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Atmospheric Chemistry and Physics Discussions

SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications

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Abstract

Atmospheric new particle formation is generally thought to occur due to homogeneous or ion-induced nucleation of sulphuric acid. We compare ambient nucleation rates with laboratory data from nucleation experiments involving either sulphuric acid or oxidized SO_2. Atmospheric nucleation occurs at H_2SO_4 concentrations 2–4 orders of magnitude lower than binary or ternary H_2SO_4 nucleation. In contrast, the atmospheric nucleation rates and H_2SO_4 concentrations are very well replicated in the SO_2 oxidation experiments. We explain these features by the formation of free HSO_5 radicals in pace with H_2SO_4 during the SO_2 oxidation. We suggest that at temperatures above ~250 K these radicals produce nuclei of new aerosols much more efficiently than H_2SO_4. These nuclei are activated to further growth by H_2SO_4 and possibly other trace species. However, at lower temperatures the atmospheric relative acidity is high enough for the H_2SO_4–H_2O nucleation to dominate.

1 Introduction

The formation of aerosol particles in atmospheric nucleation events is a source of cloud condensation nuclei (CCN) (Laaksonen et al., 2005; Komppula et al., 2005) missing from most current climate models, and constitutes therefore a considerable uncertainty in climate change predictions. The new particle formation is generally thought to occur due to homogeneous or ion-induced nucleation of sulphuric acid (H_2SO_4) (Kulmala, 2003) formed in oxidation of sulphur dioxide (SO_2). However, it has so far remained unclear why the binary classical nucleation theory (CNT) seems to explain ambient observations of nucleation above the altitude of 4 km (Weber et al., 1999) as well as laboratory nucleation experiments with vaporized sulphuric acid (Ball et al., 1999; Zhang et al., 2004), but severely underpredicts nucleation below 4 km (Weber et al., 1999) and in laboratory experiments involving oxidized SO_2 (Friend et al., 1980; Berndt et al. 2005, 2006).

A further puzzle related to boundary layer nucleation events was noticed by Weber et al. (1996), who compared particle formation rates with the measured gas-phase concentrations of sulphuric acid, and deduced that the dependence is consistent with a mechanism in which the rate of appearance of new particles is proportional to the rate of sulphuric acid - sulphuric acid collisions in the gas. However, in the boundary layer, clusters containing just two H_2SO_4 molecules should not be stable even if the possibility of immediate association of water molecules is allowed for. As a solution to the problem it has been suggested that other associated molecules such as ammonia (Weber et al., 1996; Ball et al., 1999; Kulmala et al., 2000) or organic acids (Zhang et al., 2004) may have a stabilizing effect on the clusters. However, Berndt et al. (2005, 2006) recently presented measurements on particle formation in a flow chamber in which mixtures of SO_2 gas and water vapour were irradiated with UV light. The nucleation occurred at calculated sulphuric acid concentrations approximately three orders of magnitude lower than nucleation from H_2SO_4 itself. Experiments in the absence of UV light (dark reaction) showed exactly the same results indicating that irradiation itself does not influence new particle formation. This observation is qualitatively in good accord with the similar, long overlooked experiments of Friend et al. (1980).

In this paper, we compare atmospheric observations to various laboratory datasets of nucleation involving sulphuric acid or its precursors, and other substances. We suggest, in line with the companion paper (Berndt et al., 2008), a chemical mechanism that could explain the seemingly conflicting experimental results, and examine an atmospheric nucleation dataset for possible influences by other than sulphur-containing compounds. Finally, we synthesize our results, and offer a potential solution as to why the binary CNT produces better predictions of upper tropospheric than boundary layer nucleation.

2 Atmospheric and laboratory nucleation

2.1 Determination of atmospheric nucleation rates

Atmospheric nucleation rates were measured during 10 nucleation events during the spring 2003 QUEST measurement campaign in Hyytiälä, Finland. The atmospheric nucleation rate is obtained from particle size distribution measurements that were carried in 10 min intervals during the campaign. The primary quantity we obtain is the 3 nm particle appearance rate (J_3), determined from the increase of 3–6 nm particle concentrations between the measurement cycles, taking account of coagulational losses, and the flow of particles out of this size range as they grow by condensation of supersaturated vapors (Dal Maso et al., 2005). The actual nucleation rate, on the other hand, is the rate of critical cluster (diameter ~1.5 nm) formation. We therefore also calculated the 1.5 nm particle formation rates ($J_{1.5}$) from the J_3 data by accounting for the observed particle growth rates and coagulation of 1.5–3 nm particles with larger aerosols (Kerminen et al., 2002). The 1.5 nm particle formation rate is taken to represent atmospheric nucleation rate.

