

Mechanistic investigations on the formation of atmospheric H₂SO₄/H₂O particles

T. Berndt, O. Böge and F. Stratmann

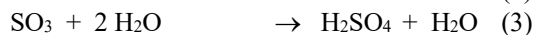
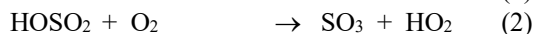
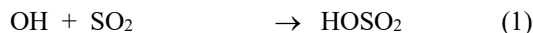
Leibniz-Institut für Troposphärenforschung e.V., Permoserstr. 15, 04318 Leipzig, Germany

Keywords: H₂SO₄, nucleation, particle formation.

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 H₂SO₄ 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 under near-atmospheric conditions was found with H₂SO₄ concentrations of $\sim 10^7$ molecule cm⁻³ (Berndt *et al.*, 2005). Here, H₂SO₄ was produced in situ via the reaction of OH radicals with SO₂ in the presence of water vapour. In contrast, taking H₂SO₄ from a liquid sample $\sim 10^{10}$ molecule cm⁻³ of H₂SO₄ are needed for producing new particles (Ball *et al.*, 1999).

In the atmosphere, the gas-phase oxidation of SO₂ is initiated by the attack of OH radicals. The following reaction sequence is currently accepted leading finally to H₂SO₄ vapour.



Subject of this study is to investigate the formation of new particles in the system H₂SO₄/H₂O starting either from OH + SO₂ or from SO₃ or taking H₂SO₄ vapour from a liquid H₂SO₄ sample.

The experiments have been performed in the *I/T-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 ($d_p > 2$ 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). Total particle numbers were measured by means of different types of UCPC's to be directly attached at the outlet of the *I/T-LFT*. In the case of in situ H₂SO₄ formation via OH + SO₂ the needed OH radicals were formed either by O₃ photolysis in the presence of water vapour or by ozonolysis of *t*-butene (dark reaction), c.f. (Berndt *et al.*, 2005). In experiments starting with SO₃, this species was produced outside the *I/T-LFT* in a pre-reactor oxidizing SO₂ in a

catalytic reaction on a Pt surface at 525°C. The conversion of SO₂ to SO₃ was followed by on-line UV spectroscopy. For experiments using H₂SO₄ vapour from a liquid sample, H₂SO₄ concentrations were measured at the outlet of the saturator by means of a denuder system with subsequent analysis of SO₄²⁻ ions by ion chromatography.

Figure 1 shows the experimental results using the different approaches for H₂SO₄ formation. Roughly the same behaviour is observed using SO₃ or starting with H₂SO₄ from a liquid sample. From these findings it can be speculated that in the course of SO₂ conversion to SO₃ via pathways (1) and (2) other, additional steps probably take place being important for the particle formation observed.

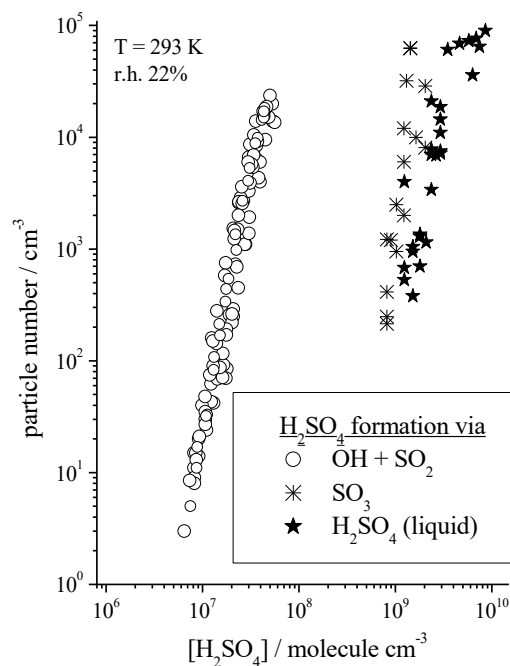


Figure 1. Measured particle numbers vs. H₂SO₄ concentration for different formation ways.

- Ball, S. M., Hanson, D. R., Eisele, F. L. & McMurry, P. H. (1999), *J. Geophys. Res.*, 104(D19), 1999JD900411, 23709-23718,
Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J. & Kulmala, M. (2005), *Science*, 307, 698-700.
Weber, R. J., McMurry, P. H., Mauldin III, R. L., Tanner, D. J., Eisele, F. L., Clarke, A. D. & Kapustin, V. N. (1999), *Geophys. Res. Lett.*, 26, 307-310.