Atmos. Chem. Phys., 11, 4755–4766, 2011
www.atmos-chem-phys.net/11/4755/2011/
doi:10.5194/acp-11-4755-2011

Atmospheric Chemistry and Physics

Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere

D. R. Benson, J. H. Yu, A. Markovich, and S.-H. Lee

Kent State University, Department of Chemistry, Kent, Ohio 44240, USA

Received: 8 September 2010 – Published in Atmos. Chem. Phys. Discuss.: 29 September 2010
Revised: 10 May 2011 – Accepted: 10 May 2011 – Published: 20 May 2011

Abstract. Ternary homogeneous nucleation (THN) of H_2SO_4, NH_3 and H_2O has been used to explain new particle formation in various atmospheric regions, yet laboratory measurements of THN have failed to reproduce atmospheric observations. Here, we report first laboratory observations of THN made under conditions relevant to the lower troposphere ([H_2SO_4] of 10^6–10^7 cm^{-3}, [NH_3] of 0.08–20 ppbv, and a temperature of 288 K). Our observations show that NH_3 can enhance atmospheric H_2SO_4 aerosol nucleation and the enhancement factor (EF) in nucleation rate (J) due to NH_3 (the ratio of J measured with vs. without NH_3) increases linearly with increasing [NH_3] and increases with decreasing [H_2SO_4] and RH. Two chemical ionization mass spectrometers (CIMS) are used to measure [H_2SO_4] and [NH_3], as well as possible impurities of amines in the nucleation system. Aerosol number concentrations are measured with a water condensation counter (CPC, TSI 3786). The slopes of Log J vs. Log [H_2SO_4], Log J vs. Log RH, and Log J vs. Log [NH_3] are 3–5, 1–4, and 1, respectively. These slopes and the threshold of [H_2SO_4] required for the unity nucleation vary only fractionally in the presence and absence of NH_3. These observations can be used to improve aerosol nucleation models to assess how man-made SO_2 and NH_3 affect aerosol formation and CCN production at the global scale.

1 Introduction

Particle nucleation (gas to particle conversion) is one of the important atmospheric processes that directly control the number concentrations of aerosol particles and thus can affect global climate, air quality and human health. Nucleation events have been observed in a wide range of atmospheric regions (Kulmala et al., 2004). These newly formed particles further grow by condensation and coagulation and can contribute to a large fraction (15–55 %) of CCN concentrations at the global scale (Merikanto, 2009), but the nucleation mechanisms are not well understood. Atmospheric observations (Erupe et al., 2010; Kulmala et al., 2004; McMurry et al., 2005) and laboratory studies (Benson et al., 2008; Berndt et al., 2005; Sipilä et al., 2010; Young et al., 2008) have shown that sulfuric acid (H_2SO_4) is the main nucleation precursor, but the role of other ternary species such as ammonia (NH_3) and organic compounds is not well understood.

Chemical composition analysis of nanometer size particles made at various locations has shown these newly formed particles contain sulfate, ammonium and various organic compounds including amines (Smith et al., 2008, 2010). Global atmospheric aerosol model calculations also suggested that in a wide range of the troposphere and the lower stratosphere, nucleation rates (J) can be predicted by the ternary homogeneous nucleation (THN) of H_2SO_4, NH_3, and H_2O (Lucas and Akimoto, 2006). Especially in the eastern US, new particle formation has been successfully explained by NH_3-THN (Gaydos et al., 2005; Jung et al., 2006; Stanier et al., 2004). The above mentioned modeling predictions were based on Napari et al. (2002)'s THN parameterization, which also predicts J values for many orders of magnitude higher than binary homogeneous nucleation (BHN) of H_2SO_4 and H_2O. This THN parameterization includes the [NH_3] range from 0–100 pptv (1 pptv $\approx 2\times10^7$ cm^{-3}) and for [NH_3] greater than 100 pptv, it assumes that there is no effect on J except for [H_2SO_4] less than 10^6 cm^{-3}, while atmospherically observed [NH_3] are typically at the sub-ppbv and ppbv level (Erupe et al., 2011; Nowak et al., 2006). Later THN parameterizations included the effects of stable ammonium bisulfate formation (Anttila et al., 2005; Merikanto et al., 2007) to match the available laboratory THN observations in the NH_3 range from 0–170 pptv (Ball et al., 1999); but these

Correspondence to: S.-H. Lee
(slee19@kent.edu)

parameterizations also fail drastically due to overestimation of the degree of proton transfer from bulk liquid properties (Vehkamäki, 2010).

At present, the exact [NH_3] needed to enhance J over BHN and the magnitude of enhancement in nucleation due to NH_3 are both uncertain, mostly because there are only a very limited number of laboratory studies of NH_3-THN (Ball et al., 1999; Benson et al., 2009; Berndt et al., 2010; Hanson and Eisele, 2002; Kim et al., 1998). To produce particles, these experiments also used [H_2SO_4] $> 10^8$ cm^{-3}, two to three orders of magnitude higher than typical atmospheric concentrations (10^5–10^7 cm^{-3}) (Erupe et al., 2010; McMurry et al., 2005). These limited observations have shown that at such high [H_2SO_4], [NH_3] of ppbv or sub-ppbv can increase J up to 3 orders of magnitude, although often the enhancement factors (EF) due to NH_3 are around only one order of magnitude.

Laboratory studies of nucleation are challenging due to technical limitations and the experimental results are often not reproducible between different studies. It is also unclear how different experimental techniques and parameters affect nucleation results. The different experimental parameters include the method to produce H_2SO_4 vapor (with the $SO_2 + OH \rightarrow HSO_3$ Reaction (R1) at in-situ or vaporization from liquid H_2SO_4 samples; a point or continuous source in the nucleation reactor), determination of aerosol precursor concentrations (e.g., [H_2SO_4] are measured with mass spectrometry or calculated from the estimated [SO_2] and [OH] in the nucleation reactor), estimation of wall loss of aerosol precursors and nucleation time in the nucleation reactor, and particle detection with different cutting sizes. The detection efficiencies in particle counters are important for experiments made at low [H_2SO_4], since the majority of particles often may not grow sufficiently large enough to be detected with 100 % detection efficiency. Additionally, direct detection of gas phase precursors is also critical because nucleation is a non-linear process so J is extremely sensitive to precursor concentrations (Lee et al., 2003; Seinfeld and Pandis, 2006).

There are also several technical limitations in laboratory nucleation studies. For example, in BHN studies that usually use water vapor to produce different RH values in the nucleation reactor, it is usually assumed that ternary species do not exist in the nucleation system, but in fact NH_3 impurities are unavoidable, because even highly purified water contains some amounts of NH_3 as impurities (Benson et al., 2010; Nowak et al., 2006). Depending on the material used in the nucleation reactor, the effects of such impurity NH_3 can be also different. Experimental tests have shown that whereas adsorption of NH_3 is most effective on stainless steel material, NH_3 adsorption is minimal on fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon surfaces (Benson et al., 2010; Neuman et al., 2003; Nowak et al., 2002, 2006; Yokelson et al., 2003). Such impurities are one of the major limitations of nucleation studies, especially considering that NH_3 can increase nucleation of H_2SO_4 aerosols (Ball et al., 1999; Benson et al., 2009, 2010; Berndt et al., 2010). It is also possible that amines can co-exist with NH_3, as they both have similar sources (Ge et al., 2010). And, amines can also enhance H_2SO_4 aerosol nucleation similarly to NH_3 (Berndt et al., 2010; Erupe et al., 2011).

Here, we present laboratory observations of homogeneous nucleation involving, H_2SO_4, NH_3, and H_2O, for the first time, made under conditions typically relevant to the lower troposphere. Experiments were made at [H_2SO_4] of 10^6–10^7 cm^{-3}, [NH_3] of 0.08–2.6 ppbv (except only one occasion where 20 ppbv NH_3 was used), RH of 6–40 % and 288 K, in a temperature- and RH-controlled fast flow nucleation reactor. All aerosol precursors were also simultaneously and directly measured with CIMS to provide more constrained precursor concentrations needed for nucleation. Prior to the present study, possible impurities of NH_3 and amine concentrations present in a nucleation system have never been quantified in laboratory studies. The present study also discusses the effects of various experimental parameters on homogeneous nucleation observation results, especially in terms of growth rate (GR) estimated under low [H_2SO_4] conditions. There is another companion paper by Erupe et al. (2011), where we show the effects of trimethylamine on H_2SO_4 nucleation and our results show that trimethylamine acts in a strikingly similar manner as NH_3.

