**Atmospheric
Chemistry
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Discussions**

SO$_2$ oxidation products other than H$_2$SO$_4$ as a trigger of new particle formation – Part 1: Laboratory investigations

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Abstract

Mechanistic investigations of atmospheric H_2SO_4 particle formation have been performed in a laboratory study taking either H_2SO_4 from a liquid reservoir or using the gas-phase reaction of OH radicals with SO_2. Applying both approaches for H_2SO_4
5 generation simultaneously we found that H_2SO_4 evaporated from the liquid reservoir acts considerably less effective for the process of particle formation and growth than the products originating from the reaction of OH radicals with SO_2. Furthermore, for NO_x concentrations $>5\times10^{11}$ molecule cm^{-3} the formation of new particles from the reaction of OH radicals with SO_2 is inhibited. This suggests that substances other
10 than H_2SO_4 (likely products from sulphur-containing peroxy radicals) trigger lower tropospheric new particle formation and growth. The currently accepted mechanism for SO_2 gas-phase oxidation does not consider the formation of such substances making a revision necessary.

1 Introduction

15 For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intense studies in the field and in the laboratory. The formation mechanisms and the participating substances, however, have not been resolved yet (Kulmala, 2003). Large discrepancies between model-predicted nucleation rates for the favoured binary system H_2SO_4/H_2O and much higher atmospheric nucleation data
20 were explained by various supportive additional participants such as ammonia (Kulmala et al., 2000), organic molecules (Yu et al., 1999; Hoffmann et al., 1998) or ions (Lee et al., 2003; Lovejoy et al., 2004).

In a previous investigation of our laboratory under near-atmospheric conditions, experimental evidence for the formation of new particles in the system H_2SO_4/H_2O was
25 found for H_2SO_4 concentrations of $\sim10^7$ molecule cm^{-3} if "H_2SO_4" was produced in-situ via the reaction of OH radicals with SO_2 ("H_2SO_4" here stands for all products of

converted SO$_2$). As the OH radical source served UV-photolysis of O$_3$ or ozonolysis of alkenes in a dark reaction. The experiments have been performed in the presence and absence of organics. No clear difference concerning new particle formation was observed using the different experimental conditions (presence or absence of UV light, presence and absence of organics) pointing clearly at the SO$_2$ oxidation products ("H$_2$SO$_4$") being the exclusive precursors for the newly formed particles observed (Berndt et al., 2004, 2005, 2006). A significant increase of the nucleation rate for increasing r.h. was measurable (Berndt et al., 2005, 2006). Similar observations are reported from another flow-tube experiment (Friend et al., 1980) as well as from investigations in a chamber (Burkholder et al., 2007). In contrast, taking H$_2$SO$_4$ from a liquid reservoir concentrations of 10^9–10^{10} molecule cm^{-3} are needed for new particle formation (Ball et al., 1999, Zhang et al., 2004). This observation is roughly in line with the prediction from the binary nucleation theory H$_2$SO$_4$/H$_2$O (Kulmala et al., 1998).

In this study mechanistic investigations on H$_2$SO$_4$/H$_2$O particle formation are reported explaining the different threshold H$_2$SO$_4$ concentrations needed for nucleation, i.e., $\sim 10^7$ molecule cm^{-3} ("H$_2$SO$_4$" produced via gas-phase reaction of OH radicals with SO$_2$) vs. 10^9–10^{10} molecule cm^{-3} (H$_2$SO$_4$ via evaporation from a liquid reservoir).

2 Experimental

The experiments have been performed in the atmospheric pressure flow-tube *IfT*-LFT (i.d. 8 cm; length 505 cm) at 293±0.5 K. The first tube section (56 cm) includes an inlet system for gas entrance (humidified air premixed with SO$_2$, O$_3$, NO or hydrocarbons or H$_2$SO$_4$ vapour from a liquid reservoir premixed in dry air). The middle section (344 cm) is equipped with 8 UV lamps (Hg-lamps made of quartz-glass PN235 with a cut-off wavelength of 210 nm) for a homogeneous irradiation of the tube if needed. A non-irradiated end section (105 cm), which also holds the sampling outlet, is attached.

Gas-phase analysis was carried out using a GC-FID (HP 5890) with a cryo-enrichment unit for hydrocarbons, a humidity sensor (Vaisala), analyzers for O$_3$, SO$_2$,

and NO_x (Thermo Environmental Instruments: 49C, 43C, and 42S), a butanol-based UCPC (TSI 3025) as well as a H_2O-based UCPC (TSI 3786) for integral particle measurements, and a differential mobility particle sizer (Vienna-type DMA with UCPC, TSI 3025) for monitoring of size distributions.

5   The carrier gas consisted of synthetic air (99.9999999%, Linde and further purification with Gate Keeper, AERONEX). A small part of the total gas flow was flushed through an ozone generator (UVP OG-2) for O_3 generation outside the flow tube. SO_2 was taken from a 1ppmv or 10ppmv calibration mixture in N_2 (Messer) and NO from 0.5 vol% mixture in N_2 (Messer). In the case of experiments with H_2SO_4 vapour from a
10 liquid reservoir a part of the total gas stream of dry air was flushed through a saturator (maintained at 288 K) filled with concentrated sulphuric acid (95–98%, Aldrich). The outlet tube of the saturator served directly as the inlet for the H_2SO_4 vapour containing gas stream. In the first tube section this H_2SO_4 gas stream was brought together with humidified air.

