

# The overall process of new particle formation starting from OH + SO<sub>2</sub>

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**Abstract.** Nucleation experiments starting from the reaction of OH radicals with SO<sub>2</sub> have been performed in the *IJT-LFT* flow tube under atmospheric conditions at  $293 \pm 0.5$  K for a relative humidity of 5 - 64 %. Experimental data of measured particle numbers and derived nucleation rates were described by power law equations for “H<sub>2</sub>SO<sub>4</sub>” as well as for H<sub>2</sub>O vapour. “H<sub>2</sub>SO<sub>4</sub>” stands for all products from the reaction of OH radicals with SO<sub>2</sub>. Experimental conditions for new particle formation were chosen in such a way that the majority of nucleated particles could be detected with appropriate methods. At a constant relative humidity of 22 %, the exponent for “H<sub>2</sub>SO<sub>4</sub>” was found to be in the range of 1.58 - 2.03 for different measurement series. The overall best fit yielded an exponent of 1.76 for “H<sub>2</sub>SO<sub>4</sub>” and 1.54 for H<sub>2</sub>O vapour.

*Key Words:* Homogeneous nucleation; Tropospheric aerosol; Laminar flow tube

## INTRODUCTION

Simultaneous measurements of newly formed ultra-fine particles and H<sub>2</sub>SO<sub>4</sub> in the lower troposphere reveal that new particle formation is strongly connected to the occurrence of H<sub>2</sub>SO<sub>4</sub> with concentrations of about 10<sup>5</sup> - 10<sup>7</sup> molecule cm<sup>-3</sup> and the production rate of new particles can be described by a power law equation for H<sub>2</sub>SO<sub>4</sub> with an exponent in the range of 1 - 2 (Weber et al., 1996, Kulmala et al., 2006, Sihto et al., 2006).

From laboratory measurements a relatively wide range for the exponent of H<sub>2</sub>SO<sub>4</sub> (slope:  $\Delta \log(J) / \Delta \log([H_2SO_4])$ ) as well as for the H<sub>2</sub>SO<sub>4</sub> concentration needed for nucleation is reported. Using H<sub>2</sub>SO<sub>4</sub> from a liquid source, nucleation for different r.h. was detectable for concentrations above 10<sup>9</sup> - 10<sup>10</sup> molecule cm<sup>-3</sup> and the deduced

exponent of H<sub>2</sub>SO<sub>4</sub> ranged between 4 and 30 (Wyslouzil et al., 1991, Viisanen et al., 1997, Ball et al., 1999).

Experiments starting from the reaction of OH radicals with SO<sub>2</sub> for in-situ H<sub>2</sub>SO<sub>4</sub> formation by Young et al. (2008) yielded threshold H<sub>2</sub>SO<sub>4</sub> concentrations needed for nucleation of 10<sup>8</sup> - 10<sup>9</sup> molecule cm<sup>-3</sup> and the researchers concluded that the critical cluster contains 3 - 8 H<sub>2</sub>SO<sub>4</sub> molecules.

From our laboratory, however, using also the reaction of OH radicals with SO<sub>2</sub> for “H<sub>2</sub>SO<sub>4</sub>” formation (Berndt et al., 2005, 2008), experimental evidence for the formation of new particles was found for “H<sub>2</sub>SO<sub>4</sub>” concentrations of ~10<sup>7</sup> molecule cm<sup>-3</sup>. Here, “H<sub>2</sub>SO<sub>4</sub>” stands for all products arising from the reaction of OH radicals with SO<sub>2</sub>. The analysis of integral number measurements by means of commercially available UCPCs revealed that measured slopes of log(N) vs. log(“H<sub>2</sub>SO<sub>4</sub>”) were affected by the decreasing size-dependent counting efficiency of the UCPCs used for dp < 3nm leading to an overestimation of the slopes.

The aim of this study is to find out the optimal experimental conditions for the detection of the majority of nucleated particles with appropriate methods. Such data represent the basis for a reliable description of the overall process of nucleation in term of a power equation.

## Experimental

The nucleation experiments have been carried out in the atmospheric pressure flow-tube *I/T*-LFT (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K (Berndt et al., 2005, 2008). For integral particle measurements a butanol-based UCPC (TSI 3025), a H<sub>2</sub>O-based UCPC (TSI 3786) as well as a pulse height condensation particle counter (PH-CPC) have been used. In order to measure particle size distributions a differential mobility particle sizer (DMPS) consisting of a Vienna-type DMA and a butanol-based UCPC (TSI 3025) came into operation.

“H<sub>2</sub>SO<sub>4</sub>” (all SO<sub>2</sub> oxidation products) concentrations were calculated using a model according to the following reaction scheme (Berndt et al., 2005, 2008):

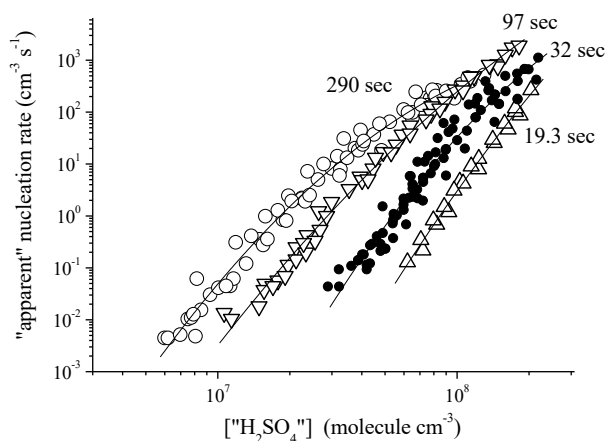


For measuring the H<sub>2</sub>SO<sub>4</sub> concentration (H<sub>2</sub>SO<sub>4</sub> represents the main fraction of “H<sub>2</sub>SO<sub>4</sub>”), the *I/T*-LFT was directly attached to a Chemical Ionization Mass spectrometer, CI-MS (Mauldin et al., 1998).

