

SO₂ oxidation products other than H₂SO₄ as a trigger of new particle formation. Part 1: Laboratory investigations

T. Berndt¹, F. Stratmann¹, S. Bräsel¹, J. Heintzenberg¹, A. Laaksonen², and M. Kulmala³

¹Leibniz-Institut für Troposphärenforschung e.V., Leipzig, Germany

²University of Kuopio, Kuopio, Finland

³University of Helsinki, Helsinki, Finland

Received: 14 April 2008 – Published in Atmos. Chem. Phys. Discuss.: 28 May 2008

Revised: 17 September 2008 – Accepted: 18 September 2008 – Published: 6 November 2008

Abstract. Mechanistic investigations of atmospheric H₂SO₄ particle formation have been performed in a laboratory study taking either H₂SO₄ from a liquid reservoir or using the gas-phase reaction of OH radicals with SO₂. Applying both approaches for H₂SO₄ generation simultaneously it was found that H₂SO₄ 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 SO₂. Furthermore, for NO_x concentrations > 5 × 10¹¹ molecule cm⁻³ the formation of new particles from the reaction of OH radicals with SO₂ is inhibited. This suggests that substances other than H₂SO₄ (potentially products from sulphur-containing peroxy radicals) trigger lower tropospheric new particle formation and growth. The currently accepted mechanism for SO₂ gas-phase oxidation does not consider the formation of such substances. The analysis of new particle formation for different reaction conditions in our experiment suggests that a contribution of impurities to the nucleation process is unlikely.

1 Introduction

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 H₂SO₄/H₂O and much higher atmospheric nucleation data 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). Nucleation events in the lower troposphere were found to be closely connected to the appearance of H₂SO₄ for concentrations of ~10⁷ molecule cm⁻³ and below measured at clean and polluted sites (Weber et al., 1996; McMurry et al., 2005; Riipinen et al., 2006).

In a previous investigation of our laboratory under near-atmospheric conditions, experimental evidence for the formation of new particles in the system H₂SO₄/H₂O was found for H₂SO₄ concentrations of ~10⁷ molecule cm⁻³ if “H₂SO₄” was produced in-situ via the reaction of OH radicals with SO₂ (“H₂SO₄” here stands for all products of converted SO₂). As the OH radical source served UV-photolysis of O₃ 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 SO₂ oxidation products (“H₂SO₄”) 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). Recently, for nucleation experiments starting from OH+SO₂ threshold H₂SO₄ (or “H₂SO₄”) concentrations of 10⁸–10⁹ molecule cm⁻³ have been measured for a nucleation rate of unity (1 cm⁻³ s⁻¹) (Benson et al., 2008, Young et al., 2008). A future detailed analysis will show whether these significantly higher threshold “H₂SO₄” concentrations (compared to our results) are simply due to the experimental conditions chosen by these researchers or an indication for a different nucleation process going on.



Correspondence to: T. Berndt
(berndt@tropos.de)

In contrast, taking H₂SO₄ from a liquid reservoir concentrations of 10⁹–10¹⁰ 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 H₂SO₄/H₂O (Kulmala et al., 1998).

In this study mechanistic investigations on H₂SO₄/H₂O particle formation are reported explaining the different threshold H₂SO₄ concentrations needed for nucleation, i.e., ~10⁷ molecule cm⁻³ (“H₂SO₄” produced via gas-phase reaction of OH radicals with SO₂) vs. 10⁹–10¹⁰ molecule cm⁻³ (H₂SO₄ via evaporation from a liquid reservoir).

2 Experimental

The experiments have been performed in the atmospheric pressure flow-tube *I/T*-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 SO₂, O₃, NO or hydrocarbons or H₂SO₄ 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 O₃, SO₂, and NO_x (Thermo Environmental Instruments: 49C, 43C, and 42S), a butanol-based UCPC (TSI 3025) as well as a H₂O-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.

The carrier gas consisted of synthetic air (99.9999999 %, Linde and further purification with GateKeeper CE-500KF-O-4R, AERONEX). Functioning of GateKeeper is based on surface reactions removing contaminants from the gas phase. Stated output gas impurity is <500 ppt for NMHCs, H₂O and CO₂.

A small part of the total gas flow was flushed through an ozone generator (UVP OG-2) for O₃ generation outside the flow tube. SO₂ was taken from a 1ppmv or 10ppmv calibration mixture in N₂ (Messer) and NO from 0.5 vol% mixture in N₂ (Messer). In the case of experiments with H₂SO₄ vapour from a 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 H₂SO₄ vapour containing gas stream. In the first tube section this H₂SO₄ gas stream was brought together with humidified air.

The total gas flow inside the *I/T*-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 s, 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 measured using a capacitive manometer (Baratron).

2.1 Determination of H₂SO₄ taken from a liquid reservoir

For experiments using H₂SO₄ vapour from a liquid reservoir, H₂SO₄ 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 times were in the range of 2–10 h. The subsequent analysis of SO₄²⁻ ions has been done by means of ion chromatography (761 compact IC, Metrohm).

