

# SO<sub>2</sub> oxidation products other than H<sub>2</sub>SO<sub>4</sub> as a trigger of new particle formation. Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications

A. Laaksonen<sup>1,7</sup>, M. Kulmala<sup>2</sup>, T. Berndt<sup>3</sup>, F. Stratmann<sup>3</sup>, S. Mikkonen<sup>1</sup>, A. Ruuskanen<sup>1</sup>, K. E. J. Lehtinen<sup>1,7</sup>, M. Dal Maso<sup>2</sup>, P. Aalto<sup>2</sup>, T. Petäjä<sup>2</sup>, I. Riipinen<sup>2</sup>, S.-L. Sihto<sup>2</sup>, R. Janson<sup>4</sup>, F. Arnold<sup>5</sup>, M. Hanke<sup>5</sup>, J. Ücker<sup>5</sup>, B. Umann<sup>5</sup>, K. Sellegri<sup>5,\*</sup>, C. D. O'Dowd<sup>6</sup>, and Y. Viisanen<sup>7</sup>

<sup>1</sup>University of Kuopio, Department of Physics, P.O. Box 1627, 70211 Kuopio, Finland

<sup>2</sup>University of Helsinki, Department of Physical Sciences, Helsinki, Finland

<sup>3</sup>Leibniz-Institut für Troposphärenforschung e.V., Permoserstraße 15, 04318 Leipzig, Germany

<sup>4</sup>Stockholm University, Department of Applied Environmental Science (ITM), Atmospheric Science Unit, 10691, Stockholm, Sweden

<sup>5</sup>Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany

<sup>6</sup>National University of Ireland, Galway, Department of Physics

<sup>7</sup>Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland

\* now at: Laboratoire de Météorologie Physique (LaMP), Observatoire de Physique du Globe de Clermont-Ferrand (OPGC), UMR 6016 CNRS, France

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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<sub>2</sub>. Atmospheric nucleation occurs at H<sub>2</sub>SO<sub>4</sub> concentrations 2–4 orders of magnitude lower than binary or ternary nucleation rates of H<sub>2</sub>SO<sub>4</sub> produced from a liquid reservoir, and atmospheric H<sub>2</sub>SO<sub>4</sub> concentrations are very well replicated in the SO<sub>2</sub> oxidation experiments. We hypothesize these features to be due to the formation of free HSO<sub>5</sub> radicals in pace with H<sub>2</sub>SO<sub>4</sub> during the SO<sub>2</sub> oxidation. We suggest that at temperatures above ~250 K these radicals produce nuclei of new aerosols much more efficiently than H<sub>2</sub>SO<sub>4</sub>. These nuclei are activated to further growth by H<sub>2</sub>SO<sub>4</sub> and possibly other trace species. However, at lower temperatures the atmospheric relative acidity is high enough for the H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O nucleation to dominate.

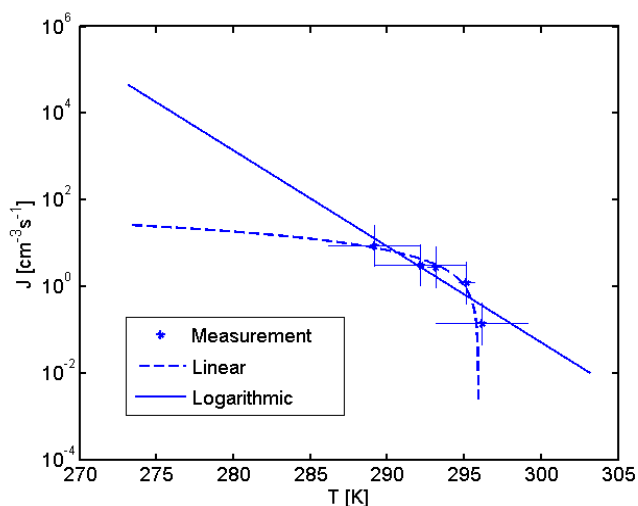
## 1 Introduction

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<sub>2</sub>SO<sub>4</sub>) (Kulmala, 2003) formed in oxidation of sulphur dioxide (SO<sub>2</sub>). 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<sub>2</sub> (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



Correspondence to: A. Laaksonen  
(ari.laaksonen@uku.fi)



**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 lines, which were used to extrapolate the temperature dependence to  $T=273$  K.