15 The total gas flow inside the *IfT*-LFT was set at 3.33, 10, 20, or 30 standard litre min^{-1} resulting in a bulk residence time (middle and end section) of 378, 126, 63, or 42 sec., respectively. It is to be noted that the given bulk residence time stands for the upper limit of the nucleation time in the flow tube. All gas flows were set by means of calibrated gas flow controllers (MKS 1259/1179) and the pressure in the tube was
20 measured using a capacitive manometer (Baratron).

2.1 Determination of H_2SO_4 taken from a liquid reservoir

For experiments using H_2SO_4 vapour from a liquid reservoir, H_2SO_4 concentrations were measured at the outlet of the saturator by means of a denuder system (Amanda, ECN). The working fluid was a 10^{-4} M NaOH solution of de-ionised water and sampling
25 times were in the range of 2–10 h. The subsequent analysis of SO_4^{2-} ions has been done by means of ion chromatography (761 compact IC, Metrohm).

2.2 Determination of "H$_2$SO$_4$"(products of converted SO$_2$) and OH concentrations

Starting from the reaction of OH radicals with SO$_2$ "H$_2$SO$_4$" concentrations were calculated using a model according to the following reaction scheme used in the case of photolysis experiments (Berndt et al., 2005, 2006):

$$O_3 \rightarrow 2\ OH \tag{1}$$

$$OH + furan/CO \rightarrow products \tag{2}$$

$$OH + SO_2 \rightarrow \ldots \rightarrow \text{"H}_2\text{SO}_4\text{"} \tag{3}$$

$$\text{"H}_2\text{SO}_4\text{"} \rightarrow wall \tag{4}$$

The effective photolysis rate coefficient k_1 was determined in each experiment measuring the O$_3$ decay. Rate coefficients $k_{2,\text{furan}}$=4.0×10^{-11} cm^3 molecule^{-1} s^{-1}, $k_{2,\text{CO}}$=2.4×10^{-13} cm^3 molecule^{-1} s^{-1}, and k_3=1.2×10^{-12} cm^3 molecule^{-1} s^{-1}, were taken from literature (Finlayson-Pitts and Pitts, 2000, and references therein). For description of the assumed, diffusion controlled wall loss of "H$_2$SO$_4$", k_4=0.017 s^{-1}, the same data as for H$_2$SO$_4$ were taken (Hanson and Eisele, 2000). The concentration of furan (or CO) was chosen such that $k_{2,\text{furan}}$×[furan]>20 s^{-1} ($k_{2,\text{furan}}$×[furan] $\sim k_{2,\text{CO}}$×[CO]) was fulfilled. Modelling studies showed that under these conditions the reactions of OH radicals with O$_3$, HO$_2$ or any impurities (impurity concentration $\leq$10^{10} molecule cm^{-3}, $k_{\text{OH+impurity}}$=10^{-10} cm^3 molecule^{-1} s^{-1}) as well as the wall loss of OH radicals were negligible allowing also the determination of OH radicals from the measured amount of reacted furan. The ratio "reacted O$_3$"/"reacted furan" was experimentally found to be 0.5±0.2 as expected from the simple reaction scheme given above. This finding confirms that OH radical concentration, and consequently the "H$_2$SO$_4$" concentrations, are well described by the model applied. For normally used initial reaction conditions (O$_3$: ~1.5×10^{11} with a conversion <25%, furan: 6.2×10^{11}

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with a conversion $\leq 6\%$ or CO: 1.0×10^{14} with a conversion $<1\%$ and SO_2: $(6.7–350) \times 10^{10}$ with a conversion $<2.5\%$; concentration unit: molecule cm^{-3}) and measured effective photolysis rate coefficient k_1 in the order of 10^{-3} s^{-1}, modelling of the reaction system yielded OH radical concentrations of about 10^7 molecule cm^{-3} being close to atmospheric levels. Given "H_2SO_4" concentrations in figures and explanations represent averaged values for the irradiated middle section.

In the case of added NO_x in the carrier gas, NO and NO_2 can undergo reactions with O_3 and OH radicals. An additional pathway for OH radical generation represents the reaction of NO with HO_2 forming OH and NO_2. Therefore, OH radical concentrations were determined experimentally using the titration procedure with furan. The OH profile in the tube was calculated from the measured furan decay assuming an exponential function for the overall decay of O_3 and for the decay of furan. With the knowledge of the axial OH radical profile "H_2SO_4" concentration according to pathways (3) and (4) were calculated. Given "H_2SO_4" concentrations represent also averaged values for the irradiated middle section.