2.2 Determination of “H₂SO₄” (products of converted SO₂) and OH concentrations

Starting from the reaction of OH radicals with SO₂ “H₂SO₄” concentrations were calculated using a model according to the following reaction scheme used in the case of photolysis experiments (Berndt et al., 2005, 2006):



The effective photolysis rate coefficient k_1 was determined in each experiment measuring the O₃ decay. Rate coefficients $k_{2,\text{furan}}=4.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, $k_{2,\text{CO}}=2.4 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, and $k_3=1.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, were taken from literature (Finlayson-Pitts and Pitts, 2000). For description of the assumed, diffusion controlled wall loss of “H₂SO₄”, $k_4=0.017$ s⁻¹, the same data as for H₂SO₄ were taken (Hanson and Eisele, 2000). The concentration of furan (or CO) was chosen in such a way that $k_{2,\text{furan}} \times [\text{furan}] > 20$ s⁻¹ ($k_{2,\text{furan}} \times [\text{furan}] \sim k_{2,\text{CO}} \times [\text{CO}]$) was fulfilled. Modelling studies showed that under these conditions the reactions of OH radicals with O₃, HO₂ or any impurities (impurity concentration ≤ 10¹⁰ molecule cm⁻³, $k_{\text{OH}+\text{impurity}}=10^{-10}$ cm³ 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 O₃”/“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 “H₂SO₄” concentrations, are well described by the model applied. For normally used initial reaction conditions (O₃: ~1.5×10¹¹ with a conversion <25%, furan: 6.2×10¹¹

with a conversion $\leq 6\%$ or CO: 1.0×10^{14} with a conversion $< 1\%$ and SO₂: $(6.7\text{--}350) \times 10^{10}$ 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 the modelling of the reaction system yielded OH radical concentrations of about 10^7 molecule cm⁻³ being close to atmospheric levels. Given “H₂SO₄” concentrations represent averaged values for the irradiated middle section. A comparison of results arising from different modelling approaches is given in Appendix A.

In the case of added NO_x in the carrier gas, NO and NO₂ can undergo reactions with O₃ and OH radicals. An additional pathway for OH radical generation represents the reaction of NO with HO₂ forming OH and NO₂. 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 O₃ and for the decay of furan. With the knowledge of the axial OH radical profile the “H₂SO₄” concentration according to pathways (3) and (4) were calculated. Given “H₂SO₄” concentrations represent also averaged values for the irradiated middle section.

2.2.1 The possible role of the reaction HO₂+SO₂ for additional H₂SO₄ production

It might be speculated that in our experiment, besides the OH radicals, also HO₂ could significantly contribute to SO₂ oxidation. Payne et al. (1973) reported for the reaction HO₂+SO₂ a rate coefficient of 8.7×10^{-16} cm³ molecule⁻¹ s⁻¹ determined in an indirect way. This data differs from the results of other researchers. Burrows et al. (1979) deduced from direct measurements an upper limit for $k_{\text{HO}_2+\text{SO}_2}$ of 2×10^{-17} cm³ molecule⁻¹ s⁻¹. The latest recommendation for atmospheric chemistry (Atkinson et al., 2004) states $k_{\text{HO}_2+\text{SO}_2} < 10^{-18}$ cm³ molecule⁻¹ s⁻¹. Assuming that there is a catalytic effect of H₂O, HO₂(H₂O)+SO₂ (Payne et al., measured in the presence of 20 torr H₂O, the other studies have been performed under dry conditions), the impact of this pathway producing OH radicals and SO₃ was investigated. SO₃ produces H₂SO₄ in a fast consecutive hydrolysis step (Jayne et al., 1997).

In the extended ideal plug model (given in Appendix A), for the rate coefficient $k_{\text{HO}_2+\text{SO}_2}$ the values 10^{-18} , 2×10^{-17} and 8.7×10^{-16} (unit: cm³ molecule⁻¹ s⁻¹) have been applied successively in an otherwise identical exemplary model setup (residence time: 97 s; initial concentrations in molecule cm⁻³: O₃: 1.6×10^{11} ; CO: 1.0×10^{14} ; SO₂: 3.5×10^{11}). With respect to the recommended value of 10^{-18} cm³ molecule⁻¹ s⁻¹ as the reference, the use of 2×10^{-17} cm³ molecule⁻¹ s⁻¹ (Burrows et al., 1979) yields an increase of less than 1% for the concentration of all SO₂ oxidation products (H₂SO₄ and “H₂SO₄”). Assumption

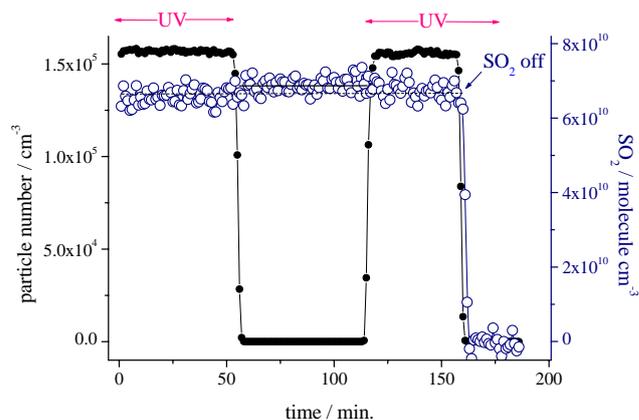


Fig. 1. Temporal behaviour of SO₂ concentration and particle number for an experiment with “H₂SO₄” formation from the reaction of OH radicals with SO₂ using CO for OH radical titration, r.h.=22%, gas flow: 3.33 sl min⁻¹. Initial concentrations were (unit: molecule cm⁻³); O₃: 3.8×10^{11} ; CO: 5.3×10^{13} . SO₂ concentration in the absence of OH radicals (UV off): $6.78 \pm 0.24 \times 10^{10}$ molecule cm⁻³ (full line) and in the presence of OH radicals (UV on): $6.63 \pm 0.24 \times 10^{10}$ molecule cm⁻³ (dashed line) results in a SO₂ consumption of 1.5×10^9 molecule cm⁻³ (uncertainty by a factor of ~ 2.3).

of $k_{\text{HO}_2+\text{SO}_2} = 8.7 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ (Payne et al., 1973) results in an 26% enhancement. Consequently, additional SO₂ oxidation from the assumed H₂O-catalysed reaction HO₂(H₂O)+SO₂ is of minor importance even when considering the rate coefficient reported by Payne et al. (1973).

