

The effect of trimethylamine on atmospheric nucleation involving H_2SO_4

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Abstract. Field observations and quantum chemical calculations have shown that organic amine compounds may be important for new particle formation involving H_2SO_4 . Here, we report laboratory observations that investigate the effect of trimethylamine (TMA) on H_2SO_4 - H_2O nucleation made under aerosol precursor concentrations typically found in the lower troposphere ($[\text{H}_2\text{SO}_4]$ of 10^6 – 10^7 cm^{-3} ; $[\text{TMA}]$ of 180–1350 pptv). The threshold $[\text{H}_2\text{SO}_4]$ needed to produce the unity J was from 10^6 – 10^7 cm^{-3} and the slopes of $\text{Log } J$ vs. $\text{Log } [\text{H}_2\text{SO}_4]$ and $\text{Log } J$ vs. $\text{Log } [\text{TMA}]$ were 4–6 and 1, respectively, strikingly similar to the case of ammonia (NH_3) ternary nucleation (Benson et al., 2011). At lower RH, however, enhancement in J due to TMA was up to an order of magnitude greater than that due to NH_3 . These findings imply that both amines and NH_3 are important nucleation species, but under dry atmospheric conditions, amines may have stronger effects on H_2SO_4 nucleation than NH_3 . Aerosol models should therefore take into account inorganic and organic base compounds together to fully understand the widespread new particle formation events in the lower troposphere.

1 Introduction

New particle formation (NPF) is a global phenomenon (Kulmala et al., 2004) that can impact the nature and amount of clouds through formation of cloud condensation nuclei (CCN) in the atmosphere (Merikanto, 2009). NPF therefore has important climate implications and an understanding of the aerosol nucleation processes (formation of solid or liquid particles from gas phase species) is vital in reducing the current uncertainties associated with climate-aerosol interac-

tions (IPCC, 2007). But the nucleation mechanisms are not well understood, and the identity of the possible species involved in the nucleation processes is yet unclear. Although several theories including binary homogeneous nucleation (BHN) (Vehkamäki et al., 2002) and ternary homogeneous nucleation (THN) with NH_3 (Merikanto et al., 2007) have been proposed to explain nucleation in the atmosphere, most of them come short of reproducing the observed nucleation rates (J) and the number of molecules in the critical cluster, especially at the typical conditions of the lower troposphere.

Laboratory experiments (Benson et al., 2008; Berndt et al., 2005; Sipilä et al., 2010; Young et al., 2008) and field observations (Erupe et al., 2010; Kulmala et al., 2004; Riipinen et al., 2007; Weber et al., 1999) have shown that H_2SO_4 is important in NPF in the atmosphere. However, other species are also needed to explain atmospherically observed J . Possible species include NH_3 (Ball et al., 1999; Benson et al., 2009, 2011) and volatile organic compounds (VOCs) such as organic acids (Bonn and Moortgat, 2003; Hoffmann et al., 1998; Kavouras et al., 1998; O'Dowd et al., 2002; Zhang et al., 2004), 1,3,5-trimethylbenzene (Paasonen et al., 2010), and amines (Barsanti et al., 2009; Smith et al., 2010). While there are thousands of organic compounds in the atmosphere, amines have become increasingly important, since recent quantum chemical calculations have shown that they can form neutral and ion clusters with H_2SO_4 molecules more efficiently than NH_3 (Kurtén et al., 2008), even though amine concentrations are lower than that of NH_3 . This is further supported by a recent experiment which shows that amines can substitute ammonium to aminium in sub-3 nm ammonium sulfate clusters (Bzdek et al., 2010). More evidence on the possible role of amines in NPF was found in field measurements which showed the presence of aminium ions in nanoparticles (Makela et al., 2001; Smith et al., 2004, 2008).

