Ternary homogeneous nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O under conditions relevant to the lower troposphere

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Received: 8 September 2010 – Accepted: 9 September 2010
– Published: 29 September 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Ternary homogeneous nucleation (THN) of $\text{H}_2\text{SO}_4$, $\text{NH}_3$, and $\text{H}_2\text{O}$ has been used to explain new particle formation in various atmospheric regions, yet laboratory measurements have failed to reproduce atmospheric observations. Here, we report laboratory observations of THN made under conditions relevant to the lower troposphere ($\text{H}_2\text{SO}_4$ of $10^6–10^7\ \text{cm}^{-3}$, $\text{NH}_3$ of 0.08–20 ppbv, and 288 K). Our observations show that $\text{NH}_3$ can enhance atmospheric $\text{H}_2\text{SO}_4$ aerosol nucleation and the enhancement factor (EF) in nucleation rate due to $\text{NH}_3$ increases linearly with increasing $\text{NH}_3$ and increases exponentially with decreasing $\text{H}_2\text{SO}_4$ and RH. The critical clusters of ternary homogeneous nucleation contain 3–5 molecules of $\text{H}_2\text{SO}_4$, 1–4 molecules of $\text{H}_2\text{O}$, and only 1 molecule of $\text{NH}_3$. The composition of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ in critical clusters and the threshold of $\text{H}_2\text{SO}_4$ concentrations required for the unit nucleation rate both do not vary in the presence and absence of $\text{NH}_3$. These observations can be directly used to improve aerosol nucleation models to correctly assess how man-made $\text{SO}_2$ and $\text{NH}_3$ affect aerosol formation and CCN production at the global scale.

1 Introduction

Nucleation (gas to particle conversion) is one of the most 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 (40%) 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; Sipila et al., 2010; Young et al., 2008) have shown that sulfuric acid ($\text{H}_2\text{SO}_4$) is the main nucleation precursor, but the role of other ternary species such as ammonia ($\text{NH}_3$) and organic compounds is unclear.
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, 2009). Global atmospheric aerosol model calculations also suggested that in a wide range of the troposphere and the lower stratosphere, nucleation rates can be predicted by the ternary homogeneous nucleation (THN) of H$_2$SO$_4$, NH$_3$, and H$_2$O (Lucas and Akimoto, 2006). Especially in the Eastern US, new particle formation has been explained by THN for many years (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 over-predicts nucleation rates of THN over binary homogeneous nucleation (BHN) of H$_2$SO$_4$ and H$_2$O. This THN parameterization includes the NH$_3$ range from 0–100 pptv and for NH$_3$ greater than 100 pptv, it assumes that there is no effect on the nucleation rate except for H$_2$SO$_4$ less than 10$^6$ cm$^{-3}$, while atmospherically observed NH$_3$ are typically at the sub-ppbv and ppbv level (Erupe et al., 2010; Nowak et al., 2006). Later THN parameterizations included the effects of stable ammonium bisulfate (NH$_4$HSO$_4$) formation (Antilla 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).

At present, the exact amount of NH$_3$ needed to enhance nucleation rates 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$_2$SO$_4$ > 10$^8$ cm$^{-3}$, two to three orders of magnitude higher than typical atmospheric concentrations. These limited observations have shown that at such high concentrations of H$_2$SO$_4$, NH$_3$ of ppbv or sub-ppbv can increase nucleation rates up to 3 orders of magnitude, although often the enhancement factors (EF; defined as the ratio of nucleation rates in THN vs. in BHN) due to NH$_3$ are around one order of magnitude.
In the present laboratory study, we present laboratory observations of homogeneous nucleation involving, \( \text{H}_2\text{SO}_4 \), \( \text{NH}_3 \), and \( \text{H}_2\text{O} \). Experiments were performed at \( \text{H}_2\text{SO}_4 \) of \( 10^6 \text{--} 10^7 \text{ cm}^{-3} \), \( \text{NH}_3 \) of 0.08--2.6 ppbv (except only one occasion where 20 ppbv \( \text{NH}_3 \) was used), RH of 6--40% and 288 K, in a temperature- and RH-controlled fast flow nucleation reactor.

2 Experiments

Our nucleation experimental setup was described in detail in (Benson et al., 2008, 2009; Young et al., 2008). Briefly, the system consists of five main sections: (i) a photolysis region where OH radicals are produced from the photodissociation of \( \text{H}_2\text{O} \) vapor with a UV lamp \( (\lambda < 185 \text{ nm}) \), (ii) a mixing region where the trace gases (\( \text{SO}_2 \), \( \text{O}_2 \), and \( \text{N}_2 \)) are introduced into the flow tube and where \( \text{H}_2\text{SO}_4 \) is also produced from the \( \text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3 \) Reaction \( (R1, 2.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}) \) at a local source (as opposed to continuously formed in the nucleation reactor), (iii) a double jacket, fast flow nucleation reactor (RH- and temperature-controlled), (iv) two chemical ionization mass spectrometers (CIMSs) to measure \( \text{H}_2\text{SO}_4 \) and \( \text{NH}_3 \) at the beginning of the nucleation reactor, and (v) a CPC (TSI 3786), which is connected to the end of the nucleation reactor, to measure particle number concentrations for \( >3 \text{ nm} \) particles.