3 Results and discussion

3.1 Measurement of consumed SO₂

It was attempted to measure the amount of consumed SO₂ to evaluate the reliability of calculated “H₂SO₄” concentrations via pathways (1)–(4). In Fig. 1 the temporal behaviour of SO₂ concentration and particle number for an experiment with CO for OH radical titration is given. SO₂ measurement using Thermo Environmental Instruments 43C in the absence of OH radicals (UV off) yielded: $6.78 \pm 0.24 \times 10^{10}$ molecule cm⁻³ (full line) and in the presence of OH radicals (UV on): $6.63 \pm 0.24 \times 10^{10}$ molecule cm⁻³ (dashed line) resulting in a SO₂ 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 “H₂SO₄”) shows an average “H₂SO₄” concentration in the tube of 2.46×10^8 molecule cm⁻³ and a SO₂ consumption of 1.46×10^9 molecule cm⁻³. Simulated and measured SO₂ consumption are in good agreement. The particle number exceeded the counting range of TSI 3025 (particle number $> 10^5$ cm⁻³). Integration of simultaneously

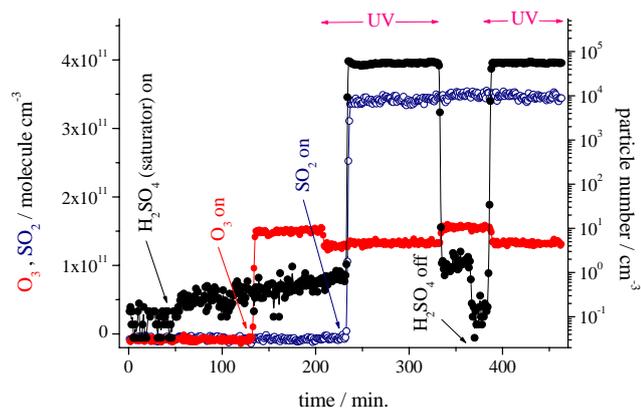


Fig. 2. Temporal behaviour of O₃ and SO₂ concentration and particle number for an experiment using H₂SO₄ from the liquid reservoir as well as in-situ formation of “H₂SO₄” (SO₂ products) with CO for OH radical titration, r.h.=22%, gas flow: 10 sl min⁻¹, bulk residence time (middle and end section): 126 sec. Initial concentrations were (unit: molecule cm⁻³): H₂SO₄ (saturator): (1–2) × 10⁹; O₃: 1.6 × 10¹¹; CO: 1.0 × 10¹⁴; SO₂: 3.5 × 10¹¹.

performed size distribution measurement yielded a particle number of 3.6 × 10⁵ cm⁻³.

The determination of reacted SO₂ stands for a complementary measure of “H₂SO₄” and the good agreement between measured and calculated SO₂ conversion shows explicitly that the “true” concentration of “H₂SO₄” in the experiment cannot exceed the modelling data considerably.

3.2 New particle formation in the presence of in-situ produced “H₂SO₄” and H₂SO₄ from a liquid reservoir

In a first set of experiments in-situ formation of “H₂SO₄” via OH+SO₂ was coupled with evaporation of H₂SO₄ from the liquid reservoir as background in order to investigate the role of H₂SO₄ for the new particle formation and growth process. Initial H₂SO₄ concentration from the liquid reservoir was (1–2) × 10⁹ molecule cm⁻³, i.e., close to the threshold concentration needed for binary H₂SO₄/H₂O nucleation in our experiment. The bulk residence time in the reaction zone (irradiated middle section) was 97 s and the end-H₂SO₄ concentration (from liquid reservoir) was estimated to be (2–4) × 10⁸ 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 H₂SO₄-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 H₂SO₄/H₂O (Kulmala et al., 1998). The particle number was not affected by the presence of O₃ and the photolysis products (OH radicals, HO₂, and H₂O₂) after switching on UV irradiation. With addition of SO₂ (time=235 min), in-situ particle precursor formation in the gas phase started and

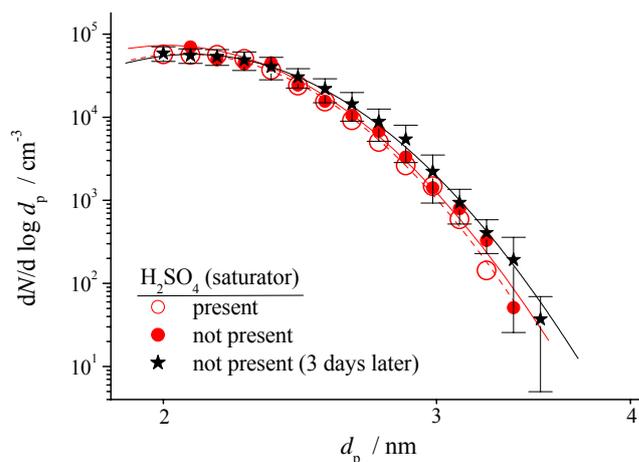


Fig. 3. Measured size distributions in the range $d=2\text{--}4$ nm from the experiment depicted in Fig. 2. The distribution with H₂SO₄ from the saturator was recorded between 275 and 325 min and that without H₂SO₄ from the saturator between 410 and 460 min, cf. Fig. 2. After a 3 day flushing of the flow tube with pure air the distribution with black symbols in absence of H₂SO₄ from the saturator was measured.

a constant particle number of 5 × 10⁴ cm⁻³ was observed for in-situ “H₂SO₄” concentration of 2.3 × 10⁸ molecule cm⁻³. Immediately after switching off UV (time=330 min), particle number went down to the level being attributed to binary H₂SO₄/H₂O nucleation. At 360 min the supply of H₂SO₄ from the liquid reservoir was stopped resulting in a decrease of particle number down to background noise level. Switching on UV, i.e., restarting the in-situ “H₂SO₄” production without background H₂SO₄, led to a particle number of 5 × 10⁴ cm⁻³ again. This behaviour is a strong indication that H₂SO₄ from the liquid reservoir (now absent) did not participate in the nucleation process. To illustrate the influence of background H₂SO₄ on particle growth, Fig. 3 shows measured size distributions in the diameter range $d=2\text{--}4$ nm recorded in the time period 275 to 325 min (presence of background H₂SO₄) and between 410 and 460 min (absence of background H₂SO₄). 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 H₂SO₄ from the liquid reservoir was repeated. Figure 3 shows that the three measured size distributions are nearly identical. This indicates that H₂SO₄ from 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 “H₂SO₄” (cf. Fig. 4), does not significantly contribute to particle growth. Obviously, condensational growth by H₂SO₄ evaporated from the liquid reservoir is of less importance under the chosen conditions and cannot be resolved.

