

Supporting Information for Manuscript “PTR3: An Instrument for Studying the Lifecycle of Reactive Organic Carbon in the Atmosphere”

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CALCULATIONS OF REVERSE REACTION CHANNELS OF THE PROTON TRANSFER REACTION

For proton transfer reactions at high water concentrations and long reaction times the reverse proton transfer reaction has to be taken into account if the difference of proton affinities is small. Vlasenko et al¹ demonstrated that in a standard PTR-MS at 2 mbar the reaction time is too short to reach equilibrium between forward and reverse reaction. This is not any more valid for the PTR3 because the enhanced reaction time and the increased pressure assure that equilibrium between forward and reverse proton transfer reactions is achieved.

The reverse reaction rate constant can be calculated using Arrhenius law,

$$k_r = k_{r,kin} e^{-\frac{\Delta PA}{E}},$$

where $k_{r,kin}$ is the reverse collision rate constant, ΔPA the exothermicity of the forward proton transfer reaction and E the mean kinetic energy of ion-molecule collisions in the center-of-mass system under investigation. E is calculated using the Wannier expression^{2,3}:

$$E = \frac{1}{2} \frac{(m_{ion} + m_{air}) \cdot m_N}{m_{ion} + m_N} \cdot v_d^2 + \frac{3}{2} k_b T;$$

m_{ion} , m_{air} and m_N are the molecular masses of the protonated ion (RH^+), the mean mass of the buffer gas (air) and the mass of the water molecule, respectively. The calculation of drift velocities (ions do drift with respect to the buffer gas due to the rotating electric field) of protonated species is based on reduced mobilities K_0 from a fit described by Mäkelä et al.⁴:

$$K_0 = e^{-0.0347 \cdot \ln(m_{ion}^2) - 0.0376 \cdot \ln(m_{ion}) + 1.46662}.$$

For $k_{r,kin}$ describing the reverse *kinetic* collision rate we use the parametrization of T. Su⁵ together with the dipole moment of H_2O (1.82 Debye) and a polarizability of 1.5 \AA^3 ⁶. Solving the equation

$$\frac{dI_{RH^+}}{dt} = k_f [R] I_{H_3O^+} - k_r [H_2O] I_{RH^+}$$

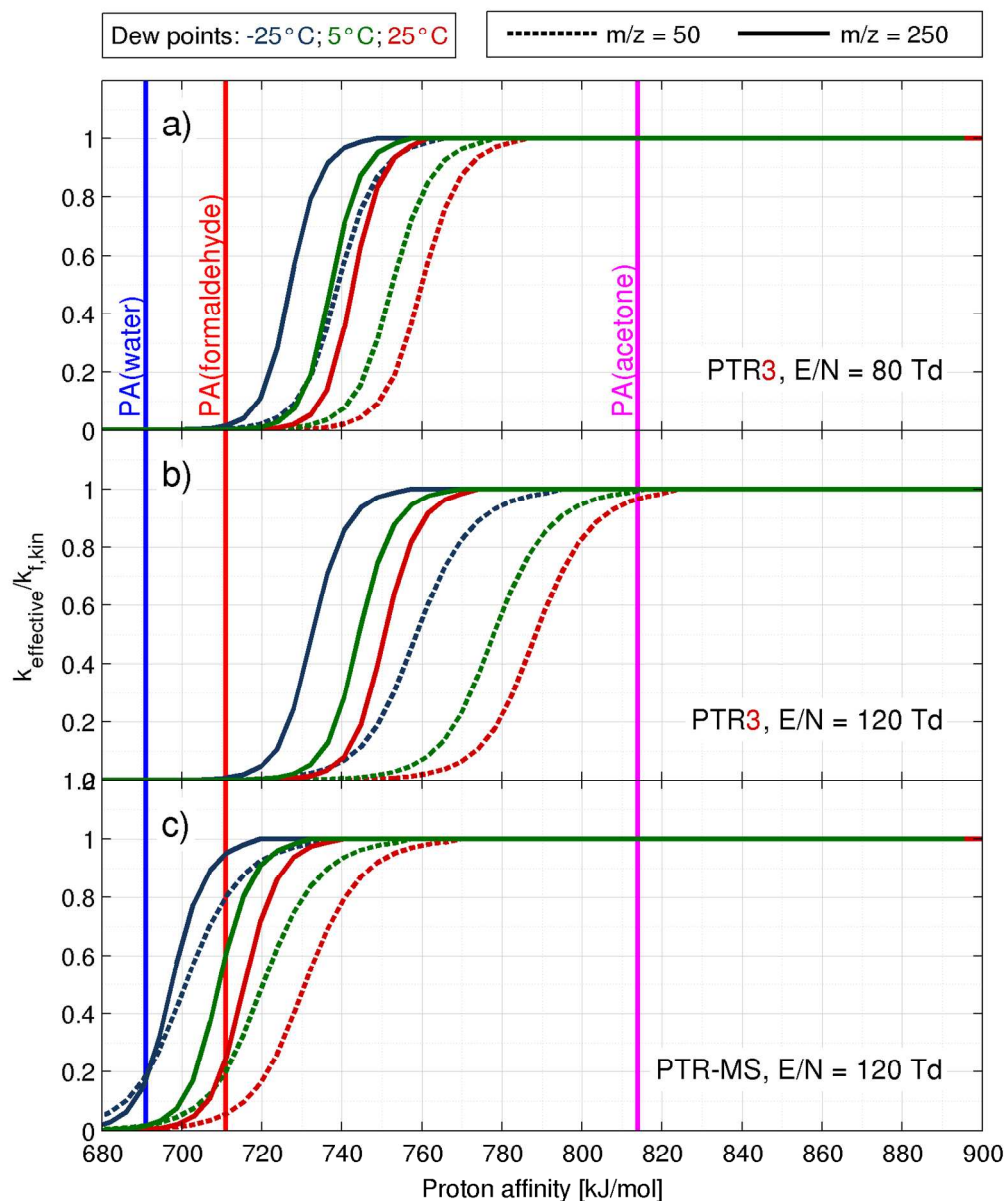
for the proton transfer reaction $H_3O^+ + R \rightleftharpoons RH^+ + H_2O$ leads to

$$I_{RH^+}(t = t_{react}) = \frac{k_f [R] I_{H_3O^+}}{k_r [H_2O]} (1 - e^{-k_r [H_2O] t})$$

Where I_{RH^+} and $I_{H_3O^+}$ are the ion currents for the protonated molecule R and the hydronium ion, respectively (primary ion current, $[R]$ and $[H_2O]$ is assumed constant over the entire length of the tripole).

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Supplementary Figure S1. Comparison of effective reaction rates taking into account the reverse reaction of the PTR3 (for E/N values of 80 and 120 Td, panels a and b, respectively) with conventional PTR-MS instruments (panel c) as a function of proton affinity for different humidities. The onset of decreasing sensitivities for the PTR3 with an p·t product of 240 mbar·ms for an E/N value of 120 Td is approximately 50 kJ/mol higher compared to a standard PTR-MS instrument (p·t = 0.2 mbar·ms). For smaller masses the reverse reactions are more pronounced, since their drift velocity and hence mean kinetic energy to overcome endothermicity of the reverse reaction is higher. Furthermore, the onsets are strongly dependent on the reduced electric field, which makes the choice of E/N for a particular application (i.e., humidity of the sample and targeted species) even more important for the PTR3 as compared to conventional PTR-MS instruments.