3 Results and Discussion

3.1 Measurement of consumed SO_2

It was attempted to measure the amount of consumed SO_2 to evaluate the reliability of calculated "H_2SO_4" concentrations via pathways (1)–(4). In Fig. 1 the temporal behaviour of SO_2 concentration and particle number for an experiment with CO for OH radical titration is given. SO_2 measurement using Thermo Environmental Instruments 43C in the absence of OH radicals (UV off) yielded: $(6.78\pm0.24) \times 10^{10}$ molecule cm^{-3} (full line) and in the presence of OH radicals (UV on): $(6.63\pm0.24) \times 10^{10}$ molecule cm^{-3} (dashed line) resulting in a SO_2 consumption of 1.5×10^9 molecule cm^{-3} with an uncertainty by a factor of ~2.3. Modelling of this example (including wall loss for "H_2SO_4")

shows an average "H_2SO_4" concentration in the tube of 2.46×10^8 molecule cm^{-3} and a SO_2 consumption of 1.46×10^9 molecule cm^{-3}. Simulated and measured SO_2 consumption are in good agreement. The particle number exceeded the counting range of the TSI 3025 (particle number $>10^5$ cm^{-3}). Integration of simultaneously performed size distribution measurement yielded a particle number of 3.6×10^5 cm^{-3}.

The determination of reacted SO_2 stands for a complementary measure of "H_2SO_4" and the good agreement between measured and calculated SO_2 conversion shows explicitly that the "true" concentration of "H_2SO_4" in the experiment cannot exceed the modelling data considerably.

3.1.1 New particle formation in the presence of in-situ produced "H_2SO_4" and H_2SO_4 from a liquid reservoir

In a first set of experiments in-situ formation of "H_2SO_4" via OH+SO_2 was coupled with evaporation of H_2SO_4 from the liquid reservoir as background in order to investigate the role of H_2SO_4 for the new particle formation and growth process. Initial H_2SO_4 concentration from the liquid reservoir was $(1–2) \times 10^9$ molecule cm^{-3}, i.e., close to the threshold concentration needed for binary H_2SO_4/H_2O nucleation in our experiment. The bulk residence time in the reaction zone (irradiated section) was 97 s and the end-H_2SO_4 concentration (from liquid reservoir) was estimated to be $(2–4) \times 10^8$ molecule cm^{-3} considering diffusion controlled wall loss only (Hanson and Eisele, 2000). In Fig. 2 results from a typical measurement are depicted. After turning on the flow through the H_2SO_4-saturator, a small increase of particle number above the noise level was visible with a subsequent slight rise up to 2–3 particles cm^{-3} after more than 5 h on stream. These particles are due to binary nucleation of H_2SO_4/H_2O (Kulmala et al., 1998). The particle number was not affected by the presence of O_3 and the photolysis products (OH radicals, HO_2, and H_2O_2) after switching on UV irradiation. With addition of SO_2 (time=235 min), in-situ particle precursor formation in the gas phase started and a constant particle number of 5×10^4 cm^{-3} was observed for in-situ "H_2SO_4" concentration

of 2.3×10^8 molecule cm^{-3}. Immediately after switching off UV (time=330 min), particle number went down to the level being attributed to binary H_2SO_4/H_2O nucleation. At 360 min the supply of H_2SO_4 from the liquid reservoir was stopped resulting in a decrease of particle number down to background noise level. Switching on UV, i.e.,
5 restarting the in-situ "H_2SO_4" production without background H_2SO_4, led to a particle number of 5×10^4 cm^{-3} again. This behaviour is a strong indication that H_2SO_4 from the liquid reservoir (now absent) did not participate in the nucleation process. To illustrate the influence of background H_2SO_4 on particle growth, Fig. 3 shows measured size distributions in the diameter range d=2–4 nm recorded in the time period 275 to
10 325 min (presence of background H_2SO_4) and between 410 and 460 min (absence of background H_2SO_4). To make sure that the measurements were not affected by memory effects, after a 3 day flushing of the flow tube with clean air, the experiment without background H_2SO_4 from the liquid reservoir was repeated. Figure 3 shows that the three measured size distributions are nearly identical. This indicates that H_2SO_4 from
15 the liquid reservoir, its concentration being at least in the same order or one order of magnitude higher compared to that of in-situ produced "H_2SO_4" (cf. Fig. 4), does not significantly contribute to particle growth. Obviously, condensational growth by H_2SO_4 evaporated from the liquid reservoir is of less importance under the chosen conditions and cannot be resolved. A kinetically limited collision model assuming H_2SO_4-like
20 substances as the particle precursor (probably products of $HOSO_2O_2$, see later) can roughly describe particle growth into the size range measured.

It is to be noted that integration of the size distributions ($d \geq 2$ nm) given in Fig. 3 yielded a particle number of $\sim 5 \times 10^3$ cm^{-3}, i.e., 1/10 of the total number found in the integral measurement using the UCPC. Therefore, the majority of produced particles
25 in this example were smaller than 2 nm in diameter.

To get an rough estimate concerning the H_2SO_4/"H_2SO_4" mass balance it is assumed i) that H_2SO_4 is the exclusive product from the reaction of OH radicals with SO_2 and ii) that the particles consist of H_2SO_4 (density of 1.85 g cm^{-3}) only, i.e., contributions of water to particle mass are neglected. For the example described above

(assuming 5×10^3 particle with $d = 2$ nm and 4.5×10^4 particle cm^{-3} with $d = 1.5$ nm) it follows that about 0.5% of gas phase H_2SO_4/"H_2SO_4''" can attributed to the newly formed particles.