2 Experiments

The nucleation experimental setup was described in detail in Benson et al. (2008, 2009) and Young et al. (2008). Briefly, as shown in Fig. 1, the system consists of five main sections: (i) a photolysis region where OH radicals are produced from the photodissociation of H_2O vapor with a UV lamp ($\lambda <$ 185 nm), (ii) a mixing region where the trace gases (SO_2, O_2, and N_2) are introduced into the flow tube and where H_2SO_4 is also produced from the following reaction:

$$SO_2 + OH \rightarrow HSO_3 \quad \text{(R1)}$$

at a local source, (iii) a double jacket, fast flow nucleation reactor (RH- and temperature-controlled), (iv) two chemical ionization mass spectrometers (CIMSs) to measure [H_2SO_4] and [NH_3] at the beginning of the nucleation reactor, and (v) a water CPC (TSI 3786) connected to the end of the nucleation reactor to measure particle number concentrations of particles.

There are also several improvements in the current nucleation setup. First, we have re-designed a new nucleation reactor with larger size diameters (13 cm now vs. 2.54 or 5.08 cm previously) based on Donahue et al. (1996) to significantly reduce wall loss factors (WLFs; the ratios of [H_2SO_4] at the beginning vs. at end of the nucleation reactor) of H_2SO_4 (1.5–4 now vs. 2–360 previously; Benson et al., 2008, 2009; Young et al., 2008), by using large size inner diameters and by introducing trace species from the center

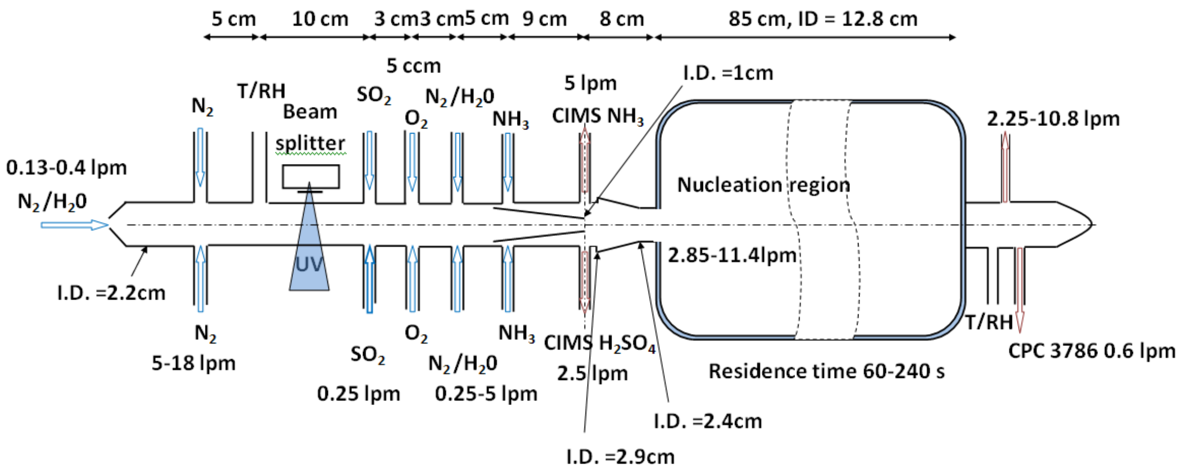

Fig. 1. A flow reactor used in KSU aerosol nucleation setup. All [H_2SO_4] and [NH_3] reported in this study were measured at the entrance of the nucleation reactor. Trimethylamine was also measured with CMS based on a similar ion chemistry used in NH_3 measurements (Erupe et al., 2011). For wall loss studies, we used two CIMSs at the entrance and the end of the nucleation reactor, to simultaneously measure H_2SO_4 (Fig. 2b).

of the flow reactor under high flow; this design is described in detail below in this section. [H_2SO_4] were changed by changing [OH] with an iris beam splitter to control the UV beam; previously, [H_2SO_4] was changed by changing [SO_2] (Benson et al., 2008, 2009; Young et al., 2008). In addition, RH values were changed by adding water vapor at the downstream end after the production of H_2SO_4, to allow independent changes in RH in the nucleation reactor and [OH] (thus [H_2SO_4]).

H_2SO_4 vapor is produced only via Reaction (R1) (rate limiting step; rate constant $k1 = 8.8 \times 10^{-13}\,\mathrm{cm^3\,s^{-1}}$; Finlayson-Pitts and Pitts, 2000) and the following two subsequent reactions:

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{R2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{R3}$$

OH radicals were produced from UV dissociation of water vapor; this allows for an ozone-free system and hence provides an advantage compared to other studies where OH was produced from ozone photolysis (Berndt et al., 2005, 2006; Sipilä et al., 2010). [OH] were also directly measured from UV photon flux measurements. This method also allows for a minimal-hydrocarbon system compared to other methods where the OH titration method was used with various hydrocarbon compounds (Berndt et al., 2005, 2006). H_2SO_4 vapor was produced at a local source at the beginning of the nucleation reactor as opposed to a continuous source in the nucleation reactor, but this fact would not affect the measured J values, because the amount of H_2SO_4 molecules used by nucleation is typically much smaller than those lost on the wall and left in the gas phase (Benson et al., 2008; Young et al., 2008).

[H_2SO_4] were detected with CIMS, using the following ion-molecule reaction:

$$(HNO_3)NO_3^- + H_2SO_4 \rightarrow HNO_3 + (NHO_3)HSO_4^- \tag{R4}$$

at atmospheric pressure, using ^{210}Po as the ion source and HNO_3 gases as reagent (Benson et al., 2008, 2009; Eisele and Tanner, 1993). The rate constant of Reaction (R5) ($k5$) is $2.32 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ with a factor of 2 uncertainties (Viggiano et al., 1997); the ion-molecule reaction time was 0.1 s. As discussed in Erupe et al. (2010), it is also possible that in the ion molecule reaction region, NO_3^- ions make clusters, such as $NO_3^-(HNO_3)_m$, where $m = 1, 2, 3\ldots$ etc., and $NO_3^-\ (H_2O)_n$, and $n = 1, 2, 3\ldots$ etc. Laboratory measurements have showed that these clusters also react with H_2SO_4 to produce HSO_4^--containing clusters (Viggiano et al., 1997):

$$(HNO_3)_mNO_3^- + H_2SO_4 \rightarrow HNO_3 + (HNO_3)_{m-1}HSO_4^- \tag{R5}$$

$$(H_2O)_nNO_3^- + H_2SO_4 \rightarrow HNO_3(H_2O)_m + HSO_4^-(H_2O)_{n-m} \tag{R6}$$

But their reaction rates, $k6$ and $k7$, are all approximately $1.8 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$, very similar to $k5$ (Viggiano et al., 1997). A collision dissociation chamber (CDC) was also used to effectively dissociate these clusters in our CIMS. Therefore, the presence of possible clusters of ion reagents would not affect the CIMS sensitivity. This is the case for the gas phase H_2SO_4 detection, but for the measurements of atmospheric neutral or charged clusters containing H_2SO_4, these ion reagent clusters can affect the mass peak identification and the instrument sensitivity of individual H_2SO_4 clusters sampled from ambient air. As shown in Young et al. (2008), calibrations of H_2SO_4 with OH have shown that

