Formation of atmospheric H_2SO_4 / H_2O particles in the absence of organics

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INTRODUCTION

Atmospheric particles have a strong impact on the Earth's radiation budget due to their radiative properties and the fact that they can act as condensation nuclei for clouds. Field measurements at ground level show atmospheric nucleation events for H_2SO_4 concentrations of $\sim 10^7$ molecule cm^{-3} (Weber *et al.*, 1999). Despite intensive research activities in the last decade, the mechanism leading to new particles has not been unambiguously revealed yet.

In a previous investigation from this laboratory, experimental evidence for the formation of new particles in the system H_2SO_4 / H_2O under near-atmospheric conditions with H_2SO_4 concentrations of $\sim 10^7$ molecule cm^{-3} was found (Berndt *et al.*, 2005). Here, H_2SO_4 was produced in situ via the reaction of OH radicals with SO_2 in the presence of water vapor. Similar observations are reported from investigations in the 590 m^3 Calspan chamber (Verheggen, 2004). In both studies organics were present in the reaction gas.

In contrast, taking H_2SO_4 from a liquid sample $\sim 10^{10}$ molecule cm^{-3} of H_2SO_4 are needed for producing new particles (Ball *et al.,* 1999).

Subject of this study is to investigate whether the low threshold H_2SO_4 concentration for nucleation of $\sim 10^7$ molecule cm^{-3} for in situ produced H_2SO_4 arises from any contributions of organic substances.

METHODS

The experiments have been performed in the *IfT*-LFT (*Institute for Tropospheric Research* – Laminar Flow Tube; i.d. 8 cm; length 505 cm) at atmospheric pressure and 293 ± 0.5 K using synthetic air as the carrier gas. Particle size distributions (dp > 2 nm) were determined using a differential mobility particle sizer (DMPS) consisting of a short Vienna-type differential mobility analyzer (DMA) and an ultrafine particle counter (UCPC, TSI 3025). From the measured mobility distributions, particle size distributions were determined using an inversion algorithm accounting for the counting efficiency of the UCPC, particle losses inside the DMA and the sampling lines connecting the outlet of the *IfT*-LFT to the DMPS system. In addition, the total number of particles was determined by a second UCPC (TSI 3025) directly at the outlet of the *IfT*-LFT.

H_2SO_4 was produced in situ via the reaction of OH radicals with SO_2. In most cases, photolysis of O_3 with the subsequent reaction of formed $O(^1D)$ with water served as source of OH radicals. Furan (organic) was added for OH radical titration. The measured furan decay allowed the calculation of the OH radical profile in the *IfT*-LFT and, consequently, the H_2SO_4 concentration. Simultaneous measurements of the furan and O_3 decay yielded a ratio "reacted O_3" / "reacted furan" = 0.5 ± 0.2 being in line with the fact that per "effective" photolyzed O_3 molecule two OH radicals were formed. Substituting furan by CO, i.e. removing the organics from the system, the H_2SO_4 concentrations in the tube were calculated using the measured O_3 decay.

In addition, in few experiments the needed OH radicals were produced via ozonolysis of *t*-butene (dark reaction).

RESULTS AND DISCUSSION

Figure 1 shows the experimental results for the different approaches for OH radical generation.
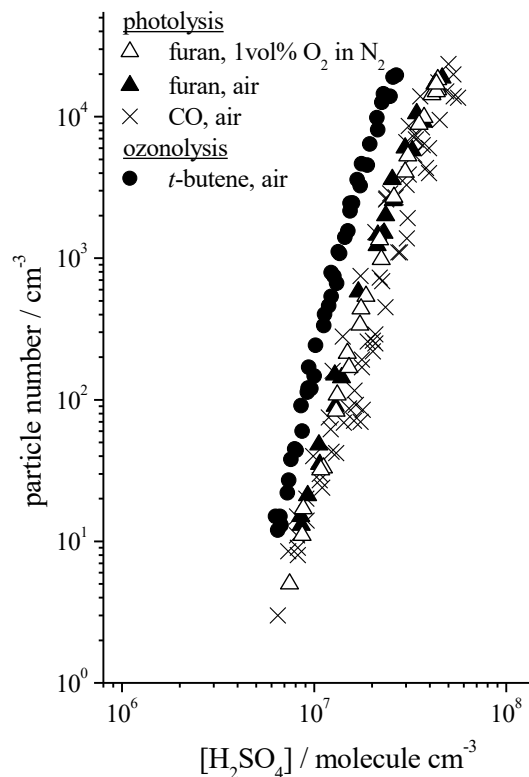

Figure 1. Observed particle numbers (TSI 3025) depending on H_2SO_4 concentration at 293 K and r.h. = 22 %.