It cannot be ruled out that probably heterogeneous processes significantly contribute to particle growth. In acidic solutions SO₂ is rapidly oxidized by H₂O₂ (Martin and

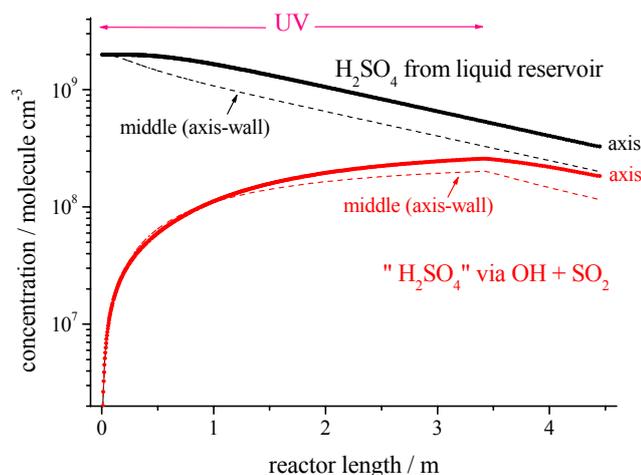


Fig. 4. CFD-Modelling: Calculated concentration profiles of H₂SO₄ from the liquid reservoir and from in-situ produced “H₂SO₄” via the reaction of OH radicals with SO₂, r.h.=22%, gas flow: 10 sl min⁻¹. Initial concentrations in the case of in situ “H₂SO₄” formation were (unit: molecule cm⁻³); O₃: 1.6×10¹¹; CO: 1.0×10¹⁴; SO₂: 3.5×10¹¹.

Damschen, 1981). Applying this behaviour to the newly formed particles, in a process of reactive uptake SO₂ and H₂O₂ molecules can react in or at the surface of the new particles forming additional SO₂ oxidation products in the particle phase. Gas-phase concentrations of SO₂ and H₂O₂ in our experiment are normally in the order of 10⁹–10¹¹ molecule cm⁻³ resulting in roughly 0.1–10 collisions s⁻¹ with SO₂ and H₂O₂ molecules per particle.

It is to be noted that integration of the size distributions (d≥2 nm) given in Fig. 3 yielded a particle number of ~5×10³ cm⁻³, i.e., 1/10 of the total number found in the integral measurement using the UCPC. Therefore, the majority of produced particles in this example were obviously smaller than 2 nm in diameter.

To get an rough estimate concerning the H₂SO₄/“H₂SO₄” mass balance it is assumed i) that H₂SO₄ is the exclusive product from the reaction of OH radicals with SO₂ and ii) that the particles consist of H₂SO₄ (density of 1.85 g cm⁻³) only, i.e., contributions of water to particle mass are neglected. For the example described above (assuming 5×10³ particle with d=2 nm and 4.5×10⁴ particle cm⁻³ with d=1.5 nm) it follows that about 0.5% of gas phase “H₂SO₄” (or H₂SO₄) can attributed to the newly formed particles.

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

These findings pose the question, why H₂SO₄ from the liquid reservoir exhibits a totally different behaviour (no clear contribution to particle formation and growth) compared to in-situ produced “H₂SO₄”? A possible reason could be that H₂SO₄ is not the particle precursor produced from the reaction of OH radicals with SO₂.

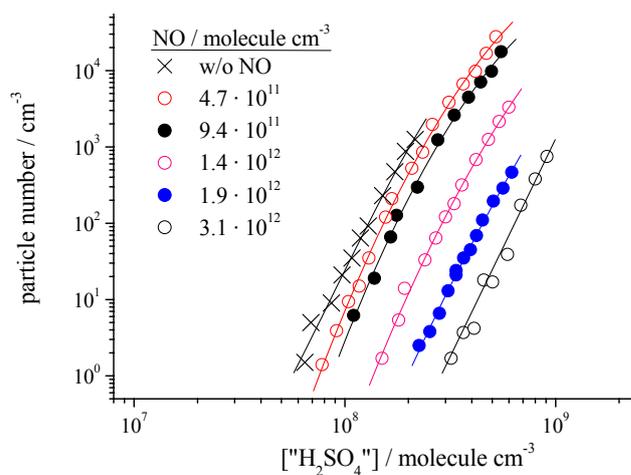
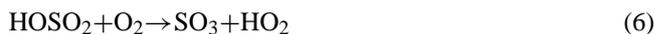
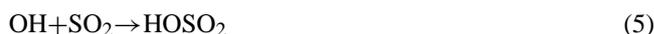


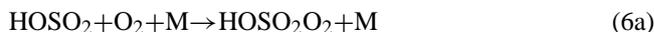
Fig. 5. Experimentally observed particle number as a function of in-situ produced “H₂SO₄” (SO₂ products) concentration for different NO additions in the carrier gas using furan for OH radical titration, OH radical formation via O₃ photolysis, r.h.=22%, gas flow: 30 sl min⁻¹, bulk residence time (middle and end section): 42 sec. Initial concentrations were (unit: molecule cm⁻³); O₃: (1.5–1.6)×10¹¹; furan: 6.2×10¹¹; furan conversion: 2.1–5.3 %; SO₂: (1.2–16)×10¹¹.