2.2 Laboratory experiments

Laboratory experiments were carried out in order to extend the results of Berndt et al. (2005; 2006) on nucleation induced by SO_2 oxidation to lower temperatures. The experiments have been performed at atmospheric pressure in the IfT-LFT (Institute for Tropospheric Research – Laminar Flow Tube, i.d. 8 cm; length 505 cm) (Berndt et al., 2004). The first tube section (56 cm) includes an inlet system for gas entrance, the middle section (344 cm) is equipped with 8 UV lamps for a homogeneous irradiation and at the non-irradiated end section (105 cm) the sampling outlets are attached. The analysis of the gas-phase species and the particles produced has been performed using an on-line GC-FID (HP 5890) with a cryo-enrichment unit for volatile hydrocarbons, an ultra-fine particle counter (TSI 3025) for integral particle measurements, and a dif-

ferential mobility particle sizer (Vienna-type DMA with UCPC, TSI 3025) for monitoring of size distributions. The carrier gas consisted of 99 vol% N_2 (99.9999999%, Linde and further purification with Gate Keeper, AERONEX) and 1 vol% O_2 (99.9996 %, Linde) used for O_3 generation outside the flow tube. SO_2 was taken from a 1ppmv calibration mixture in N_2 (Messer). The total gas flow was 3.6 l min^{-1} resulting in a bulk residence time of 420 s. Furan was added for OH radical titration. With knowledge of the amount of reacted furan and the initial concentrations for SO_2 and furan, the concentration of reacted SO_2 and the formed H_2SO_4 (assuming a H_2SO_4 yield of unity) can be easily calculated (Berndt et al., 2005).

The measured temperature dependent data was used to obtain estimates for the corresponding particle formation rates at atmospheric temperatures. This was done by fitting a line to the (T, log$J$) – data (see Fig. 1), where J refers to the particle formation rates observed in the measurements. The slope of the fitted curve (k=–0.2217 K^{-1}) was used to scale the measured particle formation rates to T=273 K. In our extrapolation we assumed an exponential relationship between the particle formation rates and temperature. The physical reasoning behind this assumption is that the formation rates are likely to depend on the saturation vapour pressures of the condensing species which show an exponential relationship with temperature.

2.3 Comparison atmospheric and laboratory nucleation rates

To investigate how the laboratory data compare with atmospheric nucleation rates we plotted the nucleation rate as a function of H_2SO_4 concentration in Fig. 2. It can be seen that the atmospheric data points (Sihto et al., 2006) are situated more or less in between the Friend et al. (1980) and Berndt et al. (2005, 2006) laboratory data sets. Uncertainties in the laboratory data on SO_2 induced nucleation include possible errors in calculated H_2SO_4 concentrations due to uncertain chemical mechanisms and not well defined wall losses of H_2SO_4; uncertainty in nucleation rate due to uncertain effective volume inside the flow chamber where nucleation occurred; and possible effects from gaseous impurities. We note that the nucleation rates of Berndt et al. (2005, 2006)

are minimum values as nucleation has been assumed to occur effectively throughout the irradiated region of the flow tube, and it is not impossible that the true rate is by up to an order of magnitude higher. On the other hand, the laboratory measurements have been performed at 293 K and the ambient measurements between 263–281 K. Taking into account laboratory data regarding the temperature dependence of nucleation (Fig. 1), we extrapolated the laboratory nucleation rates measured at 28% relative humidity (RH) to 273 K obtaining very good compatibility with the ambient data (see blue line in Fig. 1). It should be noted, however, that the slope of the extrapolated laboratory data appears somewhat steeper than that of the ambient dataset.

Figure 2 also shows two datasets of measured nucleation rates for the H_2SO_4-H_2O system both with and without a third species, which in the case of the Ball et al. (1999) measurements is ammonia and in the case of the Zhang et al. (2004) measurements is organic acids. It is clearly seen that although these species enhance the nucleation rate somewhat, the enhancement is completely inadequate to explain the atmospheric nucleation rates. This conclusion holds even if the temperature dependence of the ternary nucleation is accounted for: using the classical nucleation theory temperature dependence calculated by Napari et al. (2002) for sulphuric acid-ammonia-water, and extrapolating at constant nucleation rate from room temperature (corresponding to the ternary experiments in Fig. 2) down to around 270 K, it can be seen that the ternary curves will not come down more than two orders of magnitude in sulphuric acid concentration (besides, the experiments of Ball et al. (1999) were carried out at higher ammonia concentrations (80–170 ppt) than are usually found in Hyytiälä). All of this is in accord with the conclusion of Yu (2006), who noted that the classical ternary nucleation predicts close to 30 orders of magnitude too high nucleation rates compared with those measured by Ball et al. (1999).

