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Study of ion-molecule reactions of methyl vinyl ketone and some atmospherically important aldehydes in view of their detection through SIFT-MS.

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A laboratory study has been made of the rate constant and product ion distribution of the reactions of H_3O^+, NO^+ and O_2^+ with methacrolein (MaCR), methyl vinyl ketone (MVK), pivaldehyde, 2-methyl-butanal, glyoxal, o-, m- and p-tolualdehyde in a Selected Ion Flow Tube (SIFT) at 150 Pa and at room temperature.

For all reactions studied the corresponding theoretical collisional rate constant was derived with the Su and Chesnavich approach, using the polarizability and electric dipole moment of the compounds, inferred from quantum chemical calculations. Our experiments show that all reactions, except the NO^+/glyoxal reaction, proceed at a rate close to the calculated one.

For all H_3O^+ reactions non-dissociative proton transfer is observed, except for 2-methyl-butanal, where also fragmentation in two minor channels after protonation occurs.

In the NO^+/MVK and glyoxal reaction, association is the only pathway, whereas in all the other NO^+ reactions hydride ion transfer is the major process taking place. Elimination of CHO for pivaldehyde and association for MaCR are also non-negligible channels in their reaction with NO^+.

All the O_2^+ reactions result in the parent cation by charge transfer and in at least

one fragment ion. Ejection of C_2H_4 is the major pathway for the reaction with 2-methyl-butanal. Elimination of a H atom has been observed for o-, m-, p-tolualdehyde and MaCR, ejection of a CO molecule for glyoxal and MaCR, of CHO for glyoxal, pivaldehyde and possibly 2-methyl-butanal, of the methyl and vinyl radical for MVK.

Further hydration of the product ions was investigated by adding water vapor in the reaction zone. A simple method is proposed to infer the rate constant of the three body association of water with the product ions and to estimate the rate constants of the reactions of the hydrated precursor ions $H_3O^+.H_2O$ and $NO^+.H_2O$ with the reactants.