## RESULTS

The experimentally observed curves for particle number vs. [“H<sub>2</sub>SO<sub>4</sub>”] measured by means of a butanol-based UCPC (TSI 3025) showed a strong dependence on the residence time of the reaction gas in the flow tube. Scaling by time, reveals that also the

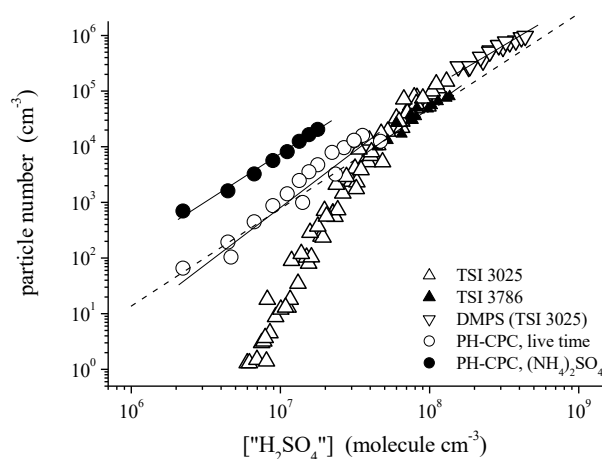
curves for nucleation rate vs. ["H<sub>2</sub>SO<sub>4</sub>"] are clearly dependent on the residence time, cf. Figure 1. It is obvious that the growth process (coupled with the size-dependent counting efficiency of the counter) governs the finally measured particle number. Consequently, the resulting nucleation rates represent only "apparent" values for J being clearly influenced by the growth process and the ability of the counter to detect small particles.



**Figure 1.** Apparent nucleation rate as a function of "H<sub>2</sub>SO<sub>4</sub>" concentration for different residence times in the *I/T*-LFT, r.h. = 22%, butanol-based UCPC (TSI 3025).

For a long residence time (290 sec), a relatively high concentrations of "H<sub>2</sub>SO<sub>4</sub>" (~10<sup>8</sup> molecule cm<sup>-3</sup>) and a mean particle diameter of ~3 nm (measured by DMPS) the majority of new particles was detectable by means of the butanol-based UCPC (TSI 3025).

In Figure 2 experimental data of measured particle numbers vs. ["H<sub>2</sub>SO<sub>4</sub>"] are depicted measured simultaneously by means of three different UCPCs (TSI 3025, TSI 3786, PH-CPC) as well as by DMPS (dp ≥ 3 nm). The *I/T*-LFT was operated with a residence time of 290 sec and r.h. = 22%.



**Figure 2.** Measured particle numbers as a function of "H<sub>2</sub>SO<sub>4</sub>" concentration at r.h. = 22 % for a residence time of 290 sec. The dashed line stands for the overall best fit.

The slopes  $\log(N)$  vs.  $\log([\text{H}_2\text{SO}_4])$  span a range of 1.58 - 2.03 (DMPS:  $1.58 \pm 0.05$ ; TSI 3786:  $1.91 \pm 0.11$ ; PH-CPC, live time:  $2.03 \pm 0.01$ ; PH-CPC,  $(\text{NH}_4)_2\text{SO}_4$ :  $1.70 \pm 0.06$ ).

In further experiments, for several fixed “ $\text{H}_2\text{SO}_4$ ” concentrations new particle formation was investigated as a function of relative humidity (or  $\text{H}_2\text{O}$  vapour concentration). Putting all measurements together, the overall best fit according to equation

$$N = k ([\text{H}_2\text{SO}_4] / \text{molecule cm}^{-3})^\alpha ([\text{H}_2\text{O}] / \text{molecule cm}^{-3})^\beta$$

yielded  $\alpha = 1.76 \pm 0.02$  and  $\beta = 1.54 \pm 0.04$ .

## CONCLUSIONS

The measured exponents of [ $\text{H}_2\text{SO}_4$ ], slopes  $\log(N)$  vs.  $\log([\text{H}_2\text{SO}_4])$ , span a range from 1.58 to 2.03. Constraining  $\alpha$  to an integer value, i.e.  $\alpha = 1$  or 2, a number of one or two “ $\text{H}_2\text{SO}_4$ ” molecules in the critical cluster follows if it is assumed that the nucleation step is rate limiting. The presence of one or two “ $\text{H}_2\text{SO}_4$ ” molecules in the critical cluster is in clear contradiction to the reported values from laboratory studies so far (Wyslouzil et al., 1991, Viisanen et al., 1997, Ball et al., 1999, Young et al., 2008). Note that in all of these laboratory studies, except Young et al., 2008,  $\text{H}_2\text{SO}_4$  was produced from evaporation from a liquid reservoir. The agreement of the exponent of [ $\text{H}_2\text{SO}_4$ ] from this study with those reported from observations in the atmosphere (Weber et al., 1996, Kulmala et al., 2006, Sihto et al., 2006), however, is very good.

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