The remaining dataset in Fig. 2, by Sorokin and Arnold (2007) shows results of ion-induced nucleation of sulphuric acid at 295 K (the different lines are for different sized ions). As with ammonia and organic acids, it appears that ions enhance the nucleation but not enough to explain atmospheric nucleation. The puzzling feature with

the Sorokin-Arnold data is that the sulphuric acid in their experiments was produced by oxidizing SO_2, hence one would expect closer agreement with the Friend et al. (1980) and Berndt et al. (2005, 2006) experiments rather than with the Ball et al. (1999) and Zhang et al. (2004) experiments. We show below that this apparent paradox can be resolved by accounting for the low total pressure (80 hPa) employed by Sorokin and Arnold (2007).

2.4 Analysis of atmospheric nucleation data

The scatter of the atmospheric nucleation rates in Fig. 2 originates from variations in temperature and RH and from measurement uncertainties (e.g. variations in aerosol size distributions caused by other factors than nucleation). Additionally, unknown species participating in the nucleation with varying contributions may have an effect. To this end, we analyzed our ambient nucleation rates using multivariate regression analysis to determine if various trace species participate in the nucleation.

The starting point of our analysis is the nucleation theorem, which can be written as $(\partial \ln(J)/\partial \ln(A_i))_{T,Aj}=n_i+\Delta_i$, where J denotes nucleation rate, A_i is the gas-phase activity (partial pressure divided by saturation vapour pressure) of species i, n_i is the number of molecules in the critical nucleus, and Δ_i is a small term originating from kinetic terms describing vapour molecule collisions with the nucleus (the sum of the individual Δ_i's is between 0 and 1; Oxtoby and Kaschiev, 1994). It has been shown using both thermodynamic (Oxtoby and Kaschiev, 1994) and statistical mechanical (MacDowell, 2003) arguments that the nucleation theorem is a very general relation that extends down to the smallest cluster sizes and holds independently of any specific nucleation theories.

In order to apply the nucleation theorem, one should determine the slope of nucleation rate as a function of the gas-phase concentration of the species in question at constant temperature and gas phase concentrations of other species participating in the nucleation process. However, we do not have enough data of atmospheric nucleation rates to obtain meaningful correlations at narrow temperature and gas concentra-

tion intervals. Furthermore, it is not certain that we know all of the species participating in the nucleation. We therefore apply nonlinear regression analysis based on nucleation theory in order to obtain information on the nucleating species.

The nucleation rates $J_{1.5}$ and J_3 were the dependent variables in the regression models. The set of independent variables consisted of gaseous H_2SO_4, NH_3, H_2O and NO_x (other meteorological and chemical variables were also tested but no improvement in statistical significance was found). The values of the nucleation rate J_3 were advanced in time by the amount of estimated growth time between 1.5 and 3 nm in comparison to the independent variables. The same model was computed for both $J_{1.5}$ and J_3.

The multiple regression equation used in our analysis is

$$\ln(J_i) = \beta_0 + \left(\beta_{1+} + \beta_{1-}\right)\ln(H_2SO_4) + (\beta_2)\ln(NOx) + \left(\beta_{3+} + \beta_{3-}\right)\ln(NH_3) + (\beta_4)\ln(H_2O) + \varepsilon,$$

where β_0 is the intercept, $\beta_1, \ldots, \beta_4$ are the regression coefficients and ε describes the zero-mean normally distributed and uncorrelated error terms. NO_x denotes gas phase concentration, and the other quantities inside the logarithms are gas-phase activities of the respective species. As suggested by a self-organising map analysis in which the data was seen to separate into two clusters distinguished by temperatures below and above freezing, respectively, the regression coefficients β_1 and β_3 were taken to depend on the temperature such that the slopes are different for temperatures of below and over 0°C. This division improved the statistical significance of the model.

The regression coefficients, standard errors of the coefficients, t-statistics and associated p-values are shown in Table 1 for $J_{1.5}$. With the exception of NO_x, the regression coefficients of the model for $J_{1.5}$ should represent the apparent numbers of molecules contained by the critical nucleus. As can be seen from Table 1, the regression model suggests that the critical nucleus contains possibly one sulphuric acid related molecule (the regression coefficient is only 0.3 at subzero temperatures, but its statistical significance is somewhat lower than that of the higher temperature regression coefficient) and no ammonia. Additionally, water vapour has a negative and NO_x a positive influ-

ence on nucleation. The regression coefficients of the J_3-model are qualitatively similar although small quantitative differences are seen.