Experiments, during which OH radicals were produced via ozonolysis of *trans*-
5 butene (dark reaction) yielded similar results.

These findings pose the question, why H_2SO_4 from the liquid reservoir exhibits a totally different behaviour (no clear contribution to particle formation and growth) compared to in-situ produced "H_2SO_4"? A possible reason could be that H_2SO_4 is not the particle precursor produced from the reaction of OH radicals with SO_2.

10 The currently accepted mechanism of atmospheric SO_2 gas-phase oxidation initiated by OH radicals is as follows (Finlayson-Pitts and Pitts, 2000, and references therein):

$$OH + SO_2 \rightarrow HOSO_2 \tag{5}$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \tag{6}$$

$$SO_3 + 2\,H_2O \rightarrow H_2SO_4 + H_2O \tag{7}$$

15 Here, $HOSO_2$ radicals produced from the primary reaction of OH radicals with SO_2 via pathway (5) react in the very fast consecutive step (6) with O_2 forming SO_3. SO_3 reacts with two water molecules or a water dimer producing H_2SO_4. According to this scheme, each attacked SO_2 molecule from pathway (5) is transformed to a H_2SO_4 molecule.

20 As a result of their pioneering work in the eighties, Stockwell and Calvert (1983) found that pathway (6) has to be important for the atmospheric fate of $HOSO_2$ as via this reaction more than 80% of $HOSO_2$ regenerates HO_2. However, an earlier way of thinking was based on a different pathway (6a) which considered the addition of O_2 to $HOSO_2$:

25 $$HOSO_2 + O_2 + M \rightarrow HOSO_2O_2 + M \tag{6a}$$

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Pathway (6) represents an endothermic reaction whereas pathway (6a) is exothermic (Benson, 1978, Majumdar et al., 2000), i.e., pathway (6a) is the thermodynamically favoured one. From the pressure-dependence of the kinetics of the HOSO$_2$+O$_2$ reaction, it was concluded that pathway (6a) accounts for <10% of the HOSO$_2$ removal (Gleason et al., 1987). Simultaneous measurements of HO$_2$ and HOSO$_2$ concentrations yielded a lower limit of 70% for pathway (6) (Howard, 1985). Taking all experimental findings into consideration, up to 30% of HOSO$_2$ can be converted to HOSO$_2$O$_2$.

It should be noted that a reduction of H$_2$SO$_4$ formation from SO$_2$ oxidation due to pathway (6a) is within the measurement uncertainty of the CIMS instruments (chemical ionization mass spectrometry) applied in laboratory and field measurements (Lovejoy et al., 1996).

HOSO$_2$O$_2$ is a peroxy-type radical and, analogous to organic peroxy radicals, it can react with HO$_2$, other peroxy radicals or with NO and NO$_2$ (Finlayson-Pitts and Pitts, 2000, and references therein). Also the reaction of HOSO$_2$O$_2$ or its hydrated species HOSO$_2$O$_2$(H$_2$O)$_n$ with SO$_2$ is imaginable (Wayne, 1991). If the reaction of HOSO$_2$O$_2$ with HO$_2$

$$HOSO_2O_2 + HO_2 \rightarrow HOSO_2O_2H + O_2 \qquad (8)$$

and/or with other peroxy radicals (RO$_2$)

$$HOSO_2O_2 + RO_2 \rightarrow products \qquad (9)$$

and/or with SO$_2$

$$HOSO_2O_2 + SO_2 \rightarrow HOSO_2OSO_3 \qquad (10)$$

is responsible for the formation of particle precursors, addition of NO and/or NO$_2$ should reduce or inhibit new particle formation as a part of the available HOSO$_2$O$_2$ will be consumed by NO and/or NO$_2$. (For simplification pathway (10) is written without hydration.)

3.1.2 New particle formation in the presence of NO/NO$_2$

New particle formation in the presence of NO/NO$_2$ using in-situ produced "H$_2$SO$_4$"

⁵ To test the hypothesis that HOSO$_2$O$_2$ is a possible precursor for the nucleating species and that in the presence of NO and/or NO$_2$ new particle formation is inhibited, experiments were carried out, with NO$_x$ (NO+NO$_2$) being present in the carrier gas. In this context it should be noted that generally NO and NO$_2$ can undergo reactions with O$_3$, OH radicals, HO$_2$ and other RO$_2$ radicals influencing the OH radical level
¹⁰ significantly. Therefore, to determine the in-situ produced "H$_2$SO$_4$" concentration, OH radical titration with furan was applied during this set of experiments. Figure 5, as an example, shows the results of measurements performed for different initial NO concentrations. In the course of the overall reaction, NO was significantly converted to NO$_2$, e.g., for the lowest initial NO concentration, 32% of NO reacted to NO$_2$. It
¹⁵ is clearly seen that with increasing amounts of NO$_x$ being present in the reaction gas, new particle formation is inhibited. Similar observations were made for relative humidities in the range 10–60 % or using NO$_2$ instead of NO. As a net inhibition of new particle formation is observed, the products from the NO$_x$ reactions, if important at all, have to be less effective particle precursors than the products from the reaction with
²⁰ HO$_2$ and/or other peroxy radicals or with SO$_2$ via pathways (8), (9) or (10), respectively. NO$_x$ cannot effect H$_2$SO$_4$ formation as described by pathways (5)–(7) because the HOSO$_2$ life-time regarding the O$_2$ reaction, pathway (6), as well as the SO$_3$ life-time regarding hydrolysis, pathway (7), are much shorter than those resulting from the corresponding NO$_x$ reactions (A more detailed explanation is given in Appendix A).
²⁵

