

Kinetics and Mechanism Investigation for Carboxylic acids (R-C(O)OH, R: -CH₂CH₃, -CH₂CH₂CH₃) Uptakes on Pure and HNO₃-Doped Ice Surfaces under UT/LS Temperature Conditions.

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In the present work, the heterogeneous interaction of CH₃CH₂C(O)OH and CH₃CH₂CH₂C(O)OH with pure and HNO₃-doped ice surfaces (1.96 and 7.69 wt % H₂O/HNO₃) under UT/LS temperature conditions was studied at the low pressure regime (~2 mTorr). Experiments were carried out in a Knudsen continuous-flow reactor coupled with quadrupole mass spectrometry (Kn-QMS). Pure and HNO₃-doped ice surfaces of ~5 – 20 μm thickness were developed at T = 206 K, by single capillary controlled flow of H₂O vapors (pure ice films) or by H₂O vapors and HNO₃/He mixture co-admission (HNO₃-doped ice films) via separate inlets in the reactor, followed by their deposition on the cold copper surface at the bottom of the Knudsen cell. The initial uptake coefficients of the title carboxylic acids were measured as a function of temperature (195-212 K), for the three different types of the ice films, varying the R-C(O)OH concentration in the range (0.18 – 17.83) × 10¹¹ molecule cm⁻³. Initial uptake coefficients, γ₀, of both carboxylic acids showed inverse temperature dependence, while the γ₀ values that were measured for butanoic acid were systematically higher compared to those of propanoic acid. The latter result is consistent with what was observed for the carboxylic acids of smaller straight-carbon chain (X-C(O)OH, X: -H, -CH₃), resulting, eventually, in a γ₀ value increase of a factor of 10, from HC(O)OH to CH₃CH₂CH₂C(O)OH.^{1,2} HNO₃ doping of the ice surfaces had a negligible effect on γ₀ values. However, noticeable differences of R-C(O)OH surface coverage on, and desorption from the ice surface were observed in case by case of the series of carboxylic acids. This can be attributed to an increase of ice surface reactivity due to in-bulk phenomena, such as diffusion or/and dissolution, and the deterioration of ice-structure smoothness that they are explicitly discussed. Finally the lifetime of propanoic and butanoic acid (τ_{het}) at dense cirrus clouds particles (~2 × 10⁻⁴ cm² cm⁻³) was estimated and the significance of the heterogeneous chemistry as a potential sink is compared to the gas phase chemistry.

References

- (1) Romanias, M.N.; Zogka, A.G.; Stefanopoulos, V.G.; Papadimitiou, V.C.; Papagiannakopoulos, P. *Chemphyschem.* **2010**, 18, 4042 – 4052.
- (2) Romanias, M.N.; Zogka, A.G.; Papadimitiou, V.C.; Papagiannakopoulos, P. *J. Phys. Chem. A* **2012**, DOI: 10.1021/jp205196t.