Note, that the negative influence of water vapour on new particle formation is in line with previous observations that nucleation events occur more frequently at dry conditions (Boy and Kulmala, 2002). It has been shown that water vapour inhibits the formation of condensable organic species formed in ozonolysis (Bonn and Moortgat, 2002, Bonn et al., 2002) that may be involved in new particle formation.

In order to see whether monoterpene oxidation products (MTOP) participate in the nucleation, we repeated the regression modelling with just two independent variables, H_2SO_4 and MTOP (Sellegri et al., 2005) concentrations. (Here, we were not able to use activity for MTOP, and for consistency we chose to use concentration for sulphuric acid as well. Note that we did not include MTOP in the above multiple regression analysis because both water vapour and NO_x appeared to be correlated with MTOP, thus all three would not have been independent variables. Because there was much less data of MTOP compared with the other gases, we left MTOP out.) The results are shown in Table 2. H_2SO_4 now shows statistically significant regression coefficients both below and above freezing, with values somewhat above unity. This is consistent with studies which have indicated one to two sulphuric acid molecules in the critical cluster (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007). At subzero temperatures MTOP shows a statistically significant regression coefficient close to unity, indicating possible organic contribution to nucleation. However, at higher temperatures this indication disappears.

3 Suggested nucleation mechanism

3.1 Chemistry

Taken together, the results from Sect. 2 above indicate that ammonia and monoterpene oxidation products play only a minor role (if any) in Boreal nucleation events, and cer-

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tainly cannot enhance binary nucleation enough to explain them. On the other hand, the SO_2 induced laboratory nucleation appears to be in quite close agreement with the atmospheric data. Here we provide a possible explanation for this agreement.

To explain their observations, Friend et al. (1980) suggested in the beginning of the 1980's a mechanism involving the formation of the free radicals HSO_3 and HSO_5 as SO_2 is oxidized by OH radicals in the presence of water vapor. Collisions of these sulphur-containing radicals would then result in the formation of stable clusters consisting of $H_2S_2O_6$ or $H_2S_2O_8$ probably associated with water molecules. The currently accepted mechanism of atmospheric SO_2 oxidation is as follows (Finlayson-Pitts and Pitts Jr., 2000):

$$OH + SO_2 \rightarrow HSO_3 \tag{1}$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{2}$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \tag{3}$$

The reaction of HSO_3 with O_2 is very fast (Gleason et al., 1987) resulting in atmospheric steady state concentrations for HSO_3 of $\sim$0.05 molecule cm^{-3} ((OH)=10^6 and (SO_2)=10^{11} molecule cm^{-3}). In competition to the stated reaction products of pathway (2), SO_3 and HO_2, also the formation of the addition product HSO_5 has to be considered:

$$HSO_3 + O_2 + M \rightarrow HSO_5 + M. \tag{2a}$$

Stockwell and Calvert (1983) found as a result of their experiments that more than 80% of initial OH radicals are regenerated as HO_2 radicals in pathway (2), whereas the work of Schmidt et al. (1985) indicates that at atmospheric pressure, the loss of OH radicals via pathway (2a) is less than 10%. That points at a dominance of pathway (2) over (2a) but does not exclude that HSO_5 is produced in substantial fractions. HSO_5 is a peroxy radical and its hydrated form could initiate the nucleation process (Wayne,

1991) rather than HSO_3. This fact is especially caused by the expected higher atmospheric concentration of HSO_5 (note that gas-phase HSO_5 has not been directly observed). In the atmosphere, HSO_5 can react with other atmospheric species such as other peroxy radicals, and we suggest that these reaction products act as the critical clusters triggering atmospheric nucleation. Gaseous H_2SO_4 is formed in the SO_2 oxidation process via pathways (2) and (3) in pace with the sulphur-containing radicals via pathway (2a) or pathway (1), partially explaining the apparent dependence of the nucleation rate on H_2SO_4 concentration. The companion paper (Berndt et al. 2008) provides experimental support for reaction (2a) to be operational and offers further discussion of the chemical mechanisms possibly contributing to new particle formation.

As an alternative explanation of the results of Friend et al. (1980), McGraw (1982) suggested that the data might be an artifact produced by sulphuric acid vapour nucleating inside the particle detector (where the RH was 300%). However, this cannot have been the case with the Berndt et al. (2005, 2006) results (where the particle detector used butanol as working fluid). As the Friend et al. (1980) and Berndt et al. (2005, 2006) data are in rather good agreement especially at high RH, it is likely that the free radical nucleation mechanism is the correct explanation of the experimental results.