There are also several improvements in the current nucleation setup. We have 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 (WLF) of \( \text{H}_2\text{SO}_4 \) (1.5--4 now vs. 2--360 previously), by using large size inner diameters and by introducing trace species from the center of the flow reactor under high flow. \( \text{H}_2\text{SO}_4 \) concentrations are changed by changing OH with an iris beam splitter to control the UV beam; previously, \( \text{H}_2\text{SO}_4 \) was changed by changing \( \text{SO}_2 \) (Benson et al., 2008, 2009; Young et al., 2008). In addition, RH values are changed by adding water vapor at the downstream end after the production of \( \text{H}_2\text{SO}_4 \), to allow independent changes in RH in the nucleation reactor and OH (thus \( \text{H}_2\text{SO}_4 \)) concentrations.
The detection scheme for the H$_2$SO$_4$-CIMS is based on NO$_3^-$ + H$_2$SO$_4$ → HNO$_3$ + HSO$_4^-$ (R2, 2.3 × 10$^{-9}$ cm$^3$ s$^{-1}$) at atmospheric pressure (Benson et al., 2008, 2009; Eisele and Tanner, 1993; Erupe et al., 2010; Young et al., 2008). NH$_3$ is detected in another CIMS using protonated ethanol ions as the reagent based on NH$_3$ + (CH$_3$CH$_2$OH)H$^+$ → NH$_4^+$ + CH$_3$CH$_2$OH (R3, 2.0 × 10$^{-9}$ cm$^3$ s$^{-1}$) at a lower pressure (20 torr) (Benson et al., 2008, 2009, 2010; Erupe et al., 2010; Nowak et al., 2006; Young et al., 2008). One issue that must be taken into account in the nucleation experiments is the amount of NH$_3$ that comes from the flow tube system, which most likely originated from water vapor (Nowak et al., 2006). This background NH$_3$, measured with CIMS, increased linearly with RH in the flow tube, but for RH from 6–40%, the NH$_3$ from water vapor in the flow tube was ∼20–100 pptv.

3 Results

Figure 1a shows the measured nucleation rate ($J$) as a function of initial [H$_2$SO$_4$] for different RH values with and without NH$_3$. The total flow through the reactor was 10.3 lpm (2.8 lpm through the nucleation region and 7.5 lpm to the two CIMSs), 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$_2$SO$_4$] from 2 × 10$^6$–2 × 10$^7$ cm$^{-3}$ and in general, was 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$_2$SO$_4$ threshold to produce the unit $J$ (1 cm$^{-3}$ s$^{-1}$) was at the 10$^6$ cm$^{-3}$ range, which is one of the main findings of the present study.

From a plot of Log $J$ vs. Log [H$_2$SO$_4$], one can obtain the number of H$_2$SO$_4$ molecules in the critical cluster ($n_{H_2SO_4}$) if saturation ratios of other components are constant, based on the first nucleation theorem (Kashchiev, 1982; McGraw and Zhang, 2008). The derived $n_{H_2SO_4}$ was 3–5 for both BHN and THN cases. Unlike (Benson et al., 2009) in which $n_{H_2SO_4}$ increased with decreasing RH, there was no clear trend in $n_{H_2SO_4}$ as
a function of RH. The $n_{H_2SO_4}$ values only slightly decreased (reduced by 0.04 to 0.4 molecules) for THN compared to BHN for the same RH.

Figure 1b shows the measured Log $J$ vs. Log RH for BHN and THN with NH$_3$ (20 ppbv). $J$ varied from $3 \times 10^{-3}$–$3 \times 10^1$ cm$^{-3}$ s$^{-1}$ for RH values 6–40%, initial [H$_2$SO$_4$] in the range of $3 \times 10^6$–$7 \times 10^6$ cm$^{-3}$ and at a residence time of 120 s, and was usually higher in the presence of NH$_3$ than without it. In both the BHN and THN cases, the H$_2$SO$_4$ threshold to produce the unit $J$ was again at the $10^6$ cm$^{-3}$ range. The slope of Log $J$ vs. Log RH, which is the same as the number of water molecules ($n_{H_2O}$) in critical clusters, was 1–4 and only slightly reduced in the presence of NH$_3$. Thus, under these experimental conditions, there was also no change in the composition of H$_2$SO$_4$ and H$_2$O molecules in critical clusters in the presence and absence of NH$_3$.

