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Mass Accommodation and Rates of Evaporation of H₂O, HNO₃ and HCl on HNO₃ hydrates (alpha-NAT, beta-NAT, NAD) in the range 175-200 K

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Experiments have been performed using a multidagnostic stirred-flow reactor (SFR) in which the gas- as well as the condensed phase have been simultaneously investigated under stratospheric temperatures in the range 175-200 K. Wall interactions of the title compounds have been taken into account using Langmuir adsorption isotherms in order to close the mass balance between deposited and desorbed (recovered) compounds. Thin solid films of 1 micrometer typical thickness have been used as a proxy for atmospheric ice particles and have been deposited on a Si window of the cryostat with the optical element being the only cold point in the deposition chamber. FTIR absorption spectroscopy in transmission in the range 650 to 4000 cm⁻¹ as well as partial and total pressure measurement using residual gas MS and sensitive pressure gauges have been employed in order to monitor growth and evaporation processes as a function of temperature using both pulsed and continuous gas admission and monitoring under SFR conditions. Thin solid H₂O ice films were used as the starting point throughout, with the initial spontaneous formation of alpha-NAT followed by the gradual transformation of alpha- to beta-NAT at T > 185 K. NAD was spontaneously formed at somewhat larger partial pressures of HNO₃ deposited on pure H₂O ice. In contrast to published reports the formation of alpha-NAT proceeded without prior formation of an amorphous HNO₃/H₂O layer and always resulted in beta-NAT. For alpha- and beta-NAT the temperature dependent accommodation coefficient $\alpha(\text{H}_2\text{O})$ and $\alpha(\text{HNO}_3)$, the evaporation flux $J_{\text{ev}}(\text{H}_2\text{O})$ and $J_{\text{ev}}(\text{HNO}_3)$ and the resulting saturation vapor pressure $P_{\text{eq}}(\text{H}_2\text{O})$ and $P_{\text{eq}}(\text{HNO}_3)$ were measured and compared to binary phase diagrams of HNO₃/H₂O in order to afford thermochemical check of the kinetic parameters. The resulting kinetic and thermodynamic parameters of activation energies for evaporation (E_{ev}) and standard heats of evaporation ΔH_{ev}^0 of H₂O and HNO₃ for alpha- and beta-NAT, respectively, led to an estimate for the relative standard enthalpy difference between alpha- and beta-NAT of -6.0 ± 20 kJ/mol in favor of beta-NAT, as expected, despite a significantly larger value of E_{ev} for HNO₃ in alpha-NAT. This in turn implies a substantial activation energy for HNO₃ accommodation in alpha- compared to beta-NAT where $E_{\text{acc}}(\text{HNO}_3)$ is essentially zero. The kinetic ($\alpha(\text{HCl})$, $J_{\text{ev}}(\text{HCl})$) and thermodynamic ($P_{\text{eq}}(\text{HCl})$) parameters of HCl-doped alpha- and beta-NAT have been determined under the assumption that HCl adsorption did not significantly affect $\alpha(\text{H}_2\text{O})$ and $\alpha(\text{HNO}_3)$ as well as the evaporation flux $J_{\text{ev}}(\text{H}_2\text{O})$. $J_{\text{ev}}(\text{HCl})$ and $P_{\text{eq}}(\text{HCl})$ on both alpha- and beta-NAT are larger than the corresponding values for HNO₃ across the investigated temperature range but significantly smaller than the values for pure H₂O ice at T < 200 K.

Significance statement

Thermochemical closure has been achieved in the measurements of mass accommodation coefficients and absolute rates of evaporation of H₂O, HCl and HNO₃ interacting with ice solids of atmospheric importance. These results provide accurate surface residence times of trace gases on ices and evaporative lifetimes of atmospheric ices.

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