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  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  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 vaporized  $\text{H}_2\text{SO}_4$ . 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 out 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 coagulative 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  $\sim 1.5$  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

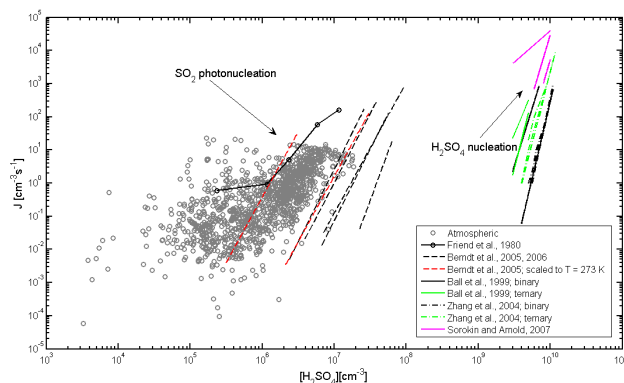
Laboratory experiments were carried out in order to extend the results of Berndt et al. (2005, 2006) on nucleation induced by  $\text{SO}_2$  oxidation to lower temperatures. The experiments have been performed at atmospheric pressure in the IFT-LFT (Institute for Tropospheric Research – Laminar Flow 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, a ultra-fine particle counter (TSI 3025) 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 99 vol%  $\text{N}_2$  (99.9999999%, Linde and further purification with Gate Keeper, AERONEX) and 1 vol%  $\text{O}_2$  (99.9996%, Linde) used for  $\text{O}_3$  generation outside the flow tube.  $\text{SO}_2$  was taken from a 1ppmv calibration mixture in  $\text{N}_2$  (Messer). The total gas flow was  $3.6 \text{ liter min}^{-1}$  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  $\text{SO}_2$  and furan, the concentration of reacted  $\text{SO}_2$  and the formed  $\text{H}_2\text{SO}_4$  (assuming a  $\text{H}_2\text{SO}_4$  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. Because the relevant

temperatures are quite a lot below the experimental range, we made two alternative extrapolations. The first 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 ( $k = -0.2217 \text{ K}^{-1}$ ) was used to scale the measured particle formation rates to  $T = 273 \text{ K}$ . In this 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. The second extrapolation was a simple linear fit to the dataset. As seen in Fig. 1, these two extrapolations result in about three orders of magnitude difference in the nucleation rate estimate at 273 K. This corresponds to a little less than one order of magnitude difference in  $\text{H}_2\text{SO}_4$  concentration (if the nucleation rate is kept constant). Quantitatively this is of course a notable difference, and additional experiments are needed to clarify the situation. However, as shown below, accounting for the temperature dependence will qualitatively result in better correspondence between the laboratory data and atmospheric data regardless of the mathematical form of the temperature dependence.

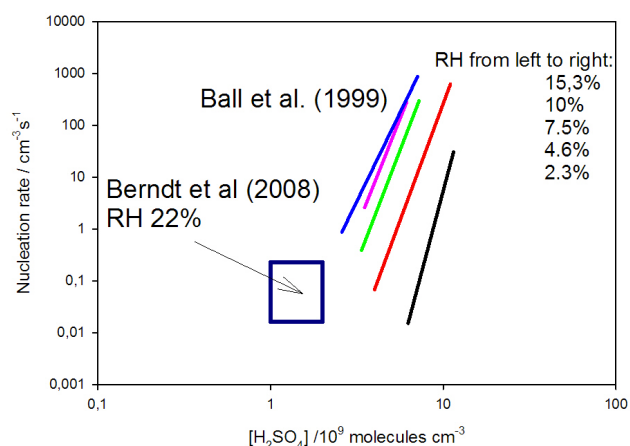
### 2.3 Comparison of atmospheric and laboratory nucleation rates

To investigate how the laboratory data compare with atmospheric nucleation rates we plotted the nucleation rate as a function of  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  induced nucleation include possible errors in calculated  $\text{H}_2\text{SO}_4$  concentrations due to uncertain chemical mechanisms and not well defined wall losses of  $\text{H}_2\text{SO}_4$ ; 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 better compatibility with the ambient data (see blue lines in Fig. 2). It should be noted, however, that the slope of the extrapolated laboratory data appears steeper than that of the ambient dataset.



