The role of selected organics for atmospheric nucleation of H_2SO_4/H_2O particles

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Motivation

Mass balances of the atmospheric aerosol have been used for more than 30 years to identify potential human influence on climate. Crucial processes, on the other hand, are controlled by the number of aerosol particles such as cloud formation, possible even certain health effects. The source processes controlling the number of secondary particles are much more complex and difficult to understand than those of the primary particles.

Recently, the formation of new particles has been investigated in a laboratory study starting from H_2SO_4 produced in situ via the reaction of OH radicals with SO_2. Newly formed particles were observed for H_2SO_4 concentrations of about 10^7 cm^{-3} (Berndt *et al.*, 2005). Laboratory data on binary sulfuric acid nucleation with water using sulfuric acid from a liquid reservoir, however, indicate particle formation for H_2SO_4 concentrations of 10^{10} cm^{-3} or more (Ball *et al.*, 1999). To date, no definite mechanistic explanation for the different H_2SO_4 concentrations needed for particle formation can be given. In a recently published study, a distinct contribution of organics to particle formation was observed experimentally (Kalberer *et al.*, 2004).

Here, results from laboratory experiments are reported which were conducted in the **I**nstitute **f**or **T**ropospheric Research-**L**aminar **F**low **T**ube (IfT-LFT).

Fig. 1: The laminar flow tube, IfT-LFT

Experimental

The experiments have been performed in an atmospheric pressure flow-tube (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K (Fig. 1). The first tube section includes an inlet system for gas entrance. The middle section is equipped with 8 UV lamps for homogeneous irradiation of the tube. A non irradiated end section is attached with the sampling outlets. The analysis of the gas-phase species and the particles produced has been performed using on-line GC-FID with cryo-enrichment, a dew point sensor, an ultra-fine particle counter for integral particle measurements, and a differential mobility particle sizer for monitoring of size distributions. For O_3 measurements, an O_3 analyzer as well as UV spectroscopy (PerkinElmer) was used. The carrier gas consisted either of 99 vol% N_2 (99.9999999 %) and 1 vol% O_2 (99.9996 %) or synthetic air (99.9999999%). SO_2 was taken from a 1 ppmv calibration mixture. The total gas flow was 3.6 liter min^{-1} resulting in a bulk residence time of 420 sec. NH_3 concentrations in the experiments were below the detection limit of the AiRRmonia system ($3.5 \cdot 10^9 cm^{-3}$) being lower than atmospheric NH_3 mixing ratios over continents of 100 - 10000 pptv.

Results

The chosen pathways leading to H_2SO_4 are equal to those in the atmosphere. O_3 is photolyzed forming $O^1(D)$ atoms and the subsequent reaction with water vapor produces OH radicals. The OH radicals attack SO_2 and after the reaction with O_2, the adduct $HOSO_2$ yields SO_3 and HO_2. In the reaction of SO_3 with water vapor, two molecules of H_2O or one dimer of H_2O per molecule of SO_3 are needed, leading finally to H_2SO_4.

$$O_3 + h\nu \rightarrow O^1(D) + O_2$$
$$O^1(D) + H_2O \rightarrow 2\ OH$$
$$OH + HC\ (furan) \rightarrow products$$
$$OH + CO \rightarrow products$$
$$OH + SO_2 \rightarrow \ldots \rightarrow H_2SO_4$$
$$H_2SO_4 \rightarrow wall$$

A hydrocarbon (furan) was added for OH radical titration consuming more than 99% of produced OH radicals. From the amount of disappeared furan (measured by GC-FID) the H_2SO_4 concentration was calculated. Experiments have been conducted in synthetic air or with 1 vol% O_2 diluted in N_2.

In the next set of experiments, furan was substituted by CO. Here, the H_2SO_4 concentrations in the flow tube were determined measuring converted O_3 by means of UV spectroscopy.

Addition of selected carbonylic substances:

Using CO for OH radical titration, the impact of acetaldehyde (Fig. 4) and acetone (Fig. 5) on particle number and particle volume was investigated. The concentrations for both carbonylic substances used here exceed atmospheric levels.