New particle formation in the presence of NO/NO$_2$ using H$_2$SO$_4$ from the liquid reservoir

Furthermore, the influence of NO_x ($NO+NO_2$) for the process of new particle formation was studied using H_2SO_4 from the liquid reservoir. Figure 6 shows the temporal behaviour of O_3 concentration and the particle number for an experiment using an initial H_2SO_4 concentration (from the liquid reservoir) of $\sim 5\times10^9$ molecule cm^{-3}. After turning on the flow through the H_2SO_4-saturator a slightly increasing particle number was observed for the whole time on stream. At 55 min NO with a concentration of 4.1×10^{12} molecule cm^{-3} was added and after turning on the external O_3 generation (O_3: 1.5×10^{11} molecule cm^{-3}) NO was partly converted to NO_2 with an end concentration of $\sim 1.1\times10^{11}$ molecule cm^{-3}, $O_3+NO\rightarrow NO_2+O_2$. Switching on UV lamps at 175 min OH radical formation started and beside OH radicals, HO_2 and H_2O_2 also HONO and HNO_3 were produced. After turning off the NO flow (time: 205 min) only the O_3 photolysis products (OH radicals, HO_2 and H_2O_2) remained. Under all conditions investigated, especially for NO_x addition, no impact of added trace gases on the number of newly formed particles was visible. The absence of a NO_x dependence on the number of new particles is a clear disagreement regarding the findings using in-situ produced "H_2SO_4". Consequently, these results represent a further indication that reaction products of SO_2 oxidation other than H_2SO_4 (most likely products of sulphur-containing peroxy-type radicals like $HOSO_2O_2$) represent possible particle precursors.

4 Summary and conclusions

It was pointed out that, under lower tropospheric conditions, H_2SO_4 evaporated from a liquid reservoir did not significantly participate in the formation and growth of particles formed from the gas phase reaction of OH radicals with SO_2. Furthermore, it was shown that for NO_x concentrations $>5\times10^{11}$ molecule cm^{-3} the formation of new particles from the reaction of OH radicals with SO_2 is inhibited. This behaviour is not in line with the currently accepted reaction mechanism describing an equal-molar formation of H_2SO_4 from SO_2. It is therefore suggested that in the course of SO_2 con-

version, sulphur-containing peroxy radicals like $HOSO_2O_2$ can be formed in substantial fractions leading to products being different from H_2SO_4. It might be speculated, that under lower tropospheric conditions, $HOSO_2O_2$ could react with HO_2 and other peroxy radicals (including the self-reaction). These reactions, being of the RO_2+RO_2 type, could result in low vapour pressure particle precursors. If, e.g., $HOSO_2O_2$ reacts with HO_2 (the most abundant RO_2 radical in atmosphere), peroxo sulphuric acid is formed. Peroxo sulphuric acid is a hydrophilic solid, which in the liquid phase (in water) is converted to sulphuric acid and H_2O_2 (Kolditz, 1983). Another idea for particle formation starting from $HOSO_2O_2$ is given by Wayne (1991) describing the reaction of hydrated $HOSO_2O_2$ ($HOSO_2O_2(H_2O)_n$) with SO_2 producing $HOSO_2O(H_2O)_nSO_3$. For large "n" these hydrated radicals are regarded as aerosol particles (or at least as precursors). These scenarios, however, are highly speculative at the moment.

In conclusion, this study shows, that it is not necessarily sulphuric acid triggering atmospheric new particle formation and growth and that other compounds (like peroxo sulphuric acid or $HOSO_2O(H_2O)_nSO_3$ radicals) formed during the gas phase reaction of OH radicals with SO_2 may play an important role.

In a second part a comparison of ambient and laboratory measurements are given and the atmospheric implications are discussed (Laaksonen et al., 2008).

Appendix A

Atmospheric life-times of $HOSO_2$ and SO_3

Assuming a concentration of 10^{12} molecule cm^{-3} for NO and NO_2 each, a $HOSO_2$ life-time regarding NO reaction of >2 s (Martin et al., 1986) and regarding NO_2 reaction of >10 milliseconds (assuming an upper limit for the rate coefficient of 10^{-10} cm^3 molecule^{-1} s^{-1}) follows. A comparison with the life-time regarding the overall O_2 reaction via pathway (6) of $\sim$0.5 microseconds (Gleason et al., 1987) shows clearly that NO and NO_2 cannot influence the conversion of $HOSO_2$ via pathways (6) and (6a).