Figure 1c shows the measured $J$ vs. NH$_3$ at H$_2$SO$_4$ 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 $n_{H_2SO_4}$ and $n_{H_2O}$ values did not change in BHN and THN (Fig. 1a and b).

By comparing the measured nucleation rates in THN vs. BHN taken under similar experimental conditions, enhancement factors (EF) were derived. EF values were usually lower than 10 for H$_2$SO$_4$ from $2 \times 10^6$–$2 \times 10^7$ cm$^{-3}$, NH$_3$ from 1.22–2.6 ppbv, RH from 6–16% and residence times of 60–240 s (Fig. 2a). Similarly to (Benson et al., 2009), EF was in general higher for lower H$_2$SO$_4$ (Fig. 2a) and lower RH (Fig. 2b) and higher at higher NH$_3$ (Fig. 2c).
4 Discussions

Our observations show that the onset $\text{H}_2\text{SO}_4$ for nucleation to occur ($J = 1 \text{ cm}^{-3} \text{s}^{-1}$) is on the order of $10^6 \text{ cm}^{-3}$ with or without $\text{NH}_3$. 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 $\text{H}_2\text{SO}_4$ of $10^6 - 10^8 \text{ cm}^{-3}$. On the other hand, BHN parameterizations typically require $\text{H}_2\text{SO}_4$ of $10^9 \text{ cm}^{-3}$ or higher (Vehkamäki et al., 2002). Recent laboratory studies have shown that nucleation can occur at $[\text{H}_2\text{SO}_4]$ as low as $10^6 \text{ cm}^{-3}$ (Berndt et al., 2005, 2008; Metzger et al., 2010; Sipilä et al., 2010). However, only two studies so far have shown the power dependence of $J$ on $[\text{H}_2\text{SO}_4]$ of one (Metzger et al., 2010) or two (Sipilä et al., 2010), as found from atmospheric observations. (Sipilä et al., 2010) used a newly developed particle detector that measures particles down to 1.5 nm and also incorporated a longer residence time in the nucleation reactor and a continuous source of $\text{H}_2\text{SO}_4$ production in the nucleation reactor. (Metzger et al., 2010) added organic compounds (i.e. trimethylbenzene) in the $\text{H}_2\text{SO}_4$ aerosol nucleation, but used a regular TSI CPC 3025 to detect particles.

In the present study, we found the threshold of $10^6 \text{ cm}^{-3} \text{H}_2\text{SO}_4$ and the slope of $J$ vs. $\text{H}_2\text{SO}_4$ between 3–5 for both BHN and NH$_3$-THN cases, using the same instrument used in field studies to measure particles (TSI CPC 3876). While we used a longer residence time (60–240 s) in the nucleation region, $\text{H}_2\text{SO}_4$ was also produced in a local source. The slopes (3–5, as compared to 1–2) found in BHN are, however, thermodynamically consistent with quantum chemical calculations which show that a monomer or dimer of $\text{H}_2\text{SO}_4$ would spontaneously evaporate and is difficult to form critical clusters by themselves (Lovejoy et al., 2004; McGraw and Weber, 1998; McGraw and Zhang, 2008).

One of the main principles of THN is that it could explain nucleation occurring at lower $[\text{H}_2\text{SO}_4]$ 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 $\text{H}_2\text{SO}_4$ 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$_2$SO$_4$, any enhancement with NH$_3$ would not be large enough to shift the threshold value. Most EF values were largest at three orders of magnitude for H$_2$SO$_4$ from $10^8$–$10^{10}$ cm$^{-3}$ (Ball et al., 1999; Benson et al., 2009). As shown in the present study, when H$_2$SO$_4$ ($10^6$–$10^7$ 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 $<10$ (Fig. 2). These observation results may be consistent with density functional calculations which show that NH$_3$ can lower the Gibbs free energy of H$_2$SO$_4$–H$_2$O clusters under actual atmospheric conditions, but the amount of such clusters would be also negligible due to the required temperatures and NH$_3$ (Kurten et al., 2007).

