Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 2, 235-247, 2002
www.atmos-chem-phys.net/2/235/2002/

The adsorption of nitrogen oxides on crystalline ice

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Abstract. The partitioning of nitrogen oxides between ice and air is of importance to the ozone budget in the upper troposphere. In the present study, adsorption of nitrogen oxides on ice was investigated at atmospheric pressure using a chromatographic technique with radioactively labelled nitrogen oxides at low concentrations. The measured retentions solely depended on molecular adsorption and were not influenced by dimerisation, formation of encapsulated hydrates on the ice surface, dissociation of the acids, nor by migration into a quasi-liquid layer or grain boundaries. Based on the chromatographic retention and the model of thermo-chromatography, the standard adsorption enthalpy of -20 kJ mol^{-1} for NO, -22kJ mol^{-1} for NO_2, -30kJ mol^{-1} for peroxyacetyl nitrate, -32kJ mol^{-1} for HON} and -44 kJ mol^{-1} for HNO_3 was calculated. To perform those calculations within the model of thermo-chromatography, the standard adsorption entropy was calculated based on statistical thermodynamics. In this work, two different choices of standard states were applied, and consequently different values of the standard adsorption entropy, of either between -39 kJ mol^{-1} and -45kJ mol^{-1}, or -164 kJ mol^{-1} and -169 kJ mol^{-1} for each nitrogen oxide were derived. The standard adsorption enthalpy was identical for both standard adsorption entropies and thus shown to be independent of the choice of standard state. A brief outlook on environmental implications of our findings indicates that adsorption on ice might be an important removal process of HNO_3. In addition, it might be of some importance for HONO and peroxyacetyl nitrate and irrelevant for NO and NO_2.

Final Revised Paper (PDF, 1584 KB) Discussion Paper (ACPD)

Citation: Bartels, T., Eichler, B., Zimmermann, P., Gäggeler, H. W., and Ammann, M.: The adsorption of nitrogen oxides on crystalline ice, Atmos. Chem. Phys., 2, 235-247, 2002. Bibtex EndNote Reference Manager