H}_{11}^+$	3	109	$\text{C}_8\text{H}_{13}^+$	2
109	$\text{C}_8\text{H}_{13}^+$	3	205	$\text{C}_{15}\text{H}_{25}^+$	94
149	$\text{C}_{11}\text{H}_{17}^+$	5	others		4
205	$\text{C}_{15}\text{H}_{25}^+$	83			
others		6			

*Table 1: Product ion distributions of H_3O^+ /sesquiterpene reactions. Only products with yields $\geq 2\%$ are listed. The *m/z* value refers to the first isotope of the product ions, but all isotopes are included in the yields.*

From Table 1 it is clear that H_3O^+ precursor ions are certainly useful for sesquiterpene detection, but they cannot be used to distinguish between different isomers. Therefore, as is frequently done in SIFT-MS studies, the potential of NO^+ and O_2^+ precursor ions for sesquiterpene detection will be studied in detail in the near future. Preliminary results already indicate that NO^+ also seems to be a suitable CIMS reagent, but O_2^+ /sesquiterpene reactions are less useful due to extensive fragmentation.

Because of the low vapor pressure and the stickiness of the sesquiterpenes, absolute rate constant measurements are difficult to perform. However, by simultaneously introducing H_3O^+ , NO^+ and O_2^+ precursor ions in the flow tube reactor and by monitoring the count rates of these three ions at controlled (but not measured) sesquiterpene concentrations in the reactor, the rate constant ratios of the NO^+ /sesquiterpene and O_2^+ /sesquiterpene reactions with respect to the H_3O^+ /sesquiterpene reaction could be obtained. For all sesquiterpenes and within experimental error, the relative rate constant ratios thus obtained were found to scale linearly with the

reciprocal of the square root of the reduced mass of the ion/sesquiterpene system, which is a good indication that all reactions proceed at the collision limit.

The collision rate constants k_C of the H_3O^+ /sesquiterpene reactions were subsequently obtained with the parameterized theory of Su and Chesnavich. Polarizabilities (α) and electric dipole moments (μ_D) of the sesquiterpenes, required for calculating these collision rate constants, were determined using B3LYP/aug-cc-pVDZ and are shown in Table 2. The second column of this table refers to the number of rotamers that were found and taken into account when averaging the molecular parameters and the collision rate constants. Previous experiments by the authors have shown that collision rate constants, calculated in this way for a large variety of chemical species, generally agree quite well with experimentally derived absolute rate constants obtained with the SIFT apparatus.

compound	# config.	μ_D (D)	α (\AA^3)	k_C (10^{-9} cm^3 molecule $^{-1} \text{ s}^{-1}$)
β -caryophyllene	9	0.65	26.6	3.1
α -humulene	4	0.24	27.4	3.0
longifolene	2	0.94	25.9	3.2
α -cedrene	2	0.21	25.3	2.9

Table 2: averaged polarizabilities and electric dipole moments (from B3LYP/aug-cc-pVDZ calculations) and thermal averaged Su-Chesnavich collision rate constants.

From the data presented above it can be concluded that H_3O^+ precursor ions are useful for the sensitive detection of sesquiterpenes, due to the high reaction rate constants and the fact that reactions (at least at thermal energies) mainly result in a non-dissociative proton transfer product. We are well aware that the SIFT-MS method is not sufficiently sensitive for ambient sesquiterpene detection, but the method could be used in experimental set-ups (e.g. smog chambers or fast flow reactors) for dedicated experiments, where sesquiterpene concentrations can be much larger. Because of the higher ion energies in drift tube experiments compared to SIFT conditions, H_3O^+ /sesquiterpene product ions in a PTR-MS instrument will be subjected to even more fragmentation. However, product ion distributions at thermal conditions in a SIFT will already give an indication about some of the fragments that can be expected in PTR-MS experiments. Because of the rather small electric dipole moments, the collision rate constants of H_3O^+ /sesquiterpene reactions are not expected to be much affected by the electric fields which are typically applied in a PTR-MS drift tube.

References

- [1] D. Helmig, J. Ortega, A. Guenther, J.D. Herrick, and C. Geron, *Atm. Environ.* 40, 4150-4157, 2006.
- [2] A. Lee, A.H. Goldstein, M.D. Keywood, S. Gao, V. Varutbangkul, R. Bahreini, N.L. Ng, R.C. Flagan, and J. Seinfeld, *J.Geophys. Res.*, Vol. 11, D07302, doi: 10.1029/2005JD006437, 2006.
- [3] A. Schaub et al., *Geophysical Research Abstracts*, EGU General Assembly 2006, Vienna, Austria, abstract number EGU06-A-07408.
- [4] N. Schoon, C. Amelynck, L. Vereecken and E. Arijs, *Int. J. Mass Spectrom.* 229, 231-240, 2003.
- [5] T. Su, W.J. Chesnavich, *J. Chem. Phys.* 76, 5183-5185, 1982.
- [6] T. Su, *J. Chem. Phys.* 89, 5355, 1988.
- [7] M.J. Frisch et al., *Gaussian '03*, Revision B.05, Gaussian Inc., Wallingford, CT, 2004.