Our results show that the $n_{H_2SO_4}$ and $n_{H_2O}$ values were reduced under THN compared to BHN, but $n_{H_2SO_4}$ and $n_{H_2O}$ both were also very similar in BHN and THN cases. For example, the $n_{H_2SO_4}$ value was reduced only by a fraction of a molecule (0.04 to 0.4 molecules). Thus, while the nucleation rate was enhanced, an addition of NH$_3$ did not drastically change the H$_2$SO$_4$ and H$_2$O composition of the critical clusters under atmospheric 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$_2$SO$_4$ in the presence of NH$_3$. This difference may be due to much longer nucleation times used in this study (60–240 s) or much lower H$_2$SO$_4$ concentrations used here ($10^6$–$10^7$ cm$^{-3}$). The estimated $n_{NH_3}$ was only one, which is consistent with cluster measurements by (Hanson and Eisele, 2002) and this unit value also explains the small reduction in $n_{H_2SO_4}$ and $n_{H_2O}$ in THN than in BHN. This low $n_{NH_3}$ value 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$_2$SO$_4$ 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$_2$SO$_4$, 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 present experimental conditions fall within these observational results. (McMurry et al., 2005) also showed the slope of particle concentration vs. NH$_3$ is nearly one (McMurry et al., 2005), similar to the present study showing that $n_{\text{NH}_3}$ is only one. Another study made in Kent, Ohio crossing four different seasons showed the threshold of H$_2$SO$_4$ 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$_2$SO$_4$ for the unit $J$ is $10^6$ 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$_2$SO$_4$] of $10^9$ cm$^{-3}$ for NH$_3$ of 1 ppbv at 273 K (Merikanto et al., 2007) (Fig. 3). A similar [H$_2$SO$_4$] threshold is also required in the BHN parameterization (Vekhamaki et al., 2002) (Fig. 3). We also used our typical experimental conditions of H$_2$SO$_4$, 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.

5 Conclusions

Our laboratory observations show that both the BHN and THN thresholds are $10^6$ cm$^{-3}$ H$_2$SO$_4$ and the slope of $J$ vs. H$_2$SO$_4$ (that is, $n_{\text{H}_2\text{SO}_4}$) is 3–5, $n_{\text{H}_2\text{O}}$ is 1–4, using the same particle instruments (TSI CPC 3876) used in field studies. The slope of $J$ vs. NH$_3$ ($n_{\text{NH}_3}$) was only one for THN. Nucleation enhancement factors by NH$_3$ varied depending on H$_2$SO$_4$, RH and residence times, but was for most time <10. These results imply that nucleation can be enhanced by NH$_3$, but H$_2$SO$_4$ 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 Kent field observations.

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, and John Nowak, Al Viggiano, Bob McGraw and Mark Erupe for useful discussions.

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**Fig. 1a.** The measured Log J vs. Log [H$_2$SO$_4$] for binary (filled symbols) and ammonia-ternary nucleation (open symbols) at RH = 9% (squares), 13% (triangles), 16% (circles). Solid lines show the linear fitting curve of the data. These data are for a 240 s residence time. NH$_3$ = 1.20 ppbv for THN. The horizontal and vertical bars indicate one standard deviation of H$_2$SO$_4$ concentration and nucleation rate; the solid or dashed lines show the linear fitting curve of the data.
Fig. 1b. Graph of Log $J$ vs. Log RH. The number of water molecules in the critical cluster is 1–4. This number is slightly reduced in the presence of ammonia (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. $J$ varies from $3 \times 10^{-3}$–$3 \times 10^1$ cm$^{-3}$ s$^{-1}$ for RH values 6–40% and initial $[\text{H}_2\text{SO}_4]$ in the range of $3 \times 10^6$–$7 \times 10^6$ cm$^{-3}$ and is usually higher in the presence of NH$_3$ than without it. In both the BHN and THN cases, the $\text{H}_2\text{SO}_4$ threshold to produce the unit $J$ (1 cm$^{-3}$ s$^{-1}$) is at the $10^6$ cm$^{-3}$ range.
Fig. 1c. The measured Log $J$ vs. Log [NH$_3$] for THN experiments. RH = 8%. H$_2$SO$_4$ = 8.2 $\times$ 10$^6$ cm$^{-3}$. Residence time = 170 s. The solid line shows the linear fitting curve of the data.
Fig. 2a. The measured nucleation enhancement factor (EF) as a function of \([\text{H}_2\text{SO}_4]\). RH = 6–16\%. \([\text{NH}_3]\) = 1.22–2.6 ppbv. Residence time = 60–240 s.
**Fig. 2b.** The measured nucleation enhancement factor (EF) as a function of RH. EF is defined as the ratio of nucleation rates in the NH$_3$ ternary homogeneous nucleation vs. rates in the binary homogeneous nucleation. [H$_2$SO$_4$] = 5 x 10$^6$–7 x 10$^6$ cm$^{-3}$. RH = 7–39%. [NH$_3$] = 20 ppbv. Residence time = 80–240 s.
Fig. 2c. The measured nucleation enhancement factor (EF) as a function of NH$_3$ mixing ratio. RH = 8%. [H$_2$SO$_4$] = 8.2 × 10$^6$ cm$^{-3}$. Residence time = 170 s.
Fig. 3. Log $J$ vs. Log $[\text{H}_2\text{SO}_4]$ based on predictions by (Vehkamäki et al., 2002) (BHN) and (Merikanto et al., 2007) (THN). The parameters are a temperature of 288 K, RH of 40% and $\text{NH}_3$ concentration of 100 pptv (for THN only).