The currently accepted mechanism of atmospheric SO₂ gas-phase oxidation initiated by OH radicals is as follows (Finlayson-Pitts and Pitts, 2000):



Here, HOSO₂ radicals produced from the primary reaction of OH radicals with SO₂ via pathway (5) react in the very fast consecutive step (6) with O₂ forming SO₃. SO₃ reacts with two water molecules or a water dimer producing H₂SO₄. According to this scheme, each attacked SO₂ molecule from pathway (5) is transformed to a H₂SO₄ molecule.

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 HOSO₂ as via this reaction more than 80% of HOSO₂ regenerates HO₂. However, an earlier way of thinking was based on a different pathway (6a) which considered the addition of O₂ to HOSO₂:



From the pressure-dependence of the kinetics of the reaction HOSO₂+O₂, it was concluded that pathway (6a) accounts for <10% of the HOSO₂ removal (Gleason et al., 1987). Simultaneous measurements of HO₂ and HOSO₂ concentrations yielded a lower limit of 70% for pathway (6)

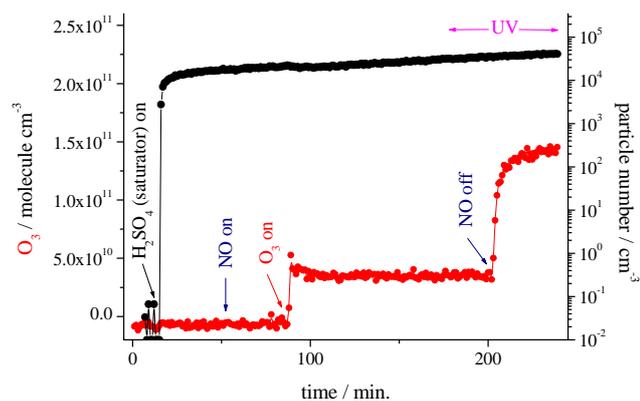


Fig. 6. Temporal behaviour of O₃ concentration and the particle number for an experiment using H₂SO₄ from the liquid reservoir, r.h.=22%, gas flow: 30 sl min⁻¹, bulk residence time (middle and end section): 42 sec. Initial concentrations were (unit: molecule cm⁻³): H₂SO₄ (saturator): $\sim 5 \times 10^9$; O₃: 1.5×10^{11} ; CO: 1.0×10^{14} ; NO: 4.1×10^{12} .

(Howard, 1985). Taking all experimental findings into consideration, up to 30% of HOSO₂ can be converted to HOSO₂O₂.

It should be noted that a reduction of H₂SO₄ formation from SO₂ 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).

HOSO₂O₂ is a peroxy-type radical and, analogous to organic peroxy radicals, it can react with HO₂, other peroxy radicals or with NO and NO₂ (Finlayson-Pitts and Pitts, 2000). Also the reaction of HOSO₂O₂ or its hydrated species HOSO₂O₂(H₂O)_n with SO₂ is imaginable (Wayne, 1991). If the reaction of HOSO₂O₂ with HO₂



and/or with other peroxy radicals (RO₂)



and/or with SO₂



is responsible for the formation of particle precursors, addition of NO and/or NO₂ should reduce or inhibit new particle formation as a part of the available HOSO₂O₂ will be consumed by NO and/or NO₂. (In pathways (8)–(10) also the hydrated species of HOSO₂O₂ can react. For simplification the hydrated form is neglected here.)

3.3 New particle formation in the presence of NO/NO₂

3.3.1 New particle formation in the presence of NO/NO₂ using in-situ produced “H₂SO₄”

To test the hypothesis that HOSO₂O₂ is a possible precursor for nucleating species and that in the presence of NO and/or NO₂ new particle formation is reduced or inhibited, experiments were carried out, with NO_x (NO+NO₂) being present in the carrier gas. In this context it should be noted that generally NO and NO₂ can undergo reactions with O₃, OH radicals, HO₂ and other RO₂ radicals influencing the OH radical level significantly. Therefore, to determine the in-situ produced “H₂SO₄” 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 NO₂, e.g., for the lowest initial NO concentration, 32% of NO reacted to NO₂. It 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 humidity in the range 10–60% or using NO₂ 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 HO₂ and/or other peroxy radicals or with SO₂ via pathways (8), (9) or (10), respectively. In this context it is to be noted, that in the presence of NO_x, under all experimental conditions new particle formation was not fully suppressed. With increasing NO_x concentrations the measured curves N vs. [“H₂SO₄”] are shifted towards the values expected for binary H₂SO₄/H₂O nucleation (new particle formation for H₂SO₄ concentrations above 10⁹ molecule cm⁻³). Even for the highest NO concentration of 3.1×10^{12} molecule cm⁻³, c.f. Fig. 5, the “binary H₂SO₄/H₂O nucleation” limit was not reached. A comparison of new particle formation data from this study with literature data is given in the accompanying paper (Laaksonen et al., 2008) for H₂SO₄ from liquid reservoir.

NO_x cannot effect H₂SO₄ formation as described by pathways (5)–(7) because the HOSO₂ life-time regarding the O₂ reaction, pathway (6), as well as the SO₃ 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 B).