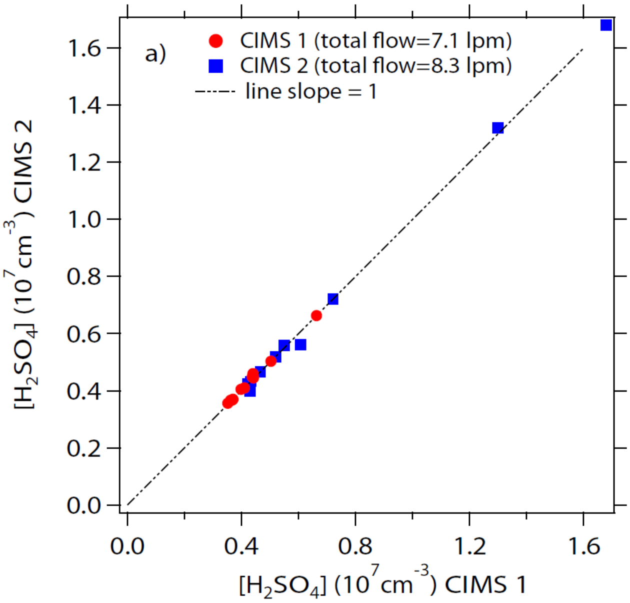

Fig. 2a. The measured [H_2SO_4] with two CIMSs at the beginning of the nucleation reactor. RH = 14 %. Dashed line shows the linear fitting of the data.

the CIMS measures all free-H_2SO_4 molecules produced in the gas phase. Figure 2a also shows the [H_2SO_4] measured with two CIMSs in the nucleation reactor, demonstrating that the two CIMSs give the similar results within <3 % in the 10^6 cm^{-3} range.

The detection limit of H_2SO_4-CIMS was 2×10^5 cm^{-3} and the uncertainty associated with our ambient measurements was estimated to be about 60 % at maximum (Erupe et al., 2010). In our previous studies (Benson et al., 2008; Young et al., 2008), we reported the residual [H_2SO_4] (measured at the end of the nucleation reactor) and further used the calculated WLFs to indicate the [H_2SO_4] range in the nucleation reactor. Here, we make a correction that these initial [H_2SO_4] should be a factor of 4.6 lower (due to the 2.3 times lower $k3$ and the 2 times lower ion molecule reaction time due to different flow rates used) than the reported values, but this error does not affect the main conclusions of these previous papers, because of the high WLFs (up to 360).

[NH_3] were measured with another CIMS (Benson et al., 2010), using protonated ethanol ions as reagent based on:

$$NH_3 + CH_3CH_2OH \cdot H^+ \rightarrow NH_4^+ + CH_3CH_2OH \quad \text{(R7)}$$

at a lower pressure (20 torr); $k8 = 2.0 \times 10^{-9}$ cm^3 s^{-1} (Nowak et al., 2006). One of the major technical challenges of measuring these sticky base molecules is to efficiently reduce the "CIMS background" signals, which are different by definition from impurity background concentrations in the nucleation reactor, and these background signals must be taken into account, as discussed in detail in Benson et al. (2010). The CIMS sensitivity for NH_3 was about 3–4 Hz pptv^{-1} for >1 MHz of reagent ion signals, with 30 % uncertainties. The estimated detection limit was ∼45 pptv (3σ) for 1 min integration time.

The [NH_3] was measured only before the nucleation region (Fig. 1). But there were no significant losses from where NH_3 was introduced to where it was measured. Figure 1 shows where all the gases are added. If we added NH_3 to the port labeled N_2/H_2O (before the flow is centered) the NH_3 was the same as if we added it directly before the NH_3-CIMS inlet. To minimize adsorption and desorption of NH_3 (Benson et al., 2010; Neuman et al., 2003; Nowak et al., 2002, 2006, 2007; Yokelson et al., 2003), the entire experimental setup was built exclusively by FEP or PFA Teflon, without any metal materials. We have also used nitrogen gases vaporized from liquid nitrogen, which has the lowest [NH_3] impurities, <∼20 pptv (Nowak et al., 2007). The impurity NH_3 gases in the system, very likely originated from deionized water, were systematically determined with CIMS as a function of RH in the system [NH_3] from water vapor increased linearly with RH in the flow tube, and was below 100 pptv for RH from 6–40 %. These values are actually similar to [NH_3] found in some remote areas (Dentener and Crutzen, 1994).

There are also possible amine impurities in deionized water, as ion exchange resins typically used for water purification often contain trimethylamine which is covalently bonded to polymer backbone of the resin to form the strong anion exchange site (for example, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0032/0901b803800326ca.pdf?filepath=liquidseps/pdfs/noreg/177-01837.pdf&fromPage=GetDoc). We also have tried to measure possible impurities of amines in the system with CIMS based on the ion chemistry shown by Erupe et al. (2010), which is similar to Reaction (R8). Our preliminary investigations show trimethylamine (the most abundant atmospheric amine compound) of <85 pptv in the nucleation reactor at RH of 6 %, but more systematic experiments are required in the future for different types of amines under different RH conditions with higher CIMS sensitivities. Due to the presence of such impurities of NH_3 (<100 pptv, or $<2 \times 10^9$ cm^{-3}) and amines (e.g., trimethylamine <85 pptv, or $<1.7 \times 10^9$ cm^{-3}), strictly speaking, the BHN system referred in the present study is not the absolute BHN system and is rather a "pseudo" BHN system.

Our previous setup had residence times up to 77 s (Benson et al., 2008, 2009; Young et al., 2008), and recently we have redesigned the nucleation reactor (Fig. 1) to increase the range of residence times (50–240 s). The new nucleation reactor was designed to reduce wall loss of aerosol precursors significantly, by using a larger diameter size (I.D. of 12.8 cm now vs. 2.54 or 5.08 cm previously (Benson et al., 2008, 2009) and by introducing trace gases from the center of the flow tube with fast flows (Fig. 1), based on Donahue et al. (1996). The combination of the large diameter and high flows effectively minimizes the chances for gas phase molecules to travel from the center of the flow tube to the

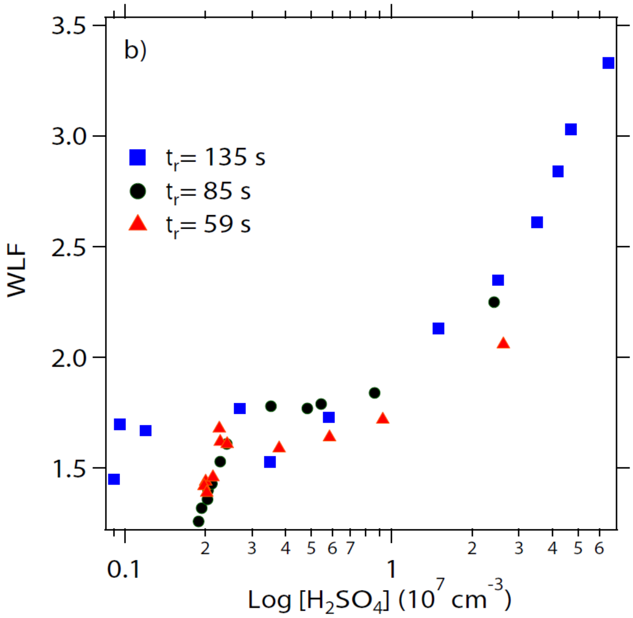

Fig. 2b. The measured WLF with two CIMSs located at the beginning (initial [H_2SO_4]) and end of the nucleation reactor (residual [H_2SO_4]) as a function of initial [H_2SO_4]. WLF is the ratio of initial to residual [H_2SO_4]. RH = 20 %.

