



Ion-molecule reaction study in support of the detection of unsaturated biogenic alcohols by chemical ionization mass spectrometry (CIMS)

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Alcohols are after isoprene and the monoterpenes, and next to the carbonyls, the most predominant group among biogenic volatile organic compounds. CIMS techniques, based upon the H_3O^+ precursor ion, have already proven to be successful for the detection and quantification of volatile organic compounds, but generally they do not allow distinction between isomers. Therefore, a Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) study has been carried out of the reactions of three precursor ions, H_3O^+ , NO^+ and O_2^+ , with the following C5, C6 and C8 unsaturated alcohols: 1-penten-3-ol (1P3), cis-2-penten-1-ol (C2P1), trans-2-penten-1-ol (T2P1), 3-methyl-2-buten-1-ol (MBO321), 2-methyl-3-buten-2-ol (MBO232), 3-methyl-3-buten-1-ol (MBO331), cis-2-hexen-1-ol (C2H1), trans-2-hexen-1-ol (T2H1), cis-3-hexen-1-ol (C3H1), trans-3-hexen-1-ol (T3H1), 1-octen-3-ol (1O3) and DL-6-methyl-5-hepten-2-ol (6M5H2). Next to the reaction rate constants, product ion distributions have been measured, in order to determine if the three precursor ions can be used to distinguish the different isomers in mixtures of the alcohols studied.

All reactions are fast and the experimental reaction rate constants are compared with the collisional rate constants, calculated with the parameterized equation of Su and Chesnavich, using dipole moments and polarizabilities derived from quantum chemical calculations. Reaction rate constants for the hydrated precursor ions are also reported.

The main reaction mechanism of the reaction of H_3O^+ with all alcohols studied is elimination of a water molecule after protonation (between 70 and 80% for MBO232, 1O3 and 6M5H2, > 85% for the other alcohols). The protonated molecule, resulting

from non-dissociative proton transfer, has not been found (< 2%) in the reaction of H_3O^+ with C2P1, T2P1, MBO321, C2H1 and T2H1, and is only a minor product with branching ratio ranging from 5 to 20% for the other alcohols. For the C8 alcohols a minor product ion at $m/z=69$ has also been observed (branching ratio ranging from 8 to 15%). The reaction of NO^+ with the C5 alcohols (except MBO331 and MBO232) and with C2H1, T2H1 and 1O3 proceeds mainly (> 60%) through hydride and hydroxide ion transfer. Non-dissociative charge transfer is dominant in the reaction of NO^+ with MBO331, T3H1, C3H1 and 6M5H2 and is a major channel (35%) in the MBO321/ NO^+ reaction. Hydroxide ion transfer is the only pathway in the reaction of NO^+ with MBO232. Elimination of a water molecule (25%) and hydride ion transfer (20-30%) are also major processes in the T3H1 and C3H1/ NO^+ reaction. The product spectra of O_2^+ with the neutral reactants are complex and show multiple fragments.

The precursor ion H_3O^+ is not well suited to distinguish isomers in mixtures. However, based upon the absence of one or more reaction pathways, the NO^+ and/or O_2^+ chemistry can be used to eliminate some isomers in mixtures. For example, the NO^+ precursor ion is an excellent choice for making the distinction between the isomers C3H1 and T2H1 in leaf wounding experiments [1].

[1] R. Fall, T. Karl, A. Jordan and W. Lindinger, Atmospheric Environment, **35**, 2001, 3905-3916