The experimental data depicted in Fig. 5 in the absence of NO_x (gas flow: 30 sl min⁻¹, bulk residence time in irradiated middle section: 32 s) show that new particle formation was observed for “H₂SO₄” concentrations above 7×10^7 molecule cm⁻³. This is about a one order of magnitude higher threshold “H₂SO₄” concentration than observed for low flow conditions (gas flow: 3.33 sl min⁻¹, bulk residence time in irradiated middle section: 290 s), cf. data in Berndt et al. (2005, 2006). Generally, the number of newly

formed particles for the same “H₂SO₄“ concentration was found to be strongly dependent on residence time and relative humidity. Furthermore, for freshly nucleated particles with $dp < 3$ nm it is obvious that the decreasing counting efficiency of the commercially available UCPCs (depending on particle size) does not permit to draw quantitative conclusions such as reliable slopes $\log(N)$ vs. $\log([\text{“H}_2\text{SO}_4\text{”}])$ and, consequently, the number of molecules in the critical cluster, c.f. Berndt et al. (2005).

3.3.2 New particle formation in the presence of NO/NO₂ using H₂SO₄ from the liquid reservoir

Furthermore, the influence of NO_x (NO+NO₂) for the process of new particle formation was studied using H₂SO₄ from the liquid reservoir. Fig. 6 shows the temporal behaviour of O₃ concentration and the particle number for an experiment using an initial H₂SO₄ concentration (from the liquid reservoir) of $\sim 5 \times 10^9$ molecule cm⁻³. After turning on the flow through the H₂SO₄ – 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 O₃ generation (O₃: 1.5×10^{11} molecule cm⁻³) NO was partly converted to NO₂ with an end concentration of $\sim 1.1 \times 10^{11}$ molecule cm⁻³, O₃+NO→NO₂+O₂. Switching on UV lamps at 175 min OH radical formation started and beside OH radicals, HO₂ and H₂O₂ also HONO and HNO₃ were produced. After turning off the NO flow (time: 205 min) only the O₃ photolysis products (OH radicals, HO₂ and H₂O₂) remained. Under all conditions investigated, especially for NO_x addition, there was no impact of added trace gases on the number of newly formed particles 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 “H₂SO₄“. Consequently, these results represent a further indication that reaction products of SO₂ oxidation other than H₂SO₄ (potentially products of sulphur-containing peroxy-type radicals like HOSO₂O₂) represent possible particle precursors.

3.4 Contribution of gas impurities to the process of new particle formation

Zhang et al. (2004) observed an enhancement of H₂SO₄/H₂O nucleation (H₂SO₄ from liquid reservoir) adding aromatic acids to the reaction gas. It could be speculated that also in the course of our experiments organic acids are formed in a parallel step to the SO₂ oxidation. These acids could increase H₂SO₄/H₂O nucleation in the same way as described by Zhang et al. (2004) causing probably a lowering of the H₂SO₄ threshold concentration.

The experimental findings in the presence of H₂SO₄ from liquid reservoir (absence of SO₂), however, do not support this scenario, c.f. Fig. 2 and Fig. 6. In Fig. 2, before turn-

ing on SO₂ at 235 min, and starting SO₂ oxidation, UV was switched on producing OH radicals, HO₂, H₂O₂, and CO₂ from CO oxidation. Under these conditions, gas impurities relevant as particle precursors, would be oxidized, producing probably e.g. acids. But, with and without OH radical formation (in absence of SO₂), and consequently with and without oxidized impurities, there was no change in the measured total particle number. Furthermore, as given in Fig. 6 in the presence of NO_x, there was also no change in the particle number visible when photochemistry was active. With respect to our experiments, this fact makes the occurrence of enhancing effects of oxidized impurities on H₂SO₄/H₂O nucleation very unlikely.

Assuming that non-(in situ)oxidized, but rather permanently present, impurities could influence the nucleation process, similar effects for both cases, i.e., H₂SO₄ taken from the liquid reservoir and “H₂SO₄“ produced via OH+SO₂ (if H₂SO₄ as a part of “H₂SO₄“ would be responsible for nucleation) should be observed. With this scenario, the different threshold concentrations needed for nucleation cannot be explained.

4 Summary and conclusions

It was pointed out that, under our experimental conditions being applicable to the lower troposphere, H₂SO₄ 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 SO₂. Furthermore, it was shown that for NO_x concentrations $> 5 \times 10^{11}$ molecule cm⁻³ the formation of new particles from the reaction of OH radicals with SO₂ is inhibited. This behaviour is not in line with the currently accepted reaction mechanism describing an equal-molar formation of H₂SO₄ from SO₂. Therefore, it can be hypothesized that in the course of SO₂ conversion, potentially sulphur-containing peroxy radicals like HOSO₂O₂ can be formed in substantial fractions leading to products being different from H₂SO₄. It might be further speculated, that under lower tropospheric conditions, HOSO₂O₂ (or its hydrated species) could react with HO₂ and other peroxy radicals (including the self-reaction). These reactions could result in low vapour pressure particle precursors. If, e.g., HOSO₂O₂ reacts with HO₂ (the most abundant RO₂ radical in atmosphere), peroxy sulphuric acid is formed. Peroxy sulphuric acid is a hydrophilic solid, which in the liquid phase (in water) is converted to sulphuric acid and H₂O₂ (Kolditz, 1983). Another idea for particle formation starting from HOSO₂O₂ is given by Wayne (1991) describing the reaction of hydrated HOSO₂O₂ (HOSO₂O₂(H₂O)_n) with SO₂ producing HOSO₂O(H₂O)_nSO₃. 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.

The analysis of new particle formation for different reaction conditions suggests that contributions of impurities to the nucleation process are unlikely in our experiment.

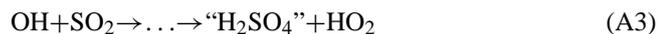
In conclusion, this study shows, that it is not necessarily sulphuric acid triggering atmospheric new particle formation and growth and that other compounds (like peroxy sulphuric acid or HOSO₂O(H₂O)_nSO₃ radicals) formed during the gas phase reaction of OH radicals with SO₂ may play an important role.