To explain the experimental result of Sorokin and Arnold (2007) who found nucleation rates consistent with sulphuric acid nucleation rather than the radical nucleation despite the fact that they produced the H_2SO_4 by oxidizing SO_2, we note that reaction (2a) is possible only in the presence of sufficient concentration of inert molecules whose collisions with the reactants ensure that excess energy is carried away and the product is stable. Apparently the 80 hPa total pressure employed by Sorokin and Arnold (2007) is too low for the HSO_5 radical production to lead to nucleation, and new particles can only form once enough H_2SO_4 has accumulated in the air to nucleate without the radicals. In the atmosphere, the efficiency of the radical production will decrease as a function of altitude (the 80 hPa pressure corresponds roughly to an altitude of 17 km) while the efficiency of H_2SO_4 nucleation will increase (because for fixed acid concentration, the relative acidity increases as temperature decreases). Note that the

work of Gleason et al. (1987) indicates that the reaction pathway (2a) is negligible at pressures below 10 hPa.

3.2 Activation and growth

It should be noted that regardless of their exact chemical composition, the reaction products from sulphur radical recombination are too small to be directly detected by the aerosol instruments used by Berndt et al. (2005, 2006) which have a lower detection limit at roughly 3 nm in particle diameter. Hence, the molecules need to grow into detectable sizes to be counted as particles. Our nucleation experiments at different temperatures indicate that this growth is due to condensation of sulphuric acid (probably together with water vapor), and that the growth is activated, i.e. triggered by heterogeneous nucleation (Kulmala et al., 2006). The reason for this conclusion is that if the new particle formation was governed solely by gas-phase reactions and molecular collisions of the reaction products, the nucleation rate should increase as a function of temperature, but we observe a decreasing trend. This decreasing trend is explained by the fact that the probability of heterogeneous nucleation of sulphuric acid on sulphur radical reaction products decreases as a function of H_2SO_4 relative acidity, which in turn decreases as a function of temperature at fixed H_2SO_4 concentration. Note that it is possible that in the atmosphere also other vapors than H_2SO_4 and water contribute to the heterogeneous nucleation.

In order to analyze the water content of critical nuclei in the laboratory experiments, we examined the slope of the nucleation rate versus RH on logarithmic scales, at fixed H_2SO_4 concentration. According to the nucleation theorem this slope very nearly gives the molecular content of the critical nucleus. The resulting numbers of water molecules were 2 for the experiments of Friend et al. (1980) and 4 for the experiments of Berndt et al. (2005, 2006). This difference causes the two experimental data sets to diverge more at drier conditions (see Fig. 1). A likely explanation for the overall discrepancies in the two data sets is the difference in particle detection efficiences. Friend et al. (1980) used a condensation nucleus counter in which the particles were made to

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grow by condensation of water vapour at 300% RH. It is conceivable that at such high supersaturation, already the sulphur radical reaction products may grow to detectable sizes. As noted above, Berndt et al. (2005, 2006) were not able to detect all of the sulphur radical reaction products, but only the fraction of them which was activated to grow to 3 nm by condensation of H_2SO_4 and water vapors.

4 Atmospheric consequences

To summarize the suggested new particle formation mechanism, we propose that (1) sulphur radicals are formed in parallel with H_2SO_4 in the SO_2 oxidation process; (2) the sulphur radicals react (possibly in hydrated form) with as yet unspecified atmospheric species; (3) H_2SO_4 vapour nucleates heterogeneously on the reaction products, starting condensational growth of the new particles. Note that it depends on the relative acidity of the H_2SO_4 vapour whether just a fraction or all of the reaction products nucleate heterogeneously (or "activate"). Thus, at constant H_2SO_4 vapour concentration, there will be some temperature at which all available nuclei will be activated, and at colder conditions the nucleation rate should thus no more depend on temperature.

Figure 3 shows calculations for classical homogeneous H_2SO_4-H_2O nucleation, and for nucleation of H_2SO_4 on pre-existing nuclei. The latter is described using so called activation nucleation mechanism (Kulmala et al., 2006), where the activation coefficient contains information of the nucleus concentrations and their sizes. The production of nuclei from the sulphur radicals followed by their activation by H_2SO_4 is consistent with this theory; however, since we do not know the sulphur radical production rate or the size of the nuclei, we fixed the activation coefficient to fit atmospheric nucleation rate data (Sihto et al., 2006). As shown in Fig. 3, the activation mechanism is more efficient than binary homogeneous nucleation at low sulphuric acid concentrations and at high temperatures. This is consistent with practically all available nucleation data both from laboratory experiments and from the atmosphere, and may explain the finding of Weber et al. (1999) that binary classical nucleation theory seems to explain observations

above the altitude of about 4 km, but not below.