**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  $\text{H}_2\text{SO}_4$  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 left red line corresponds to the exponential extrapolation and the right red line to the linear extrapolation shown in Fig. 1). The atmospheric nucleation rates (Sihto et al., 2006) were calculated from aerosol size distribution data recorded with a 10 min time resolution, and the atmospheric  $\text{H}_2\text{SO}_4$  concentrations 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.

Figure 2 also shows two datasets of measured nucleation rates for the  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  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 either by Napari et al. (2002) or by Merikanto et al. (2007) 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



**Fig. 3.** Binary homogeneous nucleation rates from vaporized  $\text{H}_2\text{SO}_4$ . See text for explanation.

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  $\text{SO}_2$ , hence one would expect close 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.

Sorokin and Arnold noted that the residence time (and hence also the nucleated cluster growth time toward the minimum detectable size limit) in the Berndt et al. (2005, 2006) experiments was 200 times longer than in their own experiments, and argued that the threshold sulphuric acid concentration for detection of nucleation should therefore be lower in the Berndt et al. experimental conditions. They furthermore calculated that their own threshold corresponds to a threshold  $[\text{H}_2\text{SO}_4]$  of  $4 \times 10^8$  at the Berndt et al. conditions, which is still considerably higher than the actual result of Berndt et al. (2005, 2006). We discuss below whether this apparent paradox can be resolved by accounting for the low total pressure (80 hPa) employed by Sorokin and Arnold (2007).

Note that we have not added in Fig. 2 the experimental results on the  $\text{SO}_2$ -derived nucleation from Part 1 (Berndt et al., 2008), which appear to indicate that the particle formation takes place at an order of magnitude higher  $\text{H}_2\text{SO}_4$  concentration than was reported by Berndt et al. (2005, 2006). This discrepancy appears to be caused by the different residence

times used in the experiments. In Part 1, the residence time was about one ninth of the residence time applied by Berndt et al. (2005, 2006). To be detected, the newly formed particles need to grow larger than the detection limit of the UCPC, about 2.5–3 nm in diameter. As the residence time is shortened, a smaller fraction of the nucleated particles have time to grow past this size range, and therefore too low particle concentrations (and nucleation rates) are observed. This residence time related problem (noticed recently also by Young et al., 2008) will be quantitatively probed in a future publication. (The Young et al., 2008, results were left out from Fig. 2 for precisely the same reason as the results from Part 1: different residence times as compared with Berndt et al. (2005, 2006).) Here we would like to point out two interesting consequences: First, it is possible that even in the experiments of Berndt et al. (2005, 2006), the residence time was too short, and a correction would cause to shift the lines shown in Fig. 2 to the left. Secondly, the correction would affect the lines more at lower  $\text{H}_2\text{SO}_4$  concentrations (because of slower particle growth), and thus the slopes of the lines would become gentler. Both effects would bring the data to better agreement with atmospheric observations.

Figure 3 shows the experimental result from Part 1 (Berndt et al., 2008) for binary homogeneous nucleation from vaporized sulphuric acid, and the experimental fits given by Ball et al. (1999). The Berndt et al. datapoint has quite large uncertainty ranges, stemming from the uncertainty ranges in  $\text{H}_2\text{SO}_4$  wall loss, and in nucleation volume inside the chamber. Nevertheless, it is clear from Fig. 3, that the datapoint is in agreement with the Ball et al. experiments, reinforcing our confidence on the proper operation of the Laminar Flow Tube.

#### 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  $(\partial \ln(J)/\partial \ln(A_i))_{T,A_j} = n_i + \Delta_i$ , 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  $\Delta_i$  is a small term originating from kinetic terms describing vapour molecule collisions with the nucleus (the sum of the individual  $\Delta_i$ '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