Assuming for the reaction of SO_3 with NO and NO_2 the rate coefficient measured for the NO_2 reaction (Penzhorn and Canosa, 1983), the SO_3 life-times regarding the NO and NO_2 reaction are in the order of 80 days. That means that also the hydrolysis of SO_3 via pathway (7) (with a life-time of $\sim$20 microseconds assuming a H_2O concentration of 3×10^{17} molecule cm^{-3}; Jayne et al., 1997) cannot be affected by NO and NO_2. Consequently, NO and NO_2 for the concentrations considered here, cannot affect H_2SO_4 formation via pathways (5)–(7).

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Interactive Discussion
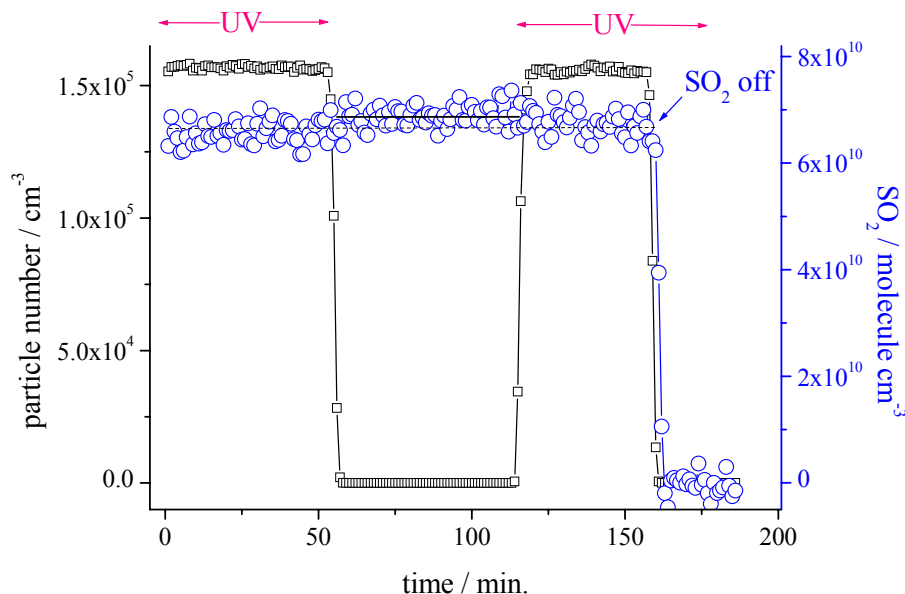
Fig. 1. Temporal behaviour of SO$_2$ concentration and particle number for an experiment with "H$_2$SO$_4$" formation from the reaction of OH radicals with SO$_2$ using CO for OH radical titration, r.h.=22%, gas flow: 3.33 sl min^{-1}. Initial concentrations were (unit: molecule cm^{-3}); O$_3$: 3.8×10^{11}; CO: 5.3×10^{13}. SO$_2$ concentration in the absence of OH radicals (UV off): (6.78±0.24)×10^{10} molecule cm^{-3} (full line) and in the presence of OH radicals (UV on): (6.63±0.24)×10^{10} molecule cm^{-3} (dashed line) results in a SO$_2$ consumption of 1.5×10^9 molecule cm^{-3} (uncertainty by a factor of ~2.3).
