Influence of NH3 on atmospheric particle formation starting from OH + SO2

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Introduction
For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intensive studies in the field and in the laboratory. The formation mechanisms and the participating substances, however, have not been resolved yet (Kulmala, 2003). Large discrepancies between model-predicted nucleation rates for the favored binary system H2SO4/H2O and much higher atmospheric nucleation data were explained by various supportive additional participants such as NH3 or organic molecules.

In a previous investigation of our laboratory under near-atmospheric conditions, experimental evidence for the formation of new particles in the system H2SO4/H2O was found for H2SO4 concentrations of 107 molecule cm−3 if ´´H2SO4´´ was produced in-situ via the reaction of OH radicals with SO2. (´´H2SO4´´ stands for all products of converted SO2) Berndt et al. (2005). In contrast, taking H2SO4 nucleation rate / cm3 / s

It can be hypothesized that HOSO2O2 or its hydrated species HOSO2O2(H2O)n play a role for the nucleation process explaining the different threshold concentrations for nucleation starting from liquid H2SO4 or from OH + SO2.

The activities focused on experimental studies regarding the influence of NH3 on new particle formation. Theoretical studies predict strong enhancement of the nucleation rate for NH3 mixing ratios at ppv-level (Coffman and Hegg, 1995). Ball et al. (1999) showed experimentally an increase of the nucleation rate for NH3 mixing ratios of 0.88 – 0.17 ppb and a relative humidity in the system of 5 - 15%. In their study H2SO4 from a liquid reservoir was used. Subject of this experimental study is the role of NH3 in the process of new particle formation starting from OH + SO2. A comparison with atmospheric measurements includes also recent results obtained in the absence of NH3 additions.

Results in absence of NH3

Influence of relative humidity

In agreement with former results, a distinct increase of total particle number with increasing rh. was observed for the measurements performed in absence of NH3. NH3 addition increased the total particle number by about one order of magnitude at rh. = 15%, by a factor of 3 – 5 at rh. = 22%, and by a factor of less than two at rh. = 47%. From mechanistic point of view it is highly speculative to explain this in a detailed manner. A possible reason could be the competing steps i) reaction of SO2 with 2 water molecules (or with the diiner) producing H2SO4 and ii) reaction of SO3 with NH3 producing sulfamic acid. Sulfinic acid can significantly contribute to particle formation and growth.

Application to the atmosphere

Laboratory: slope log N vs. log [H2SO4] = 1 - 2 (nearly independent on NH3 addition)

Figure 5: Total particle numbers vs. [H2SO4] concentration in absence of NH3 (1.2 - 2.5 ·1010 molecule cm−3) and presence of NH3 (1.2 - 1012 molecule cm−3), TSI 3025. The effective photolysis rate coefficient k4 was determined in each experiment measuring the O3 decay. With the knowledge of k4 the equation of the straight line measured in presence of NH3 was shifted by a constant factor. The effective photolysis rate coefficient k4 was determined in each experiment measuring the O3 decay. With the knowledge of k4 the equation of the straight line measured in presence of NH3 was shifted by a constant factor.

Figure 4a: Total particle numbers vs. [H2SO4] concentration in absence and presence of NH3 using TSI 3025 and PH-CPC. r.h. 22%, total flow rate: 3.33 standard litre min−1 (residence time in irradiated middle section: 290 sec).

Figure 4b: Size distributions measured in absence and presence of NH3 for [H2SO4] of 9·1010 molecule cm−3, c. 3 conditions as given in figure 4a.

Results in presence of NH3

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