OVERALL PROCESS OF NEW PARTICLE FORMATION INITIATED BY THE REACTION OH + SO$_2$

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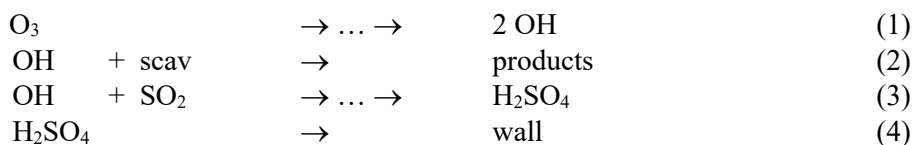Keywords: Nucleation, Sulphuric Acid, Kinetics.

INTRODUCTION

Simultaneous measurements of newly formed ultra-fine particles and H$_2$SO$_4$ in the lower troposphere reveal that new particle formation is strongly connected to the occurrence of H$_2$SO$_4$ with concentrations of about 10^5 - 10^7 molecule cm^{-3} and the production rate of new particles can be described by a power law equation for H$_2$SO$_4$ with an exponent in the range of 1 - 2 (Weber et al., 1996, Kulmala et al., 2006, Sihto et al., 2006). From our laboratory, using the reaction of OH radicals with SO$_2$ for H$_2$SO$_4$ formation (Berndt et al., 2005), experimental evidence for the formation of new particles was found for H$_2$SO$_4$ concentrations of ~10^7 molecule cm^{-3}. The analysis of integral number measurements by means of commercially available UCPCs revealed that measured slopes of log(N) vs. log([H$_2$SO$_4$]) were affected by the decreasing size-dependent counting efficiency of the UCPCs used for dp < 3 nm leading to an overestimation of the slopes.

Subject of this study are measurements of the formation rate of freshly nucleated particles by means of high-sensitivity counters with detection limits down to 1.5 nm in diameter. The influence of relative humidity as well as of ammonia on the nucleation rate is investigated.

METHODS

Experiments have been carried out in the atmospheric pressure flow-tube *IfT*-LFT (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K (Berndt et al., 2005). For integral particle measurements commercial UCPCs (TSI 3025 and TSI 3786) as well as a pulse height condensation particle counter (PH-CPC), Sipilä et al., 2008, and a mixing-type CPC (M-CPC), Vanhanen et al., 2009, came into operation. PH-CPC and M-CPC are able counting particles with a diameter of about 1.5 nm.

H$_2$SO$_4$ concentrations in the flow tube were calculated using a model according to the following reaction scheme (Berndt et al., 2005):

$$
\begin{array}{llll}
O_3 & \rightarrow \ldots \rightarrow & 2\,OH & (1) \\
OH + scav & \rightarrow & products & (2) \\
OH + SO_2 & \rightarrow \ldots \rightarrow & H_2SO_4 & (3) \\
H_2SO_4 & \rightarrow & wall & (4)
\end{array}
$$

CO, H$_2$ or mesitylene (1,3,5-trimethylbenzene) were chosen as OH radical scavenger "scav" in order to adjust atmospheric OH levels in the flow tube. For measuring the H$_2$SO$_4$ concentration, the outlet of *IfT*-LFT was directly attached to a Chemical Ionization Mass spectrometer. Measured H$_2$SO$_4$ concentrations were found to be in a good agreement with modelling results

CONCLUSIONS

Fig.1 shows experimental findings for different residence times at r.h. = 22%. Nucleation rates are obtained by dividing measured particle numbers by the bulk residence time in the reaction zone. Regression analysis of the whole data set yields for

$$J = k \, (\, [H_2SO_4]/\text{molecule cm}^{-3} \,)^{\alpha}$$

the parameters: $\alpha = 1.80$, $k = 1.3 \cdot 10^{-12}$ $cm^{-3}s^{-1}$ (full line in fig.1). Setting $\alpha = 2$ as a fixed parameter, $k = 4.2 \cdot 10^{-14}$ $cm^{-3}s^{-1}$ follows (dashed line in fig.1). The exponents α resulting from the individual measurement series are in the range 1.6 - 2.1. These parameters from the laboratory are very similar to those arising from analysis of ambient nucleation events.
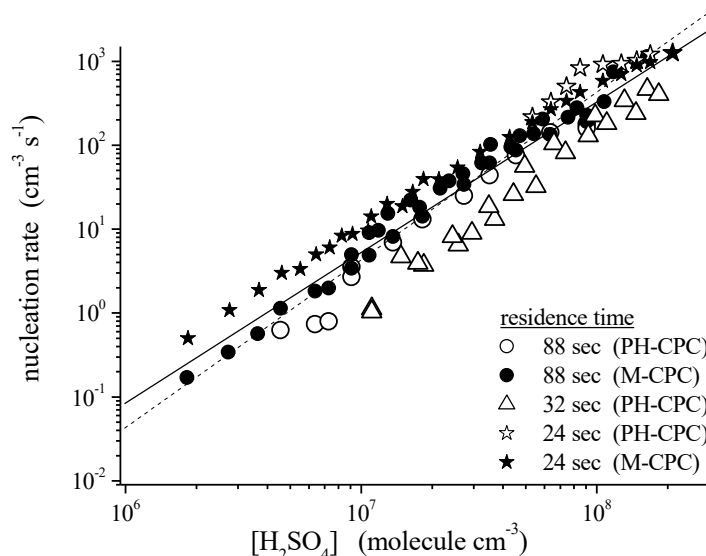

Fig.1. Nucleation rates as a function of sulphuric acid concentration for different residence times, r.h. = 22%.

For a residence time of 88 sec the relative humidity was varied in the range 22 - 61 %. With increasing r.h. there was a distinct increase of particle formation measureable. The overall best fit according to the power equation

$$N = k \, (\, [H_2SO_4]/\text{molecule cm}^{-3} \,)^{\alpha} \, (\, [H_2O]/ \, 10^{15}\text{molecule cm}^{-3} \,)^{\beta}$$

results in: $\alpha = 1.86$, $\beta = 3.08$, $k = 9.3 \cdot 10^{-18}$ cm^{-3}. It is to be noted, that the exponent for water vapour, $\beta = 3.08$, represents an upper limit caused by experimental difficulties for elevated r.h.

Measurements in the absence ($[NH_3] < 2.5 \cdot 10^9$ molecule cm^{-3}) and presence of ammonia ($[NH_3] = 1.2 \cdot 10^{12}$ molecule cm^{-3}) revealed that ammonia addition has generally a small effect on the nucleation rate. The enhancing effect is more pronounced for relatively dry conditions. A clear increase of particle diameter was observed in experiments with added ammonia.

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