

Atmospheric H₂SO₄ / H₂O Particle Formation: Mechanistic Investigations

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Abstract. The formation of H₂SO₄ / H₂O particles has been investigated in a laboratory study using a flow tube operated at atmospheric pressure. The needed H₂SO₄ vapour was produced in three different ways: i) in situ formation starting from OH + SO₂, ii) reaction of SO₃ with water vapour, iii) taking H₂SO₄ vapour from a liquid reservoir. The findings are discussed with respect to the mechanism of the formation of particle's precursors.

Key Words: atmospheric nucleation; H₂SO₄; mechanism

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 cloud condensation nuclei. Field measurements at ground level show atmospheric nucleation events for H₂SO₄ concentrations of $\sim 10^7$ molecule cm⁻³ (1). 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 our laboratory, experimental evidence for the formation of new particles in the system H₂SO₄ / H₂O under near-atmospheric conditions with H₂SO₄ concentrations of $\sim 10^7$ molecule cm⁻³ was found (2). Here, H₂SO₄ was produced in situ via the reaction OH + SO₂ in the presence of water vapour. Similar observations are reported from investigations in the 590 m³ Calspan chamber (3) as well as from another flow-tube experiment (4).

In contrast, taking H₂SO₄ from a liquid sample reservoir $\sim 10^{10}$ molecule cm⁻³ of H₂SO₄ are needed for significant new particle formation (5). This observation is roughly in line with the prediction from binary nucleation theory H₂SO₄ / H₂O (6).

Subject of this study are mechanistic investigations on H₂SO₄ / H₂O particle formation trying to explain the different threshold H₂SO₄ concentrations for nucleation, $\sim 10^7$ molecule cm⁻³ vs. $\sim 10^{10}$ molecule cm⁻³.

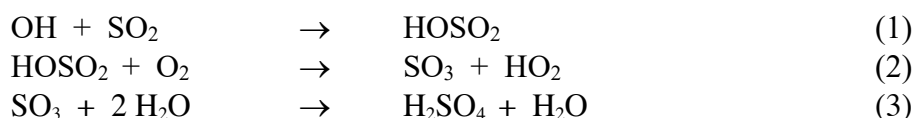
EXPERIMENTAL

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). 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. (2). Photolysis experiments were conducted using furan or CO for OH radical titration, i.e. conditions in the presence or absence of organic compound in the carrier gas. 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.

DISCUSSION

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



Produced HOSO₂ radicals from the primary reaction of OH radicals with SO₂ via pathway (1) react in a very fast consecutive reaction with O₂ leading to SO₃. For atmospheric reactant levels (OH: 2 · 10⁶; SO₂: 10¹¹; O₂: 5 · 10¹⁸; all in molecule cm⁻³) a steady state HOSO₂ concentration of 0.1 molecule cm⁻³ follows assuming that no other reactions of HOSO₂ can compete with pathway (2). SO₃ reacts with two water molecules or a water dimer producing finally H₂SO₄. This fast pathway results in the very low steady state SO₃ concentrations of ~1 molecule cm⁻³ in the atmosphere. And also here, other pathways for SO₃ conversion have to be of less importance. That means that each attacked SO₂ molecule from pathway (1) is transformed to H₂SO₄ in the atmosphere according to the scheme given above.

It is to be noted that in competition to pathway (2) also the addition of O₂ on HOSO₂ can take place leading to HOSO₂O₂.



An assessment of the importance of pathway (2a) for the conversion of HOSO₂ seems to be difficult because experimental data in the literature are sparse. *Stockwell* and *Calvert* (7) derived from a chamber experiment that less than 20% of HOSO₂ reacted via pathway (2a) and more than 80% via pathway (2). *Howard* (8) measured HOSO₂ and HO₂ simultaneously in a flow-tube experiment and found a lower limit of 70% for pathway (2).

If pathway (2a) plays a significant role for the fate of HOSO₂ radicals, less than one molecule H₂SO₄ per attacked SO₂ is formed and HOSO₂O₂ can initiate other reaction pathways not considered so far.

Figure 1 shows the experimental results using the different approaches for H₂SO₄ formation.

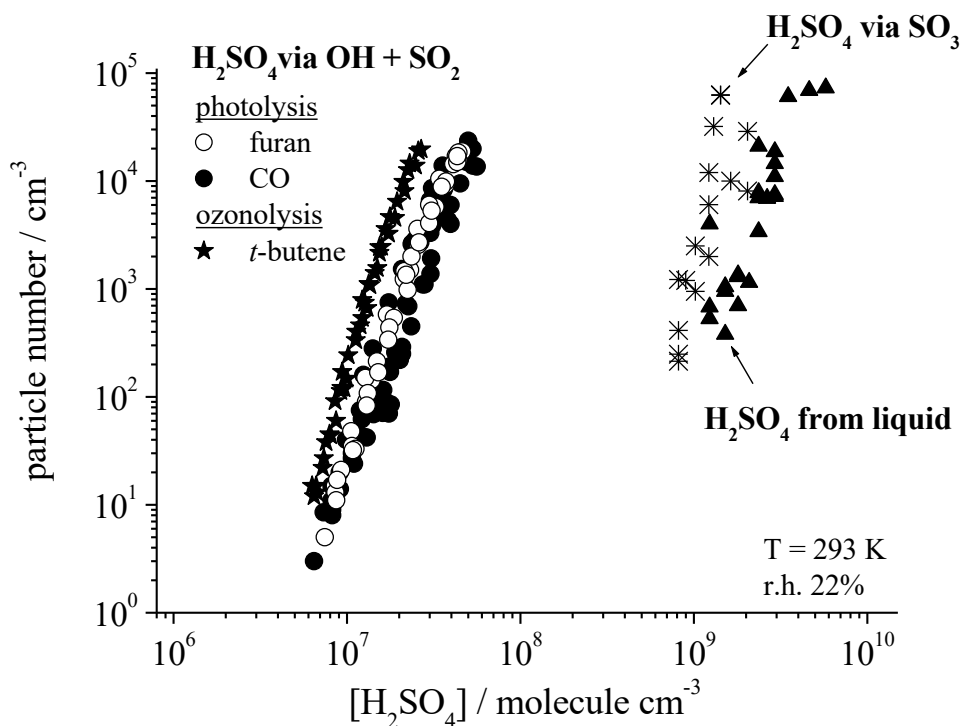


Figure 1. Measured particle numbers vs. H₂SO₄ concentration for different formation pathways.

Under conditions starting from OH + SO₂, all three series of measurements consistently demonstrate that new particle formation starts for H₂SO₄ concentrations of ~10⁷ molecule cm⁻³. Here, the small differences can be explained by uncertainties arising from different approaches for H₂SO₄ determination. On the other hand, using SO₃ or starting with H₂SO₄ from a liquid sample, H₂SO₄ concentrations of ~10⁹ molecule cm⁻³ are needed for particle formation.

From this behaviour it can be speculated that in the course of SO₂ conversion to SO₃ via pathways (1) and (2) other, additional steps may be important, for instance pathway (2a). The products of this other steps could trigger the particle formation observed for conditions starting from OH + SO₂.

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