5 Conclusions

By comparing an ambient nucleation dataset (particle formation rate vs. sulphuric acid concentration) with several different laboratory datasets, we come to the conclusion that sulphuric acid vapour produced by evaporating liquid H_2SO_4 is not capable of nucleating at as low concentrations as is observed in the atmosphere, regardless of whether or not ammonia or organic acids are participating in the nucleation. In contrast, laboratory data from nucleation experiments involving oxidized SO_2 seems to be in quite close agreement with atmospheric nucleation, in the sense that particle formation occurs at similar H_2SO_4 concentrations. We suggest that a solution to this apparent paradox is the role of sulphur radicals produced during SO_2 oxidation. In particular, we hypothesize that HSO_5 radicals are formed in a reaction between HSO_3 and O_2 in the presence of sufficient concentration of inert molecules whose collisions stabilize the reaction product. Experimental support for such a mechanism is given in the companion paper (Berndt et al., 2008). We further suggest that the HSO_5 radicals will react with other trace species, and that the resulting molecules act as nuclei for heterogeneous nucleation of H_2SO_4 vapour which will initiate the growth of the new particles. The suggested new particle formation mechanism is consistent with the so-called activation type nucleation (Kulmala et al., 2006), and may provide an explanation for the finding that binary sulphuric acid nucleation seems to explain upper tropospheric particle formation but not the boundary layer nucleation events.

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References

Ball, S. M., Hanson, D. R., Eisele, F. I., and. McMurry P. H.: Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104, 23 709–23 718, 1999.

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 H_2SO_4/H_2O particles in the absence of organics: A laboratory study, Geophys. Res. Lett, 33, L15817, doi:10.1029/2006GL026660, 2006.

Berndt, T., Stratmann,, F., Bräsel, S., Heintzenberg, J., Laaksonen, A., and Kulmala M.: SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation. Part 1: Laboratory investigations, Atmos. Chem. Phys. Discuss., accepted, 2008.

Finlayson-Pitts, B. J. and Pitts Jr., J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications. Academic Press, San Diego, CA, 2000.

Friend, J. P., Barnes, R. A., and Vasta, R. M.: Nucleation by free radicals from the photooxidation 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 $HOSO_2+O_2 \rightarrow HO_2+SO_3$, J. Phys. Chem., 91, 719–724, 1987.

Komppula, M., Lihavainen, H., Kerminen, V.-M., Kulmala, M., and Viisanen Y.: Measurements of cloud droplet activation of aerosol particles at a clean subarctic background site, J.Geophys. Res. 110, D06204, doi: 10.1029/2004JD005200, 2005.

Kulmala, M., Pirjola, L., and Mäkelä, J. M.: Stable sulfate clusters as a source of new atmospheric particles, Nature, 404, 66–69, 2000.

Kulmala, M.: How particles nucleate and grow, Science, 302, 1000–1001, 2003.

Kulmala, M., Lehtinen K. E. J., and Laaksonen A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, 2006, http://www.atmos-chem-phys.net/6/787/2006/.

Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W., Asmi, A., Fuzzi, S., and Facchini M.C.: Cloud condensation nucleus production from nucleation events at a highly polluted region, Geophys. Res. Lett., 32, L06812, doi:10.1029/2004GL022092, 2005

McGraw, R., Condensation nuclei production from sulfur dioxide photooxidation in air, J. Phys. Chem., 86, 2750–2752, 1982.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiälä, Atmos. Chem. Phys., 7, 1899–1914, 2007, http://www.atmos-chem-phys.net/7/1899/2007/.

Schmidt, V., Zhu, G. Y., Becker H., and Fink, E. H.: Study of OH reactions at high pressures by excimer laser photolysis – dye laser fluorescence, Ber. Bunsenges. Phys. Chem., 89, 321–322, 1985.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, 2006, http://www.atmos-chem-phys.net/6/4079/2006/.

Sorokin, A. and Arnold, F.: Laboratory study of cluster ions formation in H_2SO_4-H_2O system: Implications for threshold concentration of gaseous H_2SO_4 and ion-induced nucleation kinetics, Atmos. Environ., 41, 3740–3747, 2007.

Stockwell, W. R. and Calvert, J. G.: The mechanism of the HO-SO_2 reaction, Atmos. Environ., 17, 2231–2235, 1983

Vehkamäki H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res. 107, 4622, doi:10.1029/2002JD002184, 2002

Wayne, R. P.: Chemistry of Atmospheres. Clarendon Press, Oxford, 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. Commun., 151, 53–64, 1996.