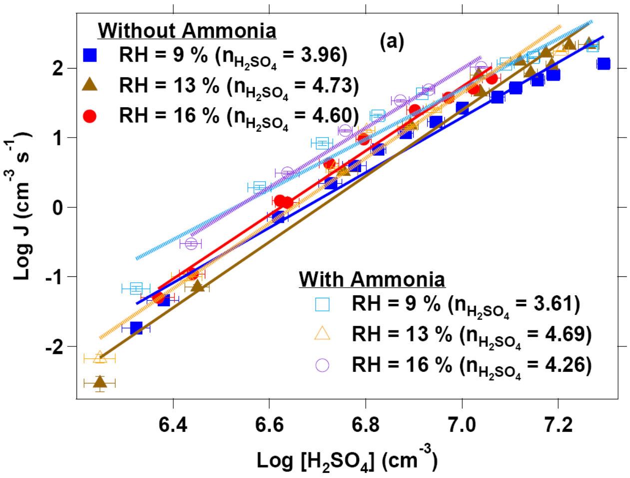

Fig. 3a. The measured Log J vs. Log [H_2SO_4] for BHN (filled symbols) and NH_3-THN (open symbols) at RH = 9 % (squares), 13 % (triangles), 16 % (circles). [NH_3] = 1.20 ppbv for THN. The horizontal and vertical bars indicate one standard deviation of [H_2SO_4] and J; the solid or dashed lines show the liner fitting curve of the data.

wall. To examine how this "cone-shaped" tube (I.D. 1 cm at the end of the cone) would affect the CIMS measurements near the entrance of the nucleation reactor, we have compared [H_2SO_4] and particle concentrations in the reactor with and without this "cone-shaped" tube, and the differences were only about 20 %.

WLFs were measured by two CIMSs located at the beginning and end of the nucleation reactor. The measured WLFs were <4 (Fig. 2b), significantly lower than those in the previous experiments (up to 360) (Benson et al., 2008; Young et al., 2008). The measured values within the estimated WLFs from a diffusion limited process (Young et al., 2008), but were also dependent on the initial [H_2SO_4] and increased with increasing the initial [H_2SO_4]. It is also possible that inhomogeneous air mixing was present in the nucleation reactor which could affect our WLF measurements. In the future, we plan to investigate flow dynamics in the air mixing region and the nucleation reactor, in order to understand how different flow conditions affect nucleation experimental conditions.

The cutting sizes of the water CPC at different detection efficiencies are 3 nm (100 % detection efficiency), 2.3 nm (50 %), 2 nm (25–30%) and 1.8 nm (∼10 %), (http://www.tsi.com/uploadedFiles/Product_Information/Literature/Spec_Sheets/3786_2980291.pdf). Using these nucleation times and the measured total particle number concentrations measured by CPC, we derived J. Therefore, it is possible that the slops of Log J vs. Log [H_2SO_4] were overestimated due to lower detection efficiencies of CPC for particles smaller than 2 nm, because at higher [H_2SO_4], more particles grow and are detected by CPC.

3 Results

Figure 3a shows the measured J as a function of initial [H_2SO_4] for different RH values with and without introducing NH_3 gases (1.2 ppb). The total flow through the reactor was 10.3 lpm, corresponding to a residence time through the nucleation region of 240 s. J values varied from 3×10^{-3}–2×10^{2} cm^{-3} s^{-1} for RH values 9–16 % and initial [H_2SO_4] from 2×10^{6}–2×10^{7} cm^{-3}. In general, J were higher in the presence of NH_3 (1.2 ppbv) than in the absence of it. However, in both BHN and THN cases, the [H_2SO_4] threshold to produce the unity J (1 cm^{-3} s^{-1}) was at the 10^{6} cm^{-3} range, which is one of the main conclusions of the present study. The slope of Log J vs. Log [H_2SO_4] was 3–5 for both BHN and THN cases. Unlike Benson et al. (2009), in which the slope increased with decreasing RH, there was no clear trend in the slope as a function of RH. This slope only slightly decreased (reduced by 0.04 to 0.4 molecules) for THN compared to BHN for the same RH.

Figure 3b shows the measured Log J vs. Log RH for BHN and THN with NH_3 (20 ppbv). J varied from 3×10^{-3}–3×10^{1} cm^{-3} s^{-1} for RH values 6–40 %, initial [H_2SO_4] in the range of 3×10^{6}–7×10^{6} cm^{-3} and at a residence time of 120 s, and was usually higher in the presence of NH_3 than without it. The slope of Log J vs. Log RH was 1–4 and only slightly reduced in the presence of NH_3. Thus, under these experimental conditions, there were also no substantial

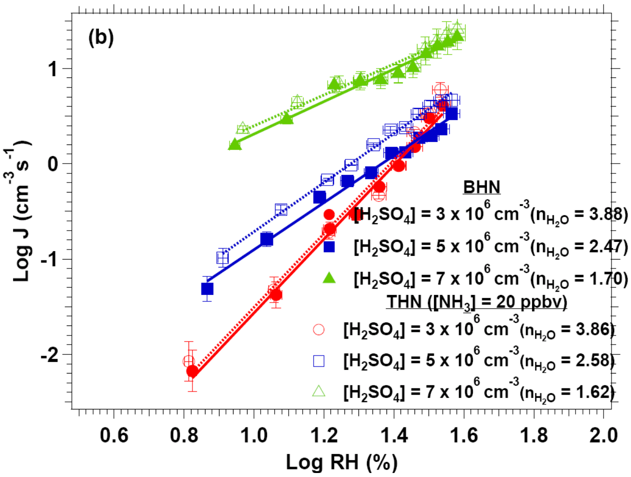

Fig. 3b. Log J vs. Log RH. $[NH_3] = 20$ ppbv. The total flow through the reactor is 13.1 lpm (5.6 lpm through the nucleation region and 7.5 lpm to the two CIMSs), corresponding to a residence time through the nucleation region of 120 s.

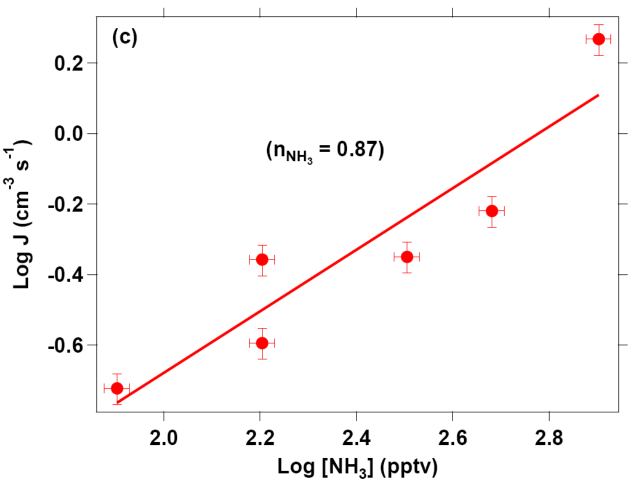

Fig. 3c. The measured Log J vs. Log $[NH_3]$ for THN experiments. RH = 8 %. $[H_2SO_4] = 8.2 \times 10^6\ cm^{-3}$. Residence time = 170 s.

changes in the composition of H_2SO_4 and H_2O molecules in critical clusters in the presence and absence of NH_3.

Figure 3c shows the measured Log J vs. Log $[NH_3]$ at $[H_2SO_4]$ of $8.2 \times 10^6\ cm^{-3}$, $[NH_3]$ from 0.08–0.80 ppbv, RH of 8 %, and a residence time of 170 s. At $[NH_3]$ from 0.08–1 ppbv, J varied from 0.2– 2 $cm^{-3}\ s^{-1}$. The slope of Log J vs. Log NH_3 was nearly one, indicating that there is only one molecule of NH_3 present in the critical clusters, consistent with the above result that the slopes of Log J vs. Log $[H_2SO_4]$ and Log J vs. Log RH did not change in BHN and THN (Fig. 3a and b).