For comparison, in Figure 1 a set of runs (O_3 photolysis in the presence of furan) using 1 vol% O_2 in N_2 as the carrier gas is also added. The findings reveal that the change of the O_2 concentration (1 vol% or 20 vol%) does not influence the particle formation. All four series of measurements consistently demonstrate that new particle formation starts for in situ produced H_2SO_4 concentrations of $\sim 7 \cdot 10^6$ molecule cm^{-3}. Therefore, it has to be concluded that organics are not implicitly needed for the process of particle formation under these conditions.

The H_2SO_4 values are affected with an uncertainty of a factor of ~ 2 caused by uncertainties of the measurements needed (reacted furan or O_3) or by the simplifications in the chemical mechanisms used for the calculation of H_2SO_4 concentrations. Differences between the four series among each other can be explained in the same way.

Experiments with enhanced H_2SO_4 concentrations allowed the determination of particle size distributions. Figure 2 shows DMPS measurements for three different H_2SO_4 concentrations at r.h. = 42 %.
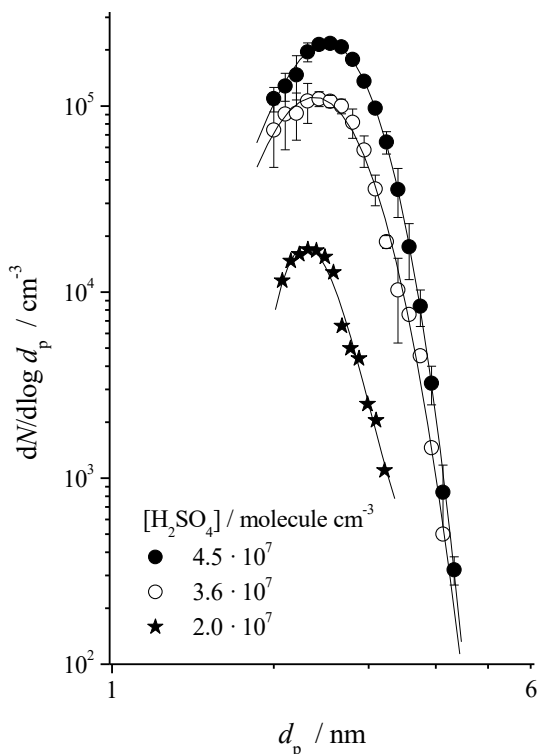

Figure 2. Particle size distributions (DMPS) for three different H_2SO_4 concentrations at r.h. = 42 %. Mean diameters of the particles are 2.5, 2.4, and 2.3 nm for H_2SO_4 concentrations of $4.5 \cdot 10^7$, $3.6 \cdot 10^7$, and $2.0 \cdot 10^7$ molecule cm^{-3}, respectively. OH radical formation via O_3 photolysis in the presence of CO.

Even for the highest H_2SO_4 concentrations, the mean particle diameter was below 3 nm. A particle diameter of ~ 2 nm for an H_2SO_4 concentration of 10^7 molecule cm^{-3} can be roughly estimated from the observed trend of decreasing particle diameter with decreasing H_2SO_4 concentration. Assuming that the particles consist of H_2SO_4 only (density: 1.85 g cm^{-3}), the upper limit of the yields of particulate H_2SO_4 formed from gaseous H_2SO_4 can be given. According to this, a yield of 0.9, 5, and 9 % was found for H_2SO_4 vapor concentrations of $2.0 \cdot 10^7$, $3.6 \cdot 10^7$, and $4.5 \cdot 10^7$ molecule cm^{-3}, respectively, cf. Figure 2.

The results from our DMPS measurements were confirmed by simultaneous runs using a Nano-SMPS system (TSI 3936-N86 with TSI 3786).

CONCLUSIONS

The results from this study show that the low threshold concentration for nucleation of $\sim 10^7$ molecule cm^{-3} in the case of in situ produced H_2SO_4 (from bulk sample $\sim 10^{10}$ molecule cm^{-3} of H_2SO_4) cannot be explained by a contribution of organics supporting the particle formation. Probably, in the course of the SO_2 oxidation ($SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$) other species than the expected H_2SO_4(-hydrates) are formed being responsible for particle formation. That is highly speculative at present and much more work is needed for clarifying the nucleation mechanism.

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