Weber, R. J., McMurry, P. H., Mauldin III, R. L., Tanner, D. J., Eisele, F. L., Clarke, A. D., and Kapustin, V. N.: New particle formation in the remote troposphere: A comparison of observations at various sites, Geophys. Res. Lett., 26, 307–310, 1999.

Yu, F.: Effect of ammonia on new particle formation: A kinetic H2SO4-H2O-NH3 nucleation model constrained by laboratory measurements, J. Geophys Res., 111, D0124, doi:

10.1029/2005JD005968, 2006.
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, 1487–1490, 2004.

Table 1. Regression coefficients, standard errors of coefficients, *t*-statistics and *p*-values for the regression model for $J_{1.5}$. The quantities inside the logarithms are gas-phase activities of H_2SO_4, NH_3 and H_2O, and concentration of NO_x. Temp class indicates temperatures below (-1) or above (1) freezing, see text for details. Number of datapoints N=316, total coefficient of determination of the model R^2= 0.62.

Parameter	Temp. class	Estimate	Standard error	T value	Pr>|t|
Intercept		–18.3773	3.342251	–5.5	<.0001
$\ln(H_2SO_4)$	–1	0.328602	0.107866	3.05	0.0025
$\ln(H_2SO_4)$	1	1.23819	0.117383	10.55	<.0001
$\ln(NO_x)$		1.248247	0.122765	10.17	<.0001
$\ln(NH_3)$	–1	0.215609	0.051582	4.18	<.0001
$\ln(NH_3)$	1	–0.2435	0.047734	–5.1	<.0001
$\ln(H_2O)$		–1.19574	0.283201	–4.22	<.0001

Table 2. Regression coefficients, standard errors of coefficients, t-statistics and p-values for the regression model for $J_{1.5}$. The quantities inside the logarithms are gas-phase concentrations of H_2SO_4 and MTOP. Temp class indicates temperatures below (–1) or above (1) freezing, see text for details. Number of datapoints N=242, total coefficient of determination of the model R^2=0.53.

Parameter	Temp. class	Estimate	Standard error	T value	Pr>|t|
Intercept		–22.6332	1.756077	–12.89	<.0001
ln(MTOP)	–1	0.854103	0.174733	4.89	<.0001
ln(MTOP)	1	0.028696	0.235999	0.12	0.9033
ln(H_2SO_4)	–1	1.271947	0.109553	11.61	<.0001
ln(H_2SO_4)	1	1.465547	0.168687	8.69	<.0001

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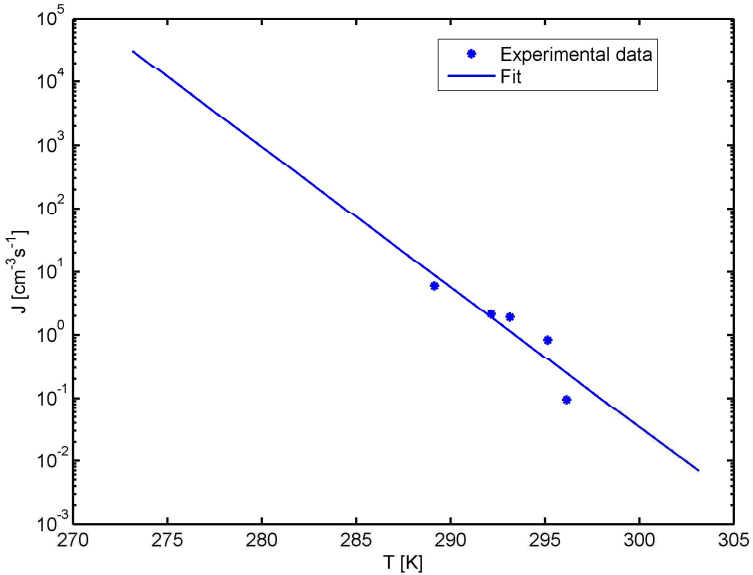

Fig. 1. Particle formation rates calculated from the particle number data for different temperatures in the flow tube (IfT-LFT) at r.h.=28% (asterisks) and the fitted line, which was used to extrapolate the temperature dependence to T=273 K.

