Determination of the bulk accommodation coefficient of NO_2 and O_3 on deliquesced aerosol particles and the effect of surfactants

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Atmospheric aerosol particles are continuously processed by gas phase oxidants, which affects their life time and climate effect. The aim of this work is to understand uptake of O_3 or NO_2 from the gas phase to deliquesced aerosol particles, with a specific eye on the bulk accommodation coefficient, α_b, i.e., the gas kinetic probability that the gas phase molecules enter the liquid phase. Experiments were performed in an aerosol flow tube, and the analysis is assisted by kinetic modelling to track reactants both in the gas and aerosol phase. We also investigated the effect organic surfactants have on the uptake of O_3.

NO_2 uptake to gentisic acid sodium salt particles. Gentisic acid trisodium salt (Na_3GA), a proxy for biomass burning derived aromatic compounds, was used as a model compound to provide a fast aerosol phase sink for NO_2. The NO_2 uptake was investigated using the ^{13}N tracer technique, by which the transfer of ^{13}N labelled NO_2 to the particles is followed as function of time in an aerosol flow reactor.

Figure 1 shows typical kinetic data of the disappearance of NO_2 from the gas phase and of the appearance of the products in the aerosol phase as a function of time in the aerosol flow tube. Adjusting the corresponding simulations all available experimental data leads to a best estimate for α_b of 0.025 and for k_2 of 3.6×10^8 $M^{-1}s^{-1}$, which is the second order liquid phase rate constant for the reaction between NO_2 and Na_3GA.

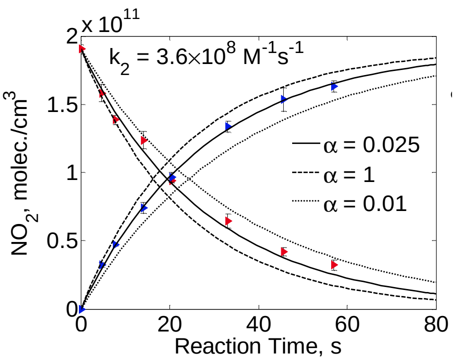

Figure 1. Typical results and simulations of an aerosol flow tube experiment of the reaction of NO_2 with gentisic acid sodium salt. Red symbols: Gas phase NO_2 concentration; blue symbols: aerosol phase nitrite product. Solid lines kinetic model simulations.

O_3 uptake to deliquesced potassium iodide particles. Similar experiments were performed with O_3 reacting with deliquesced KI particles, shown in Figure 2. The kinetic model simulations of this and similar experiments show that α_b is close to 1, if we assume that the second order rate constant between iodide and ozone is $k_b=1.2\times10^9$ $M^{-1}s^{-1}$ (Liu et al, 2001).

The values obtained for α_b for O_3 and NO_2 are significantly larger than previous estimates. This indicates that also only slightly soluble molecules are able to very rapidly enter the aqueous phase.

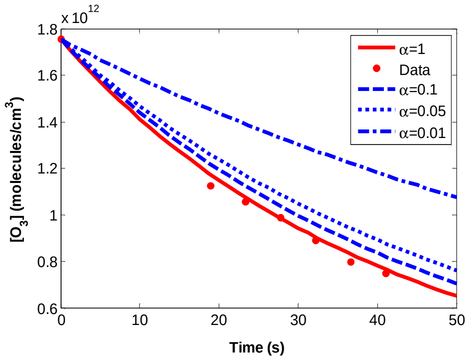

Figure 2: Temporal evolution of O_3 in the aerosol flow tube as a function of reaction time with deliquesced KI aerosol (red symbols). Kinetic model simulations are shown for different values of α_b (lines).

In a previous study, we have shown that organic coatings can reduce the mass transfer of HNO_3 between the gas and the aerosol phases (Stemmler et al, 2008). In this work, we studied the effects of fatty acids (C_9-C_{20}) on the ozone uptake to deliquesced KI particles. The results show that the degree to which ozone uptake is inhibited as a function of the fatty acid mass fraction is consistent with trends of the monolayer properties especially for C_{15}-C_{20} acids, i.e., density and surface phase state.

Acknowledgement

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References

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