To understand the effects of residence time on the slope of Log J vs. Log $[H_2SO_4]$, we also compared data taken at different residence times (thus nucleation times) using different

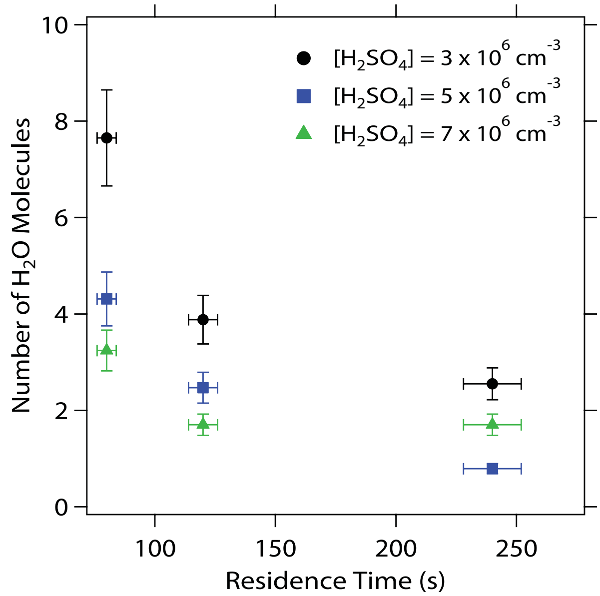

Fig. 4. The n_{H_2O} values (derived from Log J vs. Log RH) as a function of residence time and $[H_2SO_4]$. The horizontal and vertical bars indicate one standard variation in residence time and n_{H_2O}.

diameters of the nucleation reactors (not shown). We found that at shorter residence times the slopes were higher and J values were lower at similar $[H_2SO_4]$. For low $[H_2SO_4]$, increasing residence time can enhance J, because longer residence times would allow more particles grow from critical clusters to the measurable sizes by CPC (measuring particles >1.8 nm at which the TSI 3876 detection efficiency is ∼10 %). On the other hand, for high $[H_2SO_4]$, increasing residence time would decrease J, because H_2SO_4 molecules may be lost by the competitive scavenging process on the tube wall and on aerosol surfaces. As a result, the slope should be smaller at a long residence time than at a short residence time. That is, depending on different residence times and different levels of $[H_2SO_4]$, either nucleation or scavenging can be dominant, as discussed in Young et al. (2008), and such competing processes are reflected in different slopes taken at different residence times. The same trend was also observed for the slope of Log J vs. Log RH and the slope also decreased with increasing residence time (Fig. 4). Additionally, the slope of Log J vs. Log $[H_2SO_4]$ was also affected by low detection efficiencies of CPC for particles smaller than 2 nm, as discussed in the following section.

By comparing the measured J in THN vs. BHN taken under similar experimental conditions, EF was derived. EF values were usually lower than one order of magnitude for $[H_2SO_4]$ from 2×10^6–$2 \times 10^7\ cm^{-3}$, $[NH_3]$ from 1.22–2.6 ppbv, RH from 6–16 % and residence times of 60–240 s (Fig. 5a). Similarly to Benson et al. (2009), EF was in general higher for lower $[H_2SO_4]$ (Fig. 5a), lower RH (Fig. 5b) and higher at higher NH_3 (Fig. 5c).

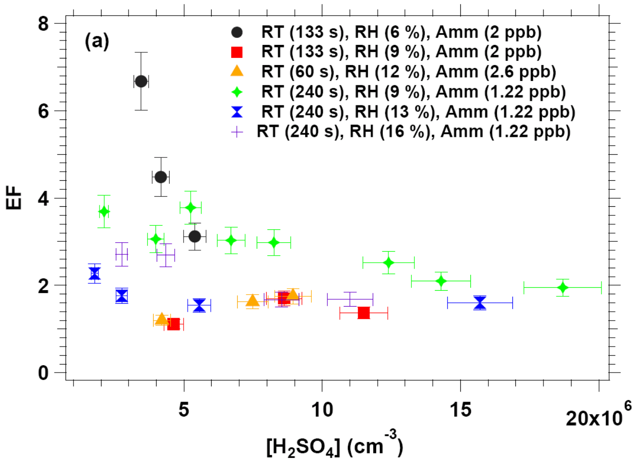

Fig. 5a. The measured EF as a function of [H_2SO_4]. [NH_3] = 1.22–2.6 ppbv. RH = 6–16 %. Residence time = 60–240 s.

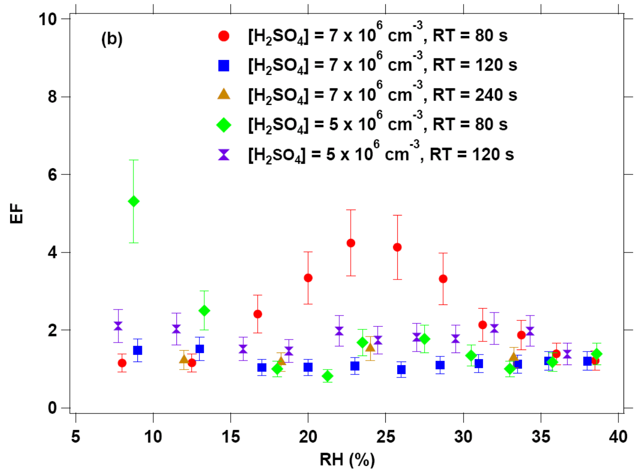

Fig. 5b. The measured EF as a function of RH. [H_2SO_4] = 5×10^6–7×10^6 cm^{-3}. [NH_3] = 20 ppbv. RH = 7–39 %. Residence time = 80–240 s.

4 Discussions

4.1 Growth Rates (GR)

The TSI 3876 (water CPC) cutting size with 10 % detection efficiency is ~1.8 nm (http://www.tsi.com/uploadedFiles/Product_Information/Literature/Spec_Sheets/3786_2980291.pdf). We have tested this detection efficiency with a particle size magnifier (PSM, Airmodus A09) (Vanhanen et al., 2011). Our results indicate that CPC measures 2 nm particles with detection efficiency of ~25 % (consistent with the above online spec sheet), while PSM has 85 % detection efficiency at this size. CPC also measures a noticeable amount of particles of 1.8 nm (e.g., 50–100 cm^{-3}). By measuring particle number concentrations with PSM at different saturator flow rates (thus different cutting sizes in PSM) and different [H_2SO_4] (thus different mode sizes of the particles generated), we also found that these particles in the nucleation reactor are all smaller than 2 nm, with the majority smaller than 1.8 nm.

Kulmala et al. (2007) have suggested critical cluster sizes to be from 1–2 nm. Considering that the critical cluster size is 1.5 nm and the produced particles in our nucleation reactor are smaller than 1.8 nm, we derived GR to be than 7.7 nm h^{-1} (residence time of 240 s in Fig. 3a). If critical size is 1.7 nm, then the GR is less than 2.6 nm h^{-1}. These GR values are well within the range of GR (1–20 nm h^{-1}), for example, measured in a less polluted US continental environment at similar [H_2SO_4] used in the present study (Erupe et al., 2010). A GR of 1 nm h^{-1} is estimated by condensation of [H_2SO_4] of 1.5×10^7 cm^{-3} (Nieminen et al., 2010) based on the kinetic regime condensation theory and accommodation coefficient of H_2SO_4 of unity. Considering an uncertainty of 60 % in H_2SO_4 detection by CIMS and an additional 20 % uncertainty in [H_2SO_4] due to the cone shaped inlet, a GR

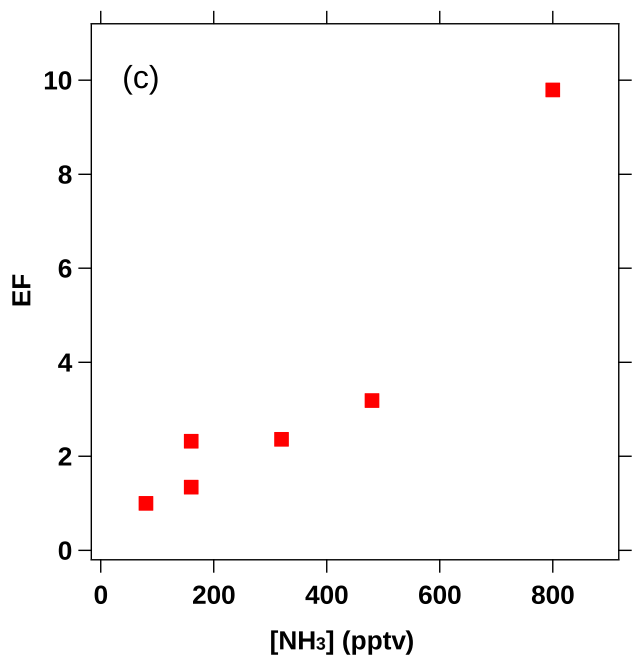

Fig. 5c. The measured EF as a function of [NH_3]. [H_2SO_4] = 8.2×10^6 cm^{-3}. RH = 8 %. Residence time = 170 s.

of 1.8 nm h^{-1} is possible under the CIMS-reported [H_2SO_4] of 1×10^7 cm^{-3}. By further considering the effects of base molecules on growth (additional 10 % discussed below), this estimated GR (1.8 nm h^{-1}) would become ~2 nm h^{-1}, as the upper limit. Coagulation of cluster size particles is negligible. This upper limit of GR value is quite close to the GR of 2.6 nm h^{-1}estimated above from our observations. Similarly high GR was also found in other laboratory studies (Berndt et al., 2005, 2006), in which particles were detected with TSI 3776 (the same detection efficiencies as TSI 3786) at [H_2SO_4] of 7×10^6 cm^{-3} and a residence time of 290 s (they reported J of 0.3–0.4 cm^{-3} s^{-1}); therefore, these reported experimental conditions imply GR was around 4 nm h^{-1}. Below we examine the possible factors that can contribute to the measured GR in our system.