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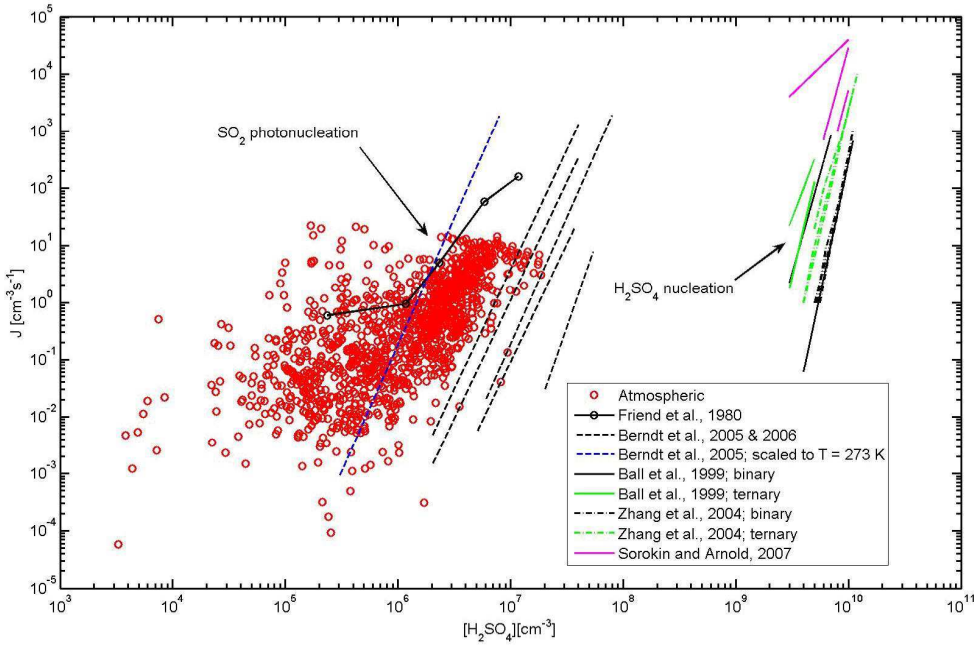

Fig. 2. Atmospheric nucleation rates (J), and nucleation rates from the experiments of Friend et al. (1980), Berndt et al. (2005, 2006), Ball et al. (1999), Zhang et al. (2004) and Sorokin and Arnold (2007) as a function of H_2SO_4 gas concentration. The RH's in the Friend et al. (1980) experiments were (from lowest data point) 1%, 5%, 10%, 25,%, 50%, and temperature was 298 K. The RH's of Berndt et al. (2005, 2006) were (from rightmost line) 11%, 22%, 28%, 42%, 60%, and temperature was 293 K. Additionally, we show nucleation rates extrapolated to 273 K at 28% RH based on the nucleation measurements of Berndt et al. (2005), and the temperature dependent measurements shown in Fig. 1. The atmospheric nucleation rates were calculated from aerosol size distribution data recorded with a 10 min time resolution, and the atmospheric H_2SO_4concentrations were recorded using a chemical ionization mass spectrometer. During the nucleation events, temperatures and RH's varied roughly between 263–281 K and 35–85%, respectively. For the rest of the experimental lines, see main text.

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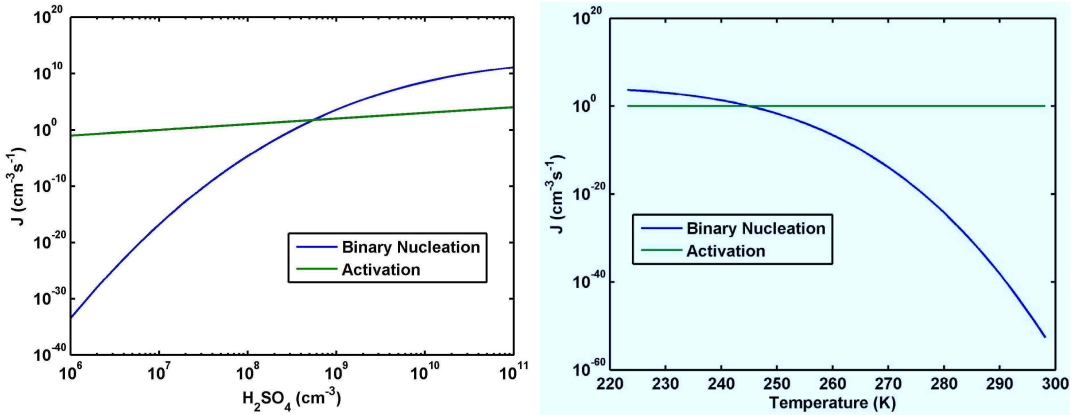

Fig. 3. Nucleation rates from activation theory (Kulmala et al., 2006) with an activation coefficient of $10^{-6}\,s^{-1}$ and binary classical nucleation theory (Vehkamäki et al., 2002). **(a)** Rates as a function of H_2SO_4 vapour concentration T=273 K. **(b)** Rates as a function of temperature, $(H_2SO_4)=10^7$. Note that the activation theory assumes that all nuclei are activated, thus there is no temperature dependence. In reality, J depends on T at least at temperatures above 288 K (see text for more details), but we expect this dependence to disappear at sufficiently low temperatures.