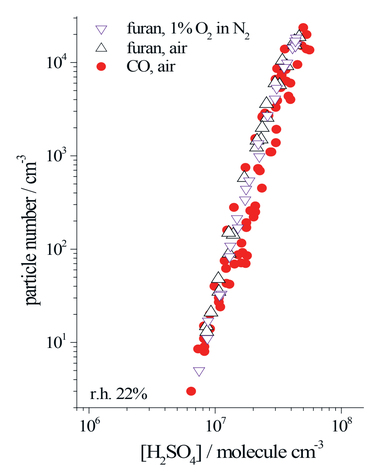

Fig. 2: Number of newly formed particles for different reaction conditions, Initial concentrations: [furan] : $1.0 \cdot 10^{12}$ cm^{-3}, [CO] : $(1.1\text{-}2.8) \cdot 10^{14}$ cm^{-3}, [SO_2] : $(1.2\text{-}7.4) \cdot 10^{10}$ cm^{-3}, [O_3] : $(1.1\text{-}4.0) \cdot 10^{11}$ cm^{-3}.

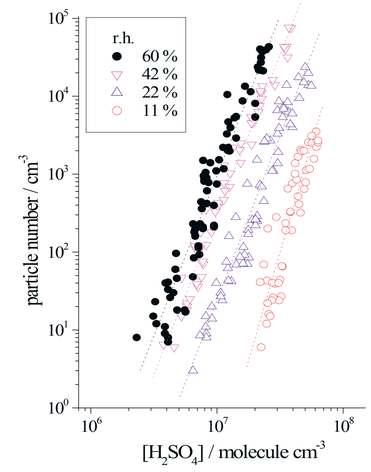

Fig. 3: Number of newly formed particles as a function of H_2SO_4 concentration, influence of relative humidity. [CO] : $1.1 \cdot 10^{14}$ cm^{-3}, [SO_2] : $(1.9\text{-}74) \cdot 10^9$ cm^{-3}, [O_3] : $(1.1\text{-}2.1) \cdot 10^{11}$ cm^{-3}.

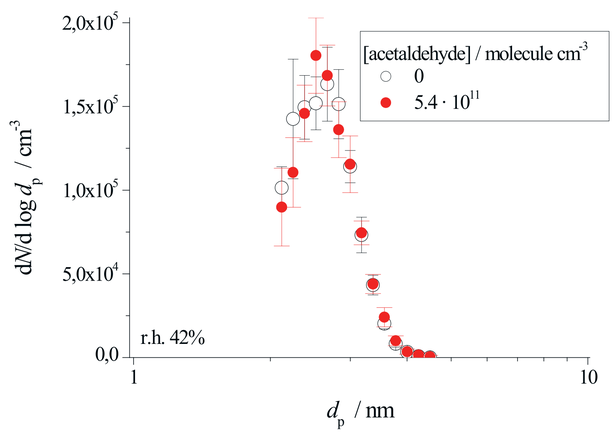

Fig. 4: Measured number size distributions in the absence and presence of additional acetaldehyde, calculated [H_2SO_4] : $3.9 \cdot 10^7$ cm^{-3}.

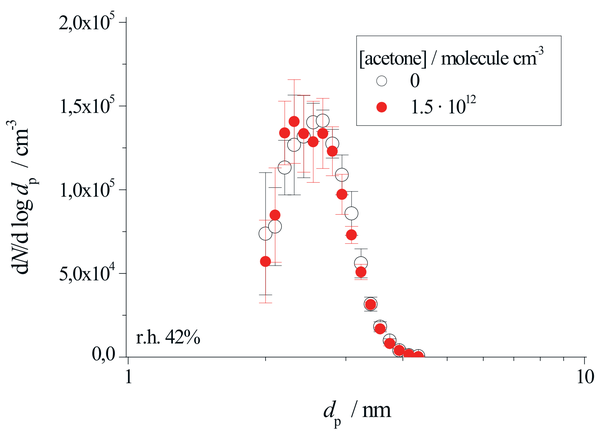

Fig. 5: Measured number size distributions in the absence and presence of additional acetone, calculated [H_2SO_4] : $3.4 \cdot 10^7$ cm^{-3}.

Summary and Conclusions

- → **No difference between experiments with furan and CO! Furan and its oxidation products do not influence particle formation!**
- → **No detectable impact of acetaldehyde and acetone on the number and volume of newly formed particles!**
- → **Detailed experiments on the influence of other atmospherical relevant organic compounds on particle formation and growth are urgently needed!**

References

Ball, S.M., Hanson, D.R., Eisele, F.L., McMurry, P.H. 1999. *J. Geophys. Res.,* 104, 23709-23718.
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Kalberer, M., Paulson, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U. 2004. *Science*, 303, 1659-1662.