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

Comparison of modelling results

Usually, calculations of “H₂SO₄” concentrations have been performed using pathways (1)–(4), calling in the following as *simple ideal plug model*. Considering also axial and radial diffusion processes in the tube, CFD modelling runs have been carried out using pathways (1)–(4) for description of the chemical processes, called *CFD model*. For a more detailed analysis of the importance of other, individual chemical steps occurring during SO₂ oxidation an *extended ideal plug model* was applied, see in the following the individual pathways:



In the same way as described for pathway (1) the used effective photolysis rate coefficient k_{1A} was determined in each experiment measuring the O₃ decay. In pathway (A3) formation of HO₂ was considered assuming a yield of unity. This represents probably an overestimation and a yield of 0.7–0.9

could be more reliable if HOSO₂O₂ is produced in substantial fraction, see text for explanation. For the rate coefficients describing the wall loss of OH radicals and HO₂, k_{A8} and k_{A12} , the diffusion limit was assumed as $k_{\text{wall}} = 3.65 D/r^2$. Corresponding diffusion coefficients were taken from Reid et al. (1987). The other rate coefficients were taken from literature (Finlayson-Pitts and Pitts, 2000; Atkinson et al., 2004). It is to be noted that for pathway (A11) also the recommended value $k_{A11} = 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was applied. The impact of $k_{A11} = 8.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Payne et al., 1973) for the resulting H₂SO₄ concentration is discussed in a separate paragraph.

For an example (r.h.=22%; gas flow: 10 sl min⁻¹; bulk residence time in the middle section: 97 s; initial concentrations in molecule cm⁻³: O₃: 1.6 × 10¹¹; CO: 1.0 × 10¹⁴; SO₂: 3.5 × 10¹¹) resulting “H₂SO₄” concentrations were calculated for the end of the middle section using the three different models. The good agreement, 2.58 × 10⁸ molecule cm⁻³ (*simple ideal plug model*), 2.63 × 10⁸ molecule cm⁻³ (*extended ideal plug model*), and 2.58 × 10⁸ molecule cm⁻³ for the centre line and 2.00 × 10⁸ molecule cm⁻³ in the middle between centre line and wall (*CFD model*), shows clearly that an application of the *simple ideal plug model* is reasonable.

Appendix B

Atmospheric life-times of HOSO₂ and SO₃

Assuming a concentration of 10¹² molecule cm⁻³ for NO and NO₂ in each case, a HOSO₂ life-time regarding NO reaction of > 2 s (Martin et al., 1986) and regarding NO₂ reaction of > 10 milliseconds (assuming an upper limit for the rate coefficient of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) follows. A comparison with the life-time regarding overall O₂ reaction via pathway (6) of ~0.5 microseconds (Gleason et al., 1987) shows clearly that NO and NO₂ cannot influence the conversion of HOSO₂ via pathways (6) and (6a). Assuming for the reaction of SO₃ with NO and NO₂ the rate coefficient measured for the NO₂ reaction (Penzhorn and Canosa, 1983), the SO₃ life-times regarding the NO and NO₂ reaction are in the order of 80 days. That means that also the hydrolysis of SO₃ via pathway (7) (with a life-time of ~20 microseconds assuming a H₂O concentration of 3 × 10¹⁷ molecule cm⁻³ (Jayne et al., 1997)) cannot be affected by NO and NO₂. Consequently, NO and NO₂ for the concentrations considered here, cannot affect H₂SO₄ formation via pathways (5)–(7).

Acknowledgements. We thank E. Brüggemann and A. Thomas for SO₄²⁻ measurements, K. Pielok, T. Conrath and H. Macholeth for technical assistance.