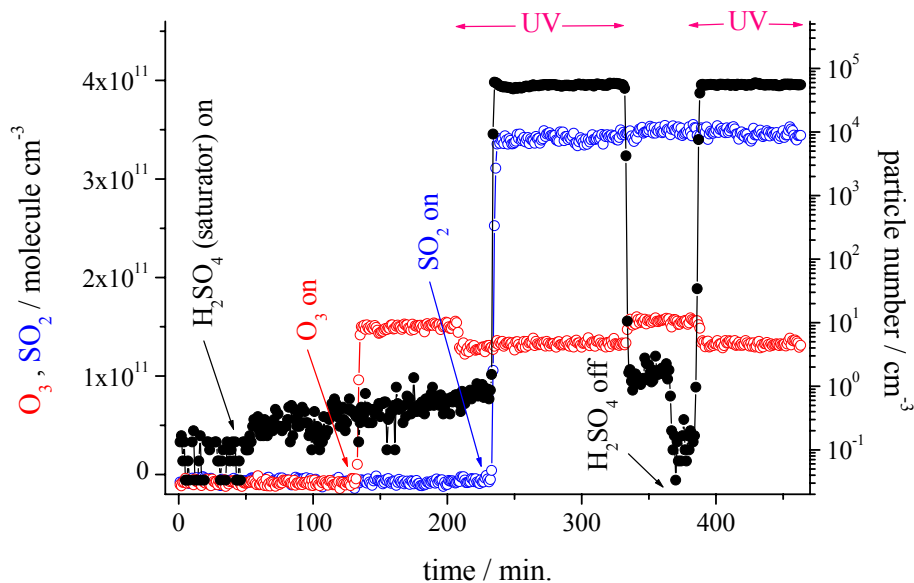
Fig. 2. Temporal behaviour of O$_3$ and SO$_2$ concentration and particle number for an experiment using H$_2$SO$_4$ from the liquid reservoir as well as in-situ formation of "H$_2$SO$_4$" (SO$_2$ products) with CO for OH radical titration, r.h.=22%, gas flow: 10 sl min^{-1}, bulk residence time (middle and end section): 126 sec. Initial concentrations were (unit: molecule cm^{-3}); H$_2$SO$_4$ (saturator): (1–2)×10^9; O$_3$: 1.6×10^{11}; CO: 1.0×10^{14}; SO$_2$: 3.5×10^{11}.
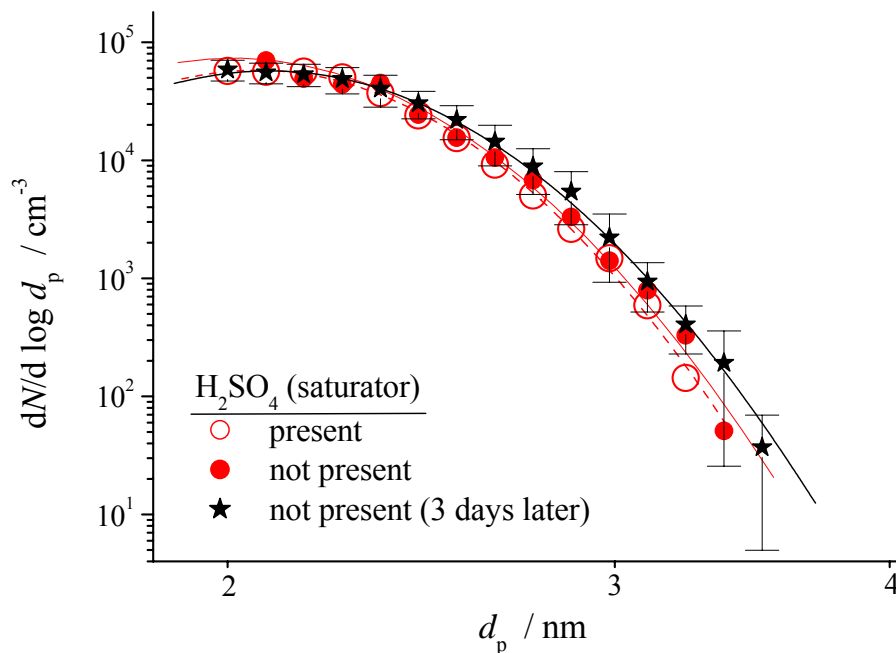
Fig. 3. Measured size distributions in the range d =2–4 nm from the experiment depicted in Fig. 2. The distribution with H$_2$SO$_4$ from the saturator was recorded between 275 and 325 min and that without H$_2$SO$_4$ from the saturator between 410 and 460 min, cf. Fig. 2. After a 3 day flushing of the flow tube with pure air the distribution with black symbols in absence of H$_2$SO$_4$ from the saturator was measured.
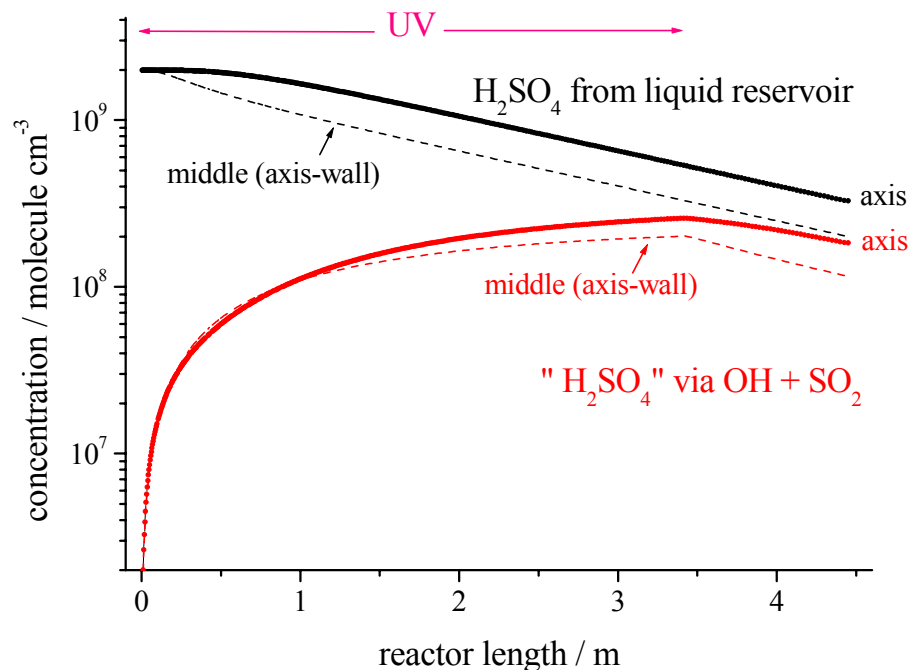