**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  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , and concentration of  $\text{NO}_x$ . The estimates for  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  represent numbers of molecules in critical cluster. 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
$\ln(\text{H}_2\text{SO}_4)$	-1	0.328602	0.107866	3.05	0.0025
$\ln(\text{H}_2\text{SO}_4)$	1	1.23819	0.117383	10.55	<.0001
$\ln(\text{NO}_x)$		1.248247	0.122765	10.17	<.0001
$\ln(\text{NH}_3)$	-1	0.215609	0.051582	4.18	<.0001
$\ln(\text{NH}_3)$	1	-0.2435	0.047734	-5.1	<.0001
$\ln(\text{H}_2\text{O})$		-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  $\text{H}_2\text{SO}_4$  and MTOP. The estimates for  $\text{H}_2\text{SO}_4$  represent numbers of molecules in critical cluster. 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
$\ln(\text{MTOP})$	-1	0.854103	0.174733	4.89	<.0001
$\ln(\text{MTOP})$	1	0.028696	0.235999	0.12	0.9033
$\ln(\text{H}_2\text{SO}_4)$	-1	1.271947	0.109553	11.61	<.0001
$\ln(\text{H}_2\text{SO}_4)$	1	1.465547	0.168687	8.69	<.0001

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 concentration 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  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_x$  (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

$$\ln(J_i) = \beta_0 + (\beta_{1+} + \beta_{1-}) \ln(\text{H}_2\text{SO}_4) + (\beta_2) \ln(\text{NO}_x) + (\beta_{3+} + \beta_{3-}) \ln(\text{NH}_3) + (\beta_4) \ln(\text{H}_2\text{O}) + \varepsilon,$$

where  $\beta_0$  is the intercept,  $\beta_1, \dots, \beta_4$  are the regression coefficients and  $\varepsilon$  describes the zero-mean normally distributed and uncorrelated error terms.  $\text{NO}_x$  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  $\beta_1$  and  $\beta_3$  were taken to depend on the temperature such that the slopes are different for temperatures of below and over  $0^\circ\text{C}$ . This division improved the statistical significance of the model. Note that temperature was found to be strongly correlated with sulphuric acid activity, and therefore we were not able to use it as an independent model variable.

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  $\text{NO}_x$ , 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 sub-zero 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  $\text{NO}_x$  a positive influence 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 (MTO) participate in the nucleation, we repeated the regression modelling with just two independent variables,  $\text{H}_2\text{SO}_4$  and MTO (Sellegrì et al., 2005) concentrations. (Here, we were not able to use activity for MTO, and for consistency we chose to use concentration for sulphuric acid as well. Note that we did not include MTO in the above multiple regression analysis because both water vapour and  $\text{NO}_x$  appeared to be correlated with MTO, thus all three would not have been independent variables. Because there was much less data of MTO compared with the other gases, we left MTO out.) The results are shown in Table 2.  $\text{H}_2\text{SO}_4$  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 – note that Sihto et al., 2006, used the same data set as we do, but a different statistical technique). At subzero temperatures MTO shows a statistically significant regression coefficient close to unity, indicating possible organic contribution to nucleation. However, at higher temperatures this indication disappears.

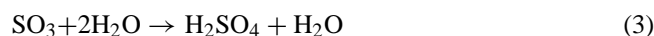
### 3 Suggested nucleation mechanism

#### 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 certainly cannot enhance binary nucleation enough to explain them. On the other hand, the  $\text{SO}_2$  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  $\text{HSO}_3$  and  $\text{HSO}_5$  as  $\text{SO}_2$  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  $\text{H}_2\text{S}_2\text{O}_6$  or  $\text{H}_2\text{S}_2\text{O}_8$  probably associated with water molecules. The currently accepted mechanism of atmospheric  $\text{SO}_2$  oxidation is as follows (Finlayson-Pitts and Pitts Jr., 2000):



The reaction of  $\text{HSO}_3$  with  $\text{O}_2$  is very fast (Gleason et al., 1987) resulting in atmospheric steady state concentrations for  $\text{HSO}_3$  of  $\sim 0.05$  molecule  $\text{cm}^{-3}$  ( $(\text{OH})=10^6$  and  $(\text{SO}_2)=10^{11}$  molecule  $\text{cm}^{-3}$ ). In competition to the stated reaction products of pathway (2),  $\text{SO}_3$  and  $\text{HO}_2$ , also the formation of the addition product  $\text{HSO}_5$  has to be considered:



Stockwell and Calvert (1983) found as a result of their experiments that more than 80% of initial OH radicals are regenerated as  $\text{HO}_2$  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  $\text{HSO}_5$  is produced in substantial fractions.  $\text{HSO}_5$  is a peroxy radical and its hydrated form could initiate the nucleation process (Wayne, 1991) rather than  $\text{HSO}_3$ . This fact is especially caused by the expected higher atmospheric concentration of  $\text{HSO}_5$  (note that gas-phase  $\text{HSO}_5$  has not been directly observed). In the atmosphere,  $\text{HSO}_5$  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  $\text{H}_2\text{SO}_4$  is formed in the  $\text{SO}_2$  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  $\text{H}_2\text{SO}_4$  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% (this is about 100%-units higher than inside modern water-based condensation particle counters, see Kulmala et al., 2007). However, this cannot have been the case with the Berndt et al. (2005, 2006) results, obtained with a particle detector that uses butanol as working fluid. (Otherwise almost all atmospheric nucleation data, which has been measured using similar apparatus, and at similar  $\text{H}_2\text{SO}_4$  concentrations

as those in the Berndt et al. experiments, would be invalidated.) 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  $\text{H}_2\text{SO}_4$  by oxidizing  $\text{SO}_2$ , 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. The 80 hPa total pressure employed by Sorokin and Arnold (2007) could thus be too low for the  $\text{HSO}_5$  radical production to lead to nucleation, delaying new particle formation until enough  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  nucleation will increase (because for fixed acid concentration, the relative acidity increases as temperature decreases).

The notion that Reaction (2a) might be pressure dependent between 1000 and 80 hPa is of course quite speculative (especially as there is no direct experimental evidence that the pathway (2a) is operative in the first place). In any case, such pressure dependence is in principle possible – for example, the effective bimolecular reaction constant of Reaction (1) decreases by a factor of about 4 in this pressure range (Atkinson et al., 1976). Note also that the work of Gleason et al. (1987) indicates that the reaction pathway (2a) is negligible at pressures below 10 hPa.

### 3.2 Nucleation 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 (Fig. 1) indicate that this growth is due to condensation of sulphuric acid (probably together with water vapor), and that the growth is 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 increases as a function of  $\text{H}_2\text{SO}_4$  relative acidity, which in turn increases as tempera-

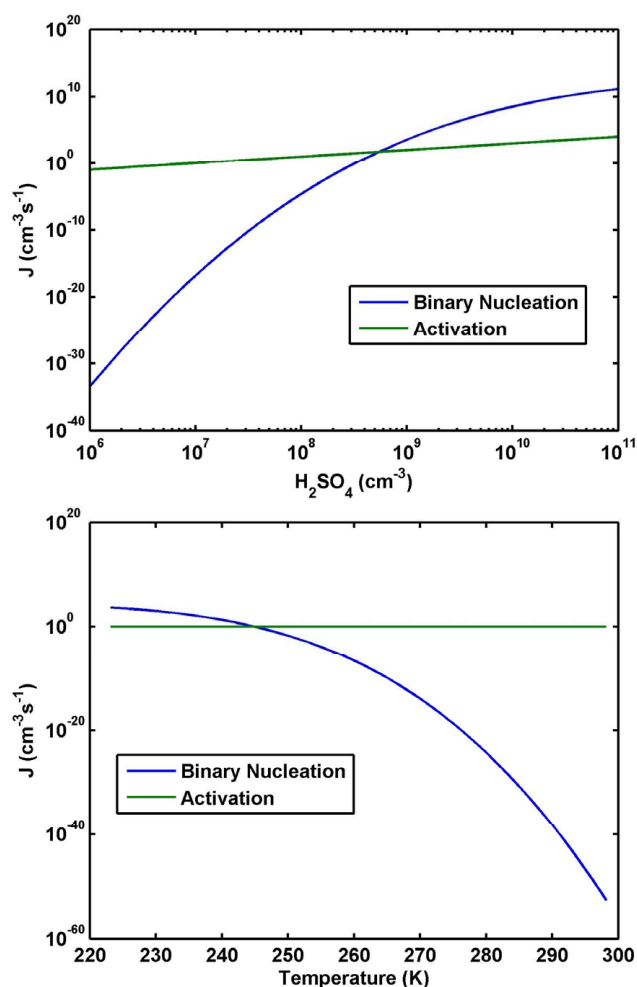
ture is decreased at fixed  $\text{H}_2\text{SO}_4$  concentration (and assuming that the production of the heterogeneous nuclei from the  $\text{HSO}_5$  – mechanism is essentially independent of temperature). However, eventually a threshold temperature will be reached, below which all nuclei will start growing. The initiation of growth is then no longer a stochastic process (which nucleation always is), and we will for clarity refer to it as “activation”. Thus, we can divide the nucleation into two regimes: the heterogeneous nucleation regime, where the observed nucleation rate is temperature dependent, and the activation regime, where the observed rate is temperature independent.