Edited by: J. Curtius

References

- Atkinson, R., Bauch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkins, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I – gas phase reactions of O_x, HO_x, NO_x and SO_x species, *Atmos. Chem. Phys.*, 4, 1461–1738, 2004, <http://www.atmos-chem-phys.net/4/1461/2004/>.
- Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H₂SO₄, H₂O, and NH₃ vapors, *J. Geophys. Res.*, 104, 23 709–23 718, doi:10.1029/1999JD900411, 1999.
- Benson, D. R., Young, L.-H., Kameel, F. R., and Lee, S.-H.: Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO₂+OH reaction, *Geophys. Res. Lett.*, 35, L11801, doi:10.1029/2008GL033387, 2008.
- Berndt, T., Böge, O., and Stratmann, F.: Atmospheric particle formation from the ozonolysis of alkenes in the presence of SO₂, *Atmos. Environ.*, 38, 2145–2153, 2004.
- Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J., and Kulmala, M.: Rapid Formation of Sulfuric Acid Particles at Near-Atmospheric Conditions, *Science*, 307, 698–700, 2005.
- Berndt, T., Böge, O., and Stratmann, F.: Formation of atmospheric H₂SO₄/H₂O particles in the absence of organics: A laboratory study, *Geophys. Res. Lett.*, 33, L15817, doi:10.1029/2006GL026660, 2006.
- Burkholder, J. B., Baynard, T., Ravishankara, A. R., and Lovejoy, E. R.: Particle nucleation following the O₃ and OH initiated oxidation of α -pinene and β -pinene between 278 and 320 K, *J. Geophys. Res.*, 112, D10216, 2007.
- Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. T.: Atmospheric reactions of the HO₂ radical studied by laser magnetic resonance spectroscopy, *Proc. R. Soc. Lond. A*, 368, 463–481, 1979.
- Finlayson-Pitts, B. J. and Pitts Jr., J. N., and references therein: *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, CA, USA, 2000.
- Friend, J. P., Barnes, R. A. and Vasta, R. M.: Nucleation by free-radicals from the photo-oxidation of sulfur-dioxide in air, *J. Phys. Chem.*, 84, 2423–2436, 1980.
- Gleason, J. F., Sinha, A., and Howard, C. J.: Kinetics of the gas-phase reaction HOSO₂+O₂→HO₂+SO₃, *J. Phys. Chem.*, 91, 719–724, 1987.
- Hanson, D. R. and Eisele, F.: Diffusion of H₂SO₄ in humidified nitrogen: Hydrated H₂SO₄, *J. Phys. Chem. A*, 104, 1715–1719, 2000.
- Hoffmann T., Bandur, R., Marggraf, U., and Linscheid, M.: Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: Implications for new particle formation processes, *J. Geophys. Res.*, 103, 25 569–25 578, 1998.
- Howard, C., Communication at the 17th Symposium on Free Radicals, Granby, 1985; see ref. (11) in: Discharge flow measurements of the rate constants for the reactions OH+SO₂+He and HOSO₂+O₂ in relation with the atmospheric oxidation of SO₂, edited by: Martin, D., Jourdain, J. L., and LeBras, G., *J. Phys. Chem.*, 90, 4143–4147, 1986.
- Jayne, J. T., Pöschl, U., Chen, Y. M., Dai, D., Molina, L. T., Worsnop, D. R., Kolb, C. E., and Molina, M. J.: Pressure and temperature dependence of the gas-phase reaction of SO₃ with H₂O and the heterogeneous reaction of SO₃ with H₂O/H₂SO₄ surfaces, *J. Phys. Chem.* 101, 10000–10011, 1997.
- Kolditz, L.: *Anorganische Chemie*, Deutscher Verlag der Wissenschaften, Berlin, 461–482, 1983.
- Kulmala, M., Laaksonen, A., and Pirjola, L.: Parameterization for sulphuric acid/water nucleation rates, *J. Geophys. Res.*, 103, 8301–8307, 1998.
- Kulmala, M., Pirjola, L., and Makela, J. M.: Stable sulphate cluster as a source of new atmospheric particles, *Nature*, 404, 66–69, 2000.
- Kulmala, M.: How particles nucleate and grow, *Science*, 302, 1000–1001, 2003.
- Martin, L. R. and Damschen, D. E.: Aqueous Oxidation of Sulfur Dioxide by Hydrogen Peroxide at Low pH, *Atmos. Environ.*, 15, 1615–1621, 1981.
- Laaksonen, A., Kulmala, M., Berndt, T., Stratmann, F., Mikkonen, S., Ruuskanen, A., Lehtinen, K. E. J., Dal Maso, M., Aalto, P., Petäjä, T., Riipinen, I., Sihto, S.-L., Janson, R., Arnold, F., Hanke, M., Ücker, J., Umann, B., Sellegri, K., ODowd, C. D., and Viisanen, Y., *Atmos. Chem. Phys. Discuss.*, 8, 9673–9695, 2008, <http://www.atmos-chem-phys-discuss.net/8/9673/2008/>.
- Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M., Ballenthin, J. O., and Lait, L. R.: *Science*, 301, 1886–1889, 2003.
- Lovejoy, E. R., Hanson, D. R., and Huey, L. G.: Kinetics and products of the gas-phase reaction of SO₃ with water, *J. Phys. Chem.*, 100, 19911–19916, 1996.
- Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulphuric acid and water, *J. Geophys. Res.*, 109, D08204, doi:10.1029/2003JD004460, 2004.
- Martin, D., Jourdain, J. L., and LeBras, G.: Discharge flow measurements of the rate constants for the reactions OH+SO₂+He and HOSO₂+O₂ in relation with the atmospheric oxidation of SO₂, *J. Phys. Chem.*, 90, 4143–4147, 1986.
- McMurry, P. H., Fink, M., Sakurai, H., Stolzenburg, M. R., Mauldin III, R. L., Smith, J., Eisele, F., Moore, K., Sjostedt, S., Tanner, D., Huey, L. G., Nowak, J. B., Edgerton, E., and Voisin, D.: A criterion for new particle formation in the sulfur-rich Atlanta atmosphere, *J. Geophys. Res.*, 110, D22S02, doi:10.1029/2005JD005901, 2005.
- Payne, W. A., Stief, L. J., and Davis, D. D.: A Kinetics Study of the Reaction of HO₂ with SO₂ and NO, *J. Am. Chem. Soc.*, 95, 7614–7619, 1973.
- Penzhorn, R. D. and Canosa, C. E.: 2nd Derivative UV Spectroscopy Study of the Thermal and Photochemical Reaction of NO₂ with SO₂ and SO₃, *Ber. Bunsen Phys. Chem.*, 87, 648–654, 1983.
- Reid, R. C., Prausnitz, J. M., and Poling, B. E.: *The Properties of Gases and Liquids*, McGraw-Hill, New York, 11, 1–20, 1987.
- Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. F. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyttälä, *Atmos. Chem. Phys.*, 7, 1899–1914, 2007, <http://www.atmos-chem-phys.net/7/1899/2007/>.
- Stockwell, W. R. and Calvert, J. G.: The mechanism of the HO-SO₂ reaction, *Atmos. Environ.*, 17, 2231–2235, 1983.

- Wayne, R.: Chemistry of Atmospheres, Clarendon Press, Oxford, 242–245, 1991.
- Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, Chem. Eng. Comm., 151, 53–64, 1996.
- Young, L.-H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H₂SO₄/H₂O binary homogeneous nucleation from the SO₂+OH reaction: evaluation of the experimental setup and preliminary results, Atmos. Chem. Phys., 8, 4997–5016, 2008, <http://www.atmos-chem-phys.net/8/4997/2008/>.
- Yu, F., Turco, R. P., and Kärcher, B.: The possible role of organics in the formation and evolution of ultrafine aircraft particles, J. Geophys. Res., 104, 4079–4087, 1999.
- Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric New Particle Formation Enhanced by Organic Acids, Science, 304, 1487–1489, 2004.