Assuming that newly nucleation H_2SO_4 particles were fully neutralized by NH_3, GR will only increase with a factor of 1.1. Similarly, amines (organic base compounds) also will not significantly contribute to the GR. GR is ultimately determined by H_2SO_4 vapor (in the absence of condensable organic compounds), whereas NH_3/amines and water can only co-condense on newly formed particles to maintain thermodynamic equilibrium with the vapor phase. Pryor et al. (2011) and Zhang et al. (2009) have shown that tens or hundreds of pptv of NH_3 actually cannot explain the elevated GR. So it is unlikely that the possible impurities of NH_3 or amines present in the system can explain the GR estimated in our nucleation reactor.

We have also ruled out the major effects of organic compounds on the GR. In our system, we did not introduce any organic compounds. However, there may be still some trace level of hydrocarbons (and carbon monoxide) gases from the highly purified gas bottles, but they would be rapidly scavenged by OH radicals. Within very short reaction times (<0.1 s in our system; Young et al., 2008), hydrocarbons do not produce highly oxidized low volatility compounds to condense on particles and even there are some higher generations of oxidation products, their concentrations are too low to affect aerosol growth in the system. We have also made additional tests to investigate the effects of organics, by introducing different functional groups of organic compounds at the ppbv to hundreds of ppbv level, but these organic compounds did not produce particles. For example, in the presence of isoprene at the sub-ppbv level, there was no effect on nucleation of H_2SO_4, but when isoprene concentrations increased to ppbv level, nucleation was abruptly suppressed because isoprene scavenges OH rapidly, similarly to (Kiendler-Scharr et al., 2009) plant chamber study. Erupe et al. (2011) have also discussed the effects of oxidation products of trimetylamine with OH; the amine oxidation products did not produce particles (implying that nucleation enhancement was likely due to formation of salts, rather than due to amine oxidation products).

4.2 THN effects

There are also differences, especially in the threshold of H_2SO_4 and the slope, between the current and the early THN study (Benson et al., 2009). The main difference between the two studies is the flow reactor used for nucleation experiments. Because the flow reactor is much larger in the present study (I.D. 12.8 cm vs. 5.08 cm previously), we had much higher residence times in the current study (up to 240 s) with the current setup. The difference in residence times will cause the slopes to be different so the behavior with respect to relative humidity may also be altered. As for the differences in EF, in the previous study (Benson et al., 2009) it was shown that EFs increase exponentially with decreasing H_2SO_4 and the same trend was also found in the present study. From these results, one would expect that EFs in the current study should actually be higher due to lower [H_2SO_4] used. However, because of the differences between these two studies (including larger I.D. for the nucleation region and higher residence times), direct extrapolation between the studies is inconclusive. It seems only when all conditions are the same that EFs are higher for lower H_2SO_4. These results also imply that, due to matrix effects of experimental conditions on nucleation, one should be extremely cautious when directly comparing different studies.

Our observations show that the onset H_2SO_4 for nucleation to occur ($J = 1$ cm^{-3} s^{-1}) is on the order of 10^6 cm^{-3}. Atmospheric observations (Birmili et al., 2000; Erupe et al., 2010; Kulmala et al., 2004; McMurry et al., 2005; Weber et al., 1999) have shown that nucleation occurs at [H_2SO_4] of 10^6–10^8 cm^{-3}. In the present study, we found the threshold of 10^6 cm^{-3} [H_2SO_4] and the slope of Log J vs. Log [H_2SO_4] between 3–5 for both BHN and NH_3-THN cases, when using TSI 3876. While we used a longer residence time (60–240 s) in the nucleation region, H_2SO_4 was also produced in a local source. These slopes were likely affected by different cuttings sizes in TSI 3876, which can measure only a fraction of 1.8–2 nm particles as discussed in the above section. Sipilä et al. (2010)'s PSM measurements have showed that the slope was only 1–2, due to higher detection efficiencies for 1–2 nm particles in PSM. Based on these slopes, Sipilä et al. (2010) have concluded that the critical clusters contain only 1–2 H_2SO_4 molecules. However, it is difficult to understand, from the thermodynamics viewpoint, how monomer (gas phase molecule) or small size dimers of H_2SO_4 can act as critical clusters, since they would not spontaneously condense to grow larger.

It has been also common practice to compare the slope of Log J vs. Log [H_2SO_4] obtained in the laboratory studies with those from field studies (Metzger et al., 2010; Sipilä et al., 2010). But there is a difference in the methods used to make these slopes in the laboratory studies and field observations. The atmospherically derived slopes are usually from ensemble data obtained at various RH and temperatures and different saturation ratios of possible ternary precursors (which are unknown currently). On the other hand, laboratory values are derived from the data taken under a constant temperature and RH, and presumably in the absence of, or at least in the possibly lowest amount of, ternary species in the binary case. Such a difference has been neglected when comparing the slopes derived from field and laboratory studies. A more rigorous approach directly applying the first nucleation theorem, in which which nucleation rates can be sorted out under the same temperature and the same supresaturation ratios of other nucleation precursors, for atmospheric observations is needed to better understand the chemical composition of the critical clusters in the atmosphere.

One of the main principles of THN is that it could explain nucleation occurring at lower [H_2SO_4] where BHN would fail (Weber et al., 1998). As shown by the present study and others (Ball et al., 1999; Benson et al., 2009), the threshold H_2SO_4 for nucleation was similar for BHN and THN. It was usually on the same order of magnitude and at most only about half of the value found in BHN, implying that while THN can occur at lower [H_2SO_4], any enhancement by NH_3 would not be large enough to shift the threshold value. Most EF values were largest at three orders of magnitude for [H_2SO_4] from 10^8–10^{10} cm^{-3} (Ball et al., 1999; Benson et al., 2009). As shown in the present study, when [H_2SO_4] (10^6–10^7 cm^{-3}) and [NH_3] (0.08–2.6 ppbv) were one or three orders of magnitude lower than in these cited studies, the EF values were mostly $<$10 (Figs. 3 and 5).

Our results show that the slope of Log J vs. Log [H_2SO_4] and Log J vs. Log RH were reduced under THN than in BHN, but the both slopes were also very similar in the BHN and THN cases. For example, the Log J vs. Log [H_2SO_4] slope was reduced only by a fraction of a molecule (0.04 to 0.4 molecules). Thus, while the J was enhanced, an addition of NH_3 did not drastically change the H_2SO_4 and H_2O composition of the critical clusters under atmospherically relevant conditions. These results are different from previous studies (Ball et al., 1999; Benson et al., 2009) which showed that the critical cluster contains 2–3 less molecules of H_2SO_4 in the presence of NH_3.

The slope of Log J vs. Log [NH_3] derived from the present study was only one, which is consistent with cluster measurements by Hanson and Eisele (2002). And, this unity value also explains the small reduction in the slope of Log J vs. Log [H_2SO_4] and Log J vs. Log RH in THN than in BHN. This low slope in Log J vs. Log [NH_3] may also imply that NH_3 actually acts rather as a catalysis agent and is less physically incorporated into the cluster formation itself during the THN process. It is also possible that there is an energy reduction due to the exothermic heat released from the acid-base neutralization reaction between H_2SO_4 and NH_3, so that even only one molecule of NH_3 is sufficient to reduce the Gibbs free energy for critical cluster formation.