Note, that in the experiments of Part 1 (Berndt et al., 2008), vaporized sulphuric acid seemingly had no effect on the growth of particles produced by  $\text{SO}_2$  oxidation. This fact is in contradiction with the reasoning above. However, as discussed in Part 1, heterogeneous oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$  may have accelerated particle growth and masked the influence of vaporized  $\text{H}_2\text{SO}_4$  on growth rates.

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  $\text{H}_2\text{SO}_4$  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. 2). A likely explanation for the overall discrepancies in the two data sets is the difference in particle detection efficiencies. Friend et al. (1980) used a condensation nucleus counter in which the particles were made to 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  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  in the  $\text{SO}_2$  oxidation process; (2) the sulphur radicals react (possibly in hydrated form) with as yet unspecified atmospheric species; (3)  $\text{H}_2\text{SO}_4$  vapour nucleates heterogeneously on the reaction products or activates them, starting condensational growth of the new particles. There is an interesting consequence from the division of the process into the two regimes. At the activation regime, the production of the nuclei is proportional to the production of sulphuric acid, and therefore we would expect the observed nucleation rate to be proportional to the



**Fig. 4.** Nucleation rates from activation theory (Kulmala et al., 2006) with an activation coefficient of  $10^{-6} \text{ s}^{-1}$  and binary classical nucleation theory (Vehkamäki et al., 2002). a) Rates as a function of  $\text{H}_2\text{SO}_4$  vapour concentration  $T=273 \text{ K}$ . b) Rates as a function of temperature,  $(\text{H}_2\text{SO}_4)=10^7$ . 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  $288 \text{ K}$  (see text for more details), but we expect this dependence to disappear at sufficiently low temperatures.

gas-phase  $\text{H}_2\text{SO}_4$ -concentration. At the heterogeneous nucleation regime, on the other hand, the dependence of the observed rate on  $\text{H}_2\text{SO}_4$ -concentration is also influenced by the number of  $\text{H}_2\text{SO}_4$  participating in the heterogeneous nucleation (see Vehkamäki et al., 2007). If just one sulphuric acid is enough to cause the nucleation, then the observed dependence should be squared. (Note that it is possible that in the atmosphere also other vapors than  $\text{H}_2\text{SO}_4$  and water contribute to the heterogeneous nucleation/activation.) This picture is of course consistent with atmospheric observations: new particle formation rate depends on  $[\text{H}_2\text{SO}_4]^y$  with  $y$

varying mostly between 1 and 2 (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008).

Figure 4 shows calculations for classical homogeneous  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  nucleation, and for nucleation of  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  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. 4, 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  $4 \text{ km}$ , 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  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  seems to be in quite close agreement with atmospheric nucleation, in the sense that particle formation occurs at similar  $\text{H}_2\text{SO}_4$  concentrations. We suggest that a solution to this apparent paradox is the role of sulphur radicals produced during  $\text{SO}_2$  oxidation. In particular, we hypothesize that  $\text{HSO}_5$  radicals are formed in a reaction between  $\text{HSO}_3$  and  $\text{O}_2$  in the presence of sufficient concentration of inert molecules whose collisions stabilize the reaction product. Indirect experimental support for such a mechanism is given in the companion paper (Berndt et al., 2008). We further suggest that the  $\text{HSO}_5$  radicals will react with other trace species, and that the resulting molecules act as nuclei for heterogeneous nucleation of  $\text{H}_2\text{SO}_4$  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. Although our hypothetical nucleation mechanism is consistent with many atmospheric and



laboratory observations of nucleation, we stress that there is no direct evidence for or against the operation of reaction pathway (2a), or for the existence of HSO<sub>5</sub> or its reaction products in the atmosphere. Experimental studies investigating these issues would therefore be valuable.

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