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Chemistry of NO_2, N_2O_4, and N_2O_5 at simulated stratospheric conditions: An aerosol chamber and modelling study

H. Saathoff, K.-H. Naumann, and R. Wagner

Institute for Meteorology and Climate Research, Forschungszentrum Karlsruhe, Germany, (Harald.Saathoff@imk.fzk.de)

For the understanding of stratospheric nitrogen oxide chemistry the knowledge of reaction probabilities for the heterogeneous hydrolysis of N_2O_5 and rate coefficients for the NO_2 + O_3 reaction at low temperatures are required. In corresponding simulation chamber experiments at ppm concentration levels the dimerisation of NO_2 has also to be taken into consideration. Below 210 K no direct measured kinetic data are available for the homogeneous reactions. Regarding the reaction probability $\gamma(N_2O_5)$ for the hydrolysis of N_2O_5 on sulphuric acid or H_2SO_4/HNO_3/H_2O ternary solution particles, the available literature data are partially contradictory. Specifically, the decrease of $\gamma(N_2O_5)$ with increasing nitrate concentration observed at room temperature has not been unambiguously confirmed for stratospheric conditions.

Therefore we used the evacuable AIDA aerosol chamber of 84 m^3 volume which can be thermostated between 183 and 323 K to investigate these reaction systems. The experiments were initiated by mixing ozone to NO_2 in the presence and absence of sulphuric acid particles at temperatures between 188 and 220 K. Observed were NO_2, N_2O_4, N_2O_5, O_3, H_2O in the gas phase and sulphate, nitrate and water in the condensed phase by in situ FTIR & TDL spectroscopy as well as by analysing filter samples with ion chromatography.

The results obtained for the N_2O_4 equilibrium constant and the rate coefficient for the O_3 + NO_2 reaction are consistent with the IUPAC recommendation extrapolated to 188 K. Detailed model analysis of the experimental data reveals a significant dependence of the reaction probability for the hydrolysis of N_2O_5 on the nitrate concentration of ternary solution droplets at 194 K.