Field studies of new particle formation made in Atlanta, Georgia in the summer 2002 showed that [H_2SO_4], [NH_3] and particle concentrations are approximately 10^6–10^8 cm^{-3}, 1–10 ppbv, and 10^3–10^5 cm^{-3}, respectively (McMurry et al., 2005). And, the precursor concentrations used in the present laboratory experiments fall within these observation results. McMurry et al. (2005) also showed the slope of logarithms of particle concentration vs. [NH_3] is nearly one (McMurry et al., 2005), similar to the present study showing that the slope of Log J vs. Log [NH_3] is only one. Another study made in Kent, Ohio crossing four different seasons showed the threshold of [H_2SO_4] is around 10^6 cm^{-3}, even when NH_3 was at the sub-ppbv level (Erupe et al., 2010). While our laboratory observations also fall within the observation results taken in Kent, the Kent measurements had a nearly constant NH_3 level (sub-ppbv) over different seasons, so it was difficult to use these data to quantitatively test the J vs. [NH_3] relationship.

Our laboratory observations show the threshold of [H_2SO_4] needed for the unity J is order of 10^6 cm^{-3}, with [NH_3] from 0.08–2.6 ppbv at 288 K. In comparison, the threshold in the THN parameterization is, for example, [H_2SO_4] of 10^9 cm^{-3} for [NH_3] of 1 ppbv at 273 K (Merikanto et al., 2007). A similar [H_2SO_4] threshold is also required in the BHN parameterization (Vehkamäki et al., 2002). We also used our typical experimental conditions of [H_2SO_4], [NH_3], RH and temperature used in the present study, but the THN parameterization (Merikanto et al., 2007) did not produce particles. As discussed in Erupe et al. (2010), this THN parameterization also did not reproduce atmospheric observations made in Kent.

Since the [H_2SO_4] threshold (10^6 cm^{-3}) found in BHN or THN (with sub-ppbv NH_3, commonly found in the atmosphere) is well within the typical atmospheric conditions (Erupe et al., 2010), one would expect that aerosol nucleation should take place instantly under most atmospheric conditions. But in the atmosphere, even at [H_2SO_4] of 10^7 cm^{-3}, nucleation often does not occur with low surface areas of preexisting aerosols (Erupe et al., 2010). These results open an important atmospheric question which requires future studies to answer: under what atmospheric conditions does new particle formation actually not occur?

While impurities of NH_3 or amines in the nucleation system have become increasingly recognizable for laboratory studies, this has become to a question whether BHN process is less important than previously thought. While this question remains to be examined in the future, our THN with NH_3 (this study) and tirmethylamine (Erupe et al., 2011), together with other laboratory studies (Berndt et al., 2005; Sipilä et al., 2010), strongly imply that H_2SO_4 is still the main aerosol nucleation precursor. There is also another important aspect that one should take into account in homogeneous nucleation studies. Even if the system has multiple chemical species, it cannot be simply assumed that nucleation would take place through THN or multicomponent processes; rather it depends on several conditions including how much these ternary species are present in the system, and sometimes nucleation can take place solely via BHN even in the presence of ternary species (McGraw and Zhang, 2008). A laboratory study has also shown that different mechanisms may occur with the same aerosol precursors, under different experimental conditions (Kim et al., 1998). A typical atmospheric example would be the upper troposphere and lower stratosphere; even when there are many other chemical species in the gas phase, ion induced nucleation dominates in this region (Lee et al., 2003), because of low temperatures and high ion production rates by cosmic rays. While nucleation takes place nearly everywhere in the atmosphere, it is essential to understand how different nucleation processes co-exist in the same condition and when a certain nucleation process dominates under different atmospheric conditions. A universal nucleation mechanism which can be applied to all atmospheric conditions would unlikely exist, because of the diverse chemical, physical, meteorological and dynamics conditions found in the real atmosphere.

5 Conclusions

Our laboratory observations show that both the BHN and THN thresholds are $10^6\,cm^{-3}$ H_2SO_4 and the slope of Log J vs. Log [H_2SO_4] and Log J vs. Log RH are 3–5 and 1–4, respectively, when a CPC (TSI CPC 3876). The slope of Log J vs. Log [NH_3] is only one for THN. EF by NH_3 varies depending on [H_2SO_4], [NH_3], RH and residence times, but was for most time <10. To our knowledge, this is first time that NH_3-THN laboratory studies were made under conditions relevant to the lower troposphere. Our results reinforce that nucleation can be enhanced by NH_3, but $H_2SO_4$is still the main nucleation precursor responsible for new particle formation in the atmosphere. While our laboratory study could reproduce atmospheric observations made in Atlanta (McMurry et al., 2005) and Kent (Erupe et al., 2010), the current THN parameterization (Antilla et al., 2005; Merikanto et al., 2007) fails to produce particles under conditions used in our laboratory study and those found in the Kent field observations (Erupe et al., 2010).

Acknowledgements. This study was supported by NOAA (NA08OAR4310537), NSF (Career ATM-0645567; ATM-0904144) and Ohio Board of Regents. We thank Greg Huey and Dave Tanner for technical support on CIMS; Jyri Mikkila for technical assistances on PSM; John Passett, Al Viggiano, Mark Erupe, Li-Hao Young, John Nowak, Neil Donahue, and Bob McGraw for useful discussions.

Edited by: A. Laaksonen

References

Anttila, T., Vehkamäki, H., Napari, I., and Kulmala, M.: Effect of ammonium bisulfate formation on atmospheric water-sulfuric acid-ammonia nucleation, Boreal Environ. Res., 10, 511–523, 2005.

Ball, S. M., Hanson, D. R., Eisele, F. L., 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, 23709–23718, 1999.

Benson, D. R., Young, L. H., Kameel, R., and Lee, S.-H.: Laboratory-Measured Sulfuric Acid and Water Homogeneous Nucleation Rates from the SO_2 + OH Reaction, Geophys. Res. Lett., 35, L11801, doi:11810.11029/12008GL033387, 2008.

Benson, D. R., Erupe, M. E., and Lee, S.-H.: Laboratory-measured H_2SO_4-H_2O-NH_3 ternary homogeneous nucleation rates: Initial observations, Geophys. Res. Lett, 36, L15818, doi:10.1029/2009GL038728, 2009.

Benson, D. R., Markovich, A., Al-Refai, M., and Lee, S.-H.: A Chemical Ionization Mass Spectrometer for ambient measurements of Ammonia, Atmos. Meas. Tech., 3, 1075–1087, doi:10.5194/amt-3-1075-2010, 2010.

Berndt, T., Boge, O., Stratmann, F., Heintzenberg, J., and Kulmala, M.: Rapid formation of sulfuric acid particles at near atmospheric conditions, Science, 307, 671–698, 2005.

Berndt, T., Boge, O., and Stratmann, F.: Formation of atmospheric H_2SO_4/H_2O in the absence of organics: A laboratory study, Geophys. Res. Lett., 33, L15817, doi:15810.11029/12006GL026660, 2006.

Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Grüner, A., Spindler, G., Lee Mauldin III, R., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory study on new particle formation from the reaction OH + SO_2: influence of experimental conditions, H_2O vapour, NH_3 and the amine tert-butylamine on the overall process, Atmos. Chem. Phys., 10, 7101–7116, doi:10.5194/acp-10-7101-2010, 2010.

Birmili, W., Wiedensohler, A., Plass-Dulmer, C., and Berresheim, H.: Evolution of newly formed aerosol particles in the continental boundary layer: A case study including OH and H_2SO_4 measurements, Geophys. Res. Lett., 27, 2205–2208, 2000.

Dentener, F. J. and Crutzen, F.: A three-dimensional model of the global ammonia cycle, J. Atmos. Chem., 19, 331–369, 1994.

Donahue, N. M., Clarke, J. S., Demerjian, K. L., and Anderson, J. G.: Free-radical kinetics at high pressure: A mathematical analysis of the flow reactor, J. Phys. Chem., 100(14), 5821–5838, 1996.

