Geophysical Research Abstracts
Vol. 14, EGU2012-9958-2, 2012
EGU General Assembly 2012

Heterogeneous interaction of carboxylic acids with pure ice and HNO_3-doped ice surfaces at upper tropospheric/lower stratospheric temperatures

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The heterogeneous interaction of atmospheric trace gases with ice surfaces plays an important role in the chemistry of the upper troposphere and lower stratosphere (UT/LS) region. In particular, the uptakes of carboxylic acids, such as formic (HC(O)OH), acetic (CH3C(O)OH), propionic (CH3CH2C(O)OH), and butyric (CH3CH2CH2C(O)OH) acids, on pure ice or HNO_3-doped ice particles in dense cirrus clouds or polar stratospheric clouds may be significant in removing these acids from the UT/LS. The aim of the present study was to investigate the adsorption of gaseous carboxylic acids on thin ice and HNO_3-doped ice films over the temperature range 195-208 K and at low gaseous pressures, using a Knudsen flow reactor combined with a quadrupole mass spectrometer. The initial uptake coefficients, γo, were measured as a function of temperature and at low surface coverage; the inverse temperature dependence of γo indicates that the uptake proceeds via the formation of an intermediate precursor state. The uptakes of formic and acetic acids were well represented by Langmuir adsorption model, and the temperature independent saturation surface coverage, Nmax, on pure ice films were (2.94 $\pm$ 0.67)$\times$1014 molecule cm-2, and (2.11 $\pm$ 0.16)$\times$1014 molecule cm-2, respectively; in excellent agreement with coated-wall laminar flow tube (CWLFT) technique values. Light nitration (1.96 and 7.69 wt%) of ice films resulted in more efficient uptakes and larger Nmax values that may be attributed to in-bulk diffusion or change in nature of gas-ice surface interaction. The uptake profiles of propionic and butyric acids on pure ice and HNO_3-doped ice films over the temperature range 195-206 K were unsaturated, which indicated high solubility and rapid diffusion of these acids into the ice bulk. The kinetics of these uptakes γ(t) were very well represented by the diffusion non-dissociating resistor model, and H*d(D)1/2 values were independent of concentration and in the range 1 to 20 m s-1/2; H*d is the Henry law coefficient and D the diffusion coefficient of the carboxylic acids in the ice bulk. Finally, it was estimated that the adsorption rate of these carboxylic acids on high-density cirrus clouds in the UT/LS is fast, and this is reflected by their short atmospheric lifetimes (1-8 min), while the amount of these uptakes is probably low on pure ice ($\approx$5%) and rather considerable ($\approx$20%) on HNO_3-doped ice particles.