Fig. 4. CFD-Modelling: Calculated concentration profiles of H_2SO_4 from the liquid reservoir and from in- situ produced "H_2SO_4" via the reaction of OH radicals with SO_2, r.h.=22%, gas flow: 10 sl min^{-1}. Initial concentrations in the case of in situ "H_2SO_4" formation were (unit: molecule cm^{-3}); O_3: 1.6×10^{11}; CO: 1.0×10^{14}; SO_2: 3.5×10^{11}.
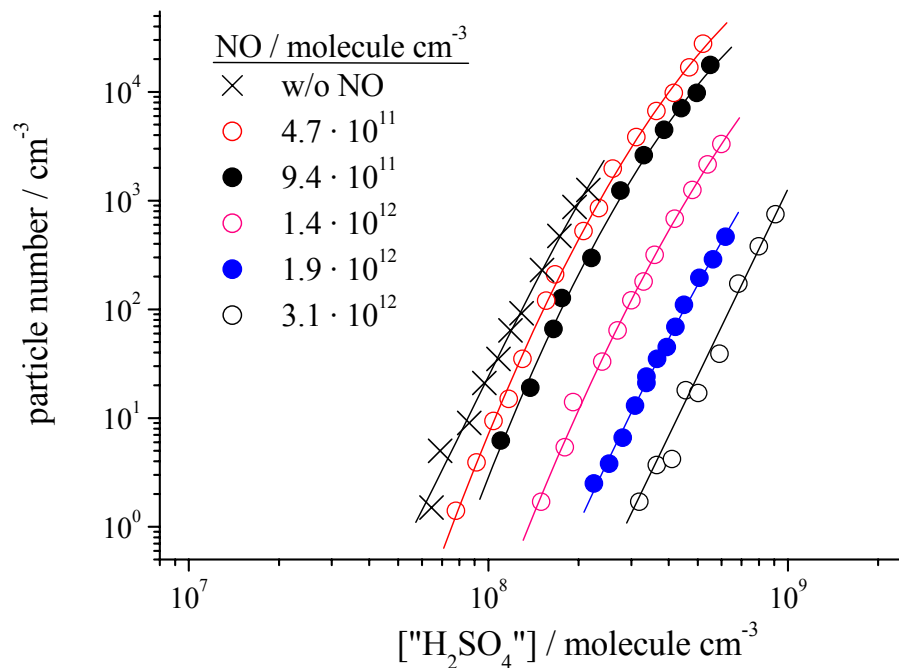
Fig. 5. Experimentally observed particle number as a function of in-situ produced "H$_2$SO$_4$" (SO$_2$ products) concentration for different NO additions in the carrier gas using furan for OH radical titration, OH radical formation via O$_3$ photolysis, r.h.=22%, gas flow: 30 sl min^{-1}, bulk residence time (middle and end section): 42 s Initial concentrations were (unit: molecule cm^{-3}); O$_3$: (1.5–1.6)×10^{11}; furan: 6.2×10^{11}; furan conversion: 2.1–5.3%; SO$_2$: (1.2–16)×10^{11}.
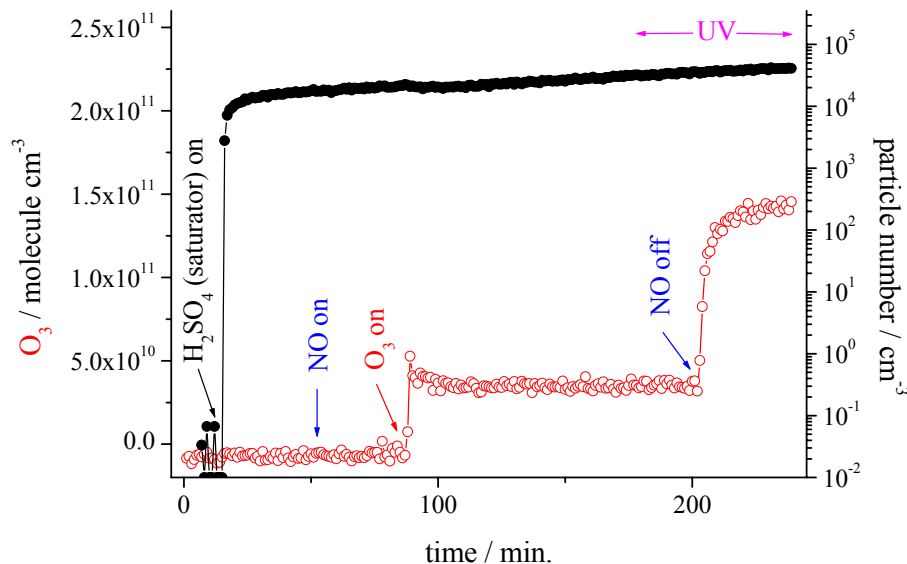
Fig. 6. Temporal behaviour of O$_3$ concentration and the particle number for an experiment using H$_2$SO$_4$ from the liquid reservoir, r.h.=22%, gas flow: 30 sl min^{-1}, bulk residence time (middle and end section): 42 s Initial concentrations were (unit: molecule cm^{-3}); H$_2$SO$_4$ (saturator): ~5×10^9; O$_3$: 1.5×10^{11}; CO: 1.0×10^{14}; NO: 4.1×10^{12}.