Eisele, F. L. and Tanner, D. J.: Measurements of gas phase concentrations of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res., 98, 9001–9010, 1993.

Erupe, M. E., Benson, D. R., Li, J., Young, L.-H., Verheggen, B., Al-Refai, M., Tahboub, O., Cunningham, V., Frimpong, F., Viggiano, A. A., and Lee, S.-H.: Correlation of Aerosol Nucleation Rate with Sulfuric Acid and Ammonia in Kent Ohio: An Atmospheric Observation, J. Geophys. Res., 115, D23216, doi:10.1029/2010JD013942, 2010.

Erupe, M. E., Viggiano, A. A., and Lee, S.-H.: The effect of trimethylamine on atmospheric nucleation involving $\mathbf{H_2SO_4}$, Atmos. Chem. Phys., 4767–4775, doi:10.5194/acp-11-4767-2011, 2011.

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

Gaydos, T. M., Stainer, C. O., and Pandis, S. N.: Modeling of in situ ultrafine atmospheric particle formation in the eastern United States, J. Geophys. Res., 110, D07S12, doi:10.1029/2004JD004683, 2005.

Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part II. Thermodynamic properties and gas/particle partitioning, Atmos. Environ., 45(3), 561–577, 2010.

Hanson, D. R. and Eisele, F. L.: Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system, J. Geophys. Res., 107, 4158, doi:4110.1029/2001JD001100, 2002.

Jung, J., Adams, P., and Pandis, S. N.: Simulating the size distribution and chemical composition of ultrafine particles during nucleation events, Atmos. Environ., 40, 2248–2259, 2006.

Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mente, T. F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A.: New particle formation in forests inhibited by isoprene emissions, Nature, 461, 381–384, 2009.

Kim, T. O., Ishada, I., Adachi, M., Okuyama, K., and Seinfeld, J. H.: Nano-meter sized particle formation from $NH_3/SO_2/H_2O/$ air mixtures by ionizing irradiation, Aerosol Sci. Tech., 29, 111–125, 1998.

Kulmala, M., Vehkamaki, H., Petaja, T., dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W. H., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: A review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M.: Toward Direct Measurement of Atmospheric Nucleation, Science, 318, 89–92, 2007.

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.: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, Science, 301, 1886–1889, 2003.

Lucas, D. D. and Akimoto, H.: Evaluating aerosol nucleation parameterization in a global atmospheric model, Geophys. Res. Lett., 33, L10808, doi:10810.11029/12006GL025672, 2006.

McGraw, R. and Zhang, R.: Multivariate analysis of homogeneous nucleation rate measurements. Nucleation in the p-toluic acid/sulfuric acid/water system, J. Chem. Phys., 128, 064508, doi:10.1063/1.2830030, 2008.

McMurry, P. H., Fink, M., Sakuri, H., Stolzenburg, M., Mauldin III., R. L., Smith, J., Eisele, F. L., 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.

Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, J. Geophys. Res., 112, D15207, doi:15210.11029/12006JD007977, 2007.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009, 2009.

Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions, P. Natl. Acad. Sci. USA, 107, 6646–6651, doi:10.1073/pnas.0911330107, 2010.

Napari, I., Noppel, M., Vehkamaki, H., and Kulmala, M.: An improved model for ternary nucleation of sulfuric acid-ammonia-water, J. Chem. Phys, 116, 4221–4227, 2002.

Neuman, J. A., Nowak, J. B., Brock, C. A., Trainer, M., Fehsenfeld, F. C., Holloway, J. S., Hübler, G., Hudson, P. K., Murphy, D. M., Nicks Jr., D. K., Orsini, D., Parrish, D. D., Ryerson, T. B., Sueper, D. T., Sullivan, A., and Weber, R.: Variability in ammonium nitrate formation and nitric acid depletion with altitude and location over California, J.Geophys. Res., 108, 4557, 12 pp., doi:10.1029/2003JD003616, 2003.

Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10, 9773–9779, doi:10.5194/acp-10-9773-2010, 2010.

Nowak, J. B., Huey, L. G., Eisele, F. L., Tanner, D., Mauldin III., R. L., Cantrell, C. A., Kosciuch, E., and Davis, D.: Chemical ionization mass spectrometry technique for the detection of dimethylsulfoxide and ammonia, J. Geophys. Res., 107(D18), 4363, doi:4310.1029/2001JD001058, 2002.

Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), J. Geophys. Res., 111, D17308, doi:17310.11029/12006JD007113, 2006.

Nowak, J. B., Newman, J. A., Kozai, K., Huey, L. G., Tanner, D., Holloway, J. S., Ryerson, T. B., Frost, G. L., McKeen, S. A., and Fehsenfeld, F. C.: A chemical ionization mass spectrometry technique for airborne measurements of ammonia, J. Geophys. Res., 112, D10S02, doi:10.1029/2006JD007589, 2007.

Pryor, S. C., Barthelmie, R. J., Sørensen, L. L., McGrath, J. G., Hopke, P., and Petäjä, T.: Spatial and vertical extent of nucleation events in the Midwestern USA: insights from the Nucleation In ForesTs (NIFTy) experiment, Atmos. Chem. Phys., 11, 1641–1657, doi:10.5194/acp-11-1641-2011, 2011.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn., John Wiley and Sons Inc., New York, 2006.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L. I., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, Science, 327, 1243–1246, 2010.

Smith, J. N., Dunn, M. J., VanReken, T. M., Iida, K., Stolzenburg, M. R., McMurry, P. H., and Huey, L. G.: Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, Geophys. Res. Lett., 35, L04808, doi:04810.01029/02007GL032523, 2008.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H: Observations of ammonium salts in atmospheric nanoparticles and possible climatic implications, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.

Stanier, C. O., Kylstov, A. Y., and Pandis, S. N.: Nucleation events during the Pittsburgh air quality study: Description and relation to key meteorological, gas phase, and aerosol parameters, Aerosol Sci. Tech., 38, 253–264, 2004.

Vanhanen, J., Mikkila, J., Lehtipalo, K., Sipila, M., Manninen, H. E., Siivola, E., Petaja, T., and Kulmala, M.: Particle size magnifier for nano-CN detection, Aerosol Sci. Tech., 45, 533–542, 2011.

Vehkamäki, H.: Molecular Modeling of Atmospheric Clusters, 2010 International Aerosol Conference, Helsinki, Finland, 2010.

Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, 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:4610.1029/2002JD002184, 2002.

Viggiano, A. A., Seeley, J. V., Mundis, J. S., Williamson, J. S., and

Morris, R. A.: Rate Constants for the Reactions of $XO_3^-(H_2O)_n$ (X = C, HC, and N) and $NO_3^-(HNO_3)_n$ with H_2SO_4: Implications for Atmospheric Detection of H_2SO_4, J. Phys. Chem. A, 101, 8275–8278, 1997.

Weber, R. J., Marti, J. J., McMurry, P. H., Mauldin III., R. L., Tanner, D., Eisele, F. L., Brechtel, F., Kreidenweis, S. M., Kok, G., Schillawski, R. D., and Baumgardner, D.: A study of new particle formation and growth involving biogenic and trace gas species measured during ACE 1, J. Geophys. Res., 103, 16385–16396, 1998.

Weber, R. J., McMurry, P. H., Mauldin III., R. L., Tanner, D., 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.

Yokelson, R. J., Christian, T. J., Bertschi, I. T., and Hao, W. M.: Evaluation of adsorption effects on measurements of ammonia, acetic acid, and methanol, J. Geophys. Res., 108(D20), 4649, doi:10.1029/2003jd003549, 2003.

Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results, Atmos. Chem. Phys., 8, 4997–5016, doi:10.5194/acp-8-4997-2008, 2008.

Zhang, R., Wang, L., Khalizov, A. F., Zhao, J., Zheng, J., McGraw, R. L., and Molina, L. T.: Formation of nanoparticles of blue haze enhanced by anthropogenic pollution, P. Natl. Acad. Sci. USA, 106(42), 17650–17654, 2009.