A comprehensive review of a large number of atmospheric amines including their thermodynamic properties was given by (Ge et al., 2010a, b). Amines are ubiquitous in the



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atmosphere with various sources that include animal husbandry, oceans, waste incinerators and cars (Cadle and Mulawa, 1980; Facchini et al., 2008; Schade, 1995). Amines and NH₃ in general have similar sources, and the relative abundance of amines vs. NH₃ varies with sources and locations. For example, a study in the sea and remote location has shown that amines may contribute up to 20% of the concentration of the bases in these areas (Gibb et al., 1999), where H₂SO₄ forms from dimethylsulfide oxidation and thus nucleation also takes place. In the continental areas, animal husbandry produces up to 108 Gg N yr⁻¹ from TMA, which is 2 orders of magnitude lower than NH₃ output (23 300 Gg N yr⁻¹) (Schade, 1995). A more recent study has indicated that amines may represent up to 20% of the measured NH₃ (Sorooshian et al., 2008). In terms of molecular structure, amines are classified into primary, secondary, or tertiary categories (Schade, 1995). Amongst tertiary amines, TMA is one of the most abundant species in the atmosphere and is one of the widely studied amine compounds (Schade, 1995; Silva et al., 2008).

There are also many similarities in the physical and chemical properties of TMA and NH₃. TMA and NH₃ compounds have similar basicities (NH₃pK_a = 9.25; TMApK_a = 10.72) and proton affinities (PA_{NH₃} = 853.6 kJ mol⁻¹; PA_{TMA} = 948.9 kJ mol⁻¹), while Henry's law coefficients are somewhat different (TMA 9.5 M atm⁻¹ at 20 °C; NH₃ 60 M atm⁻¹ at 25 °C (NIST, 2005)). Amines and NH₃ can also lower the surface tension above the solution of H₂SO₄ and H₂O and thus can potentially influence the Kelvin effect in homogeneous nucleation (Hyvarinen et al., 2004; Hyvärinen et al., 2005). Like NH₃, amines are removed from the atmosphere by reactions with common atmospheric acids such as H₂SO₄ and HNO₃. But unlike NH₃, amines are also removed efficiently through rapid oxidation reactions with atmospheric oxidants, such as OH, O₃, and NO₃ (Finlayson-Pitts and Pitts, 2000; Ge et al., 2010a, b; Malloy et al., 2009; Murphy, 2007; Pitts Jr. et al., 1978). These similarities in sources and physical and chemical properties between NH₃ and amines, and the fact that they both have been detected in atmospheric nanoparticles (Makela et al., 2001; Smith et al., 2005; Smith et al., 2008), make them ideal potential precursors for aerosol nucleation involving H₂SO₄. Currently, however, there are very few experimental studies involving amines and their possible roles in nucleation (Berndt et al., 2010; Smith et al., 2010; Wang et al., 2010a, b). Among these studies, only one study has so far examined the potential role of tert-butylamine (a primary amine) in nucleation (Berndt et al., 2010), while others have focused mainly on the possible roles of amines in the growth of newly formed particles.

In the present study, we have investigated the effect of TMA on H₂SO₄-H₂O nucleation under [H₂SO₄] of 10⁶–10⁷ cm⁻³, to compare with NH₃-THNn (Benson et al., 2011). Compared to the (Berndt et al., 2010) tert-butylamine study, the aerosol precursor concentrations (H₂SO₄ and amines)

used in the present study were one or three orders of magnitude lower, relevant to the real atmospheric conditions; H₂SO₄ was also detected directly by a chemical ionization mass spectrometer (CIMS). Particle formation rates as a function of [H₂SO₄], [TMA] and RH were studied at a constant temperature (288 K). There is another companion paper by (Benson et al., 2011), where we show the effect of NH₃ on H₂SO₄ nucleation under conditions relevant to the lower troposphere, as well as growth rates measured with CPC (TSI 3776) at low [H₂SO₄] and possible factors which contribute to growth rates.

2 Experiments

Detailed description of the instruments and the performance was given elsewhere (Benson et al., 2008, 2009, 2011; Young et al., 2008). Only the details relevant to the current experiments are reported here. OH radicals were produced by photolyzing water vapor using UV light (wavelength $\lambda < 185$ nm) with a mercury lamp (Pen-Ray 11SC-1). The OH radicals then were mixed with SO₂, O₂, humidified N₂ (to control RH), dry N₂ gases (vaporized from liquid nitrogen) and TMA, before they entered a temperature controlled fast flow reactor (288 K) where nucleation took place. H₂SO₄ vapor was produced from the



reaction, rate constant $k_1 = 8.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, (Finlayson-Pitts and Pitts, 2000) and was measured with CIMS, using (HNO₃)NO₃⁻ ions as reagent (Eisele and Tanner, 1993; Erupe et al., 2010). Variation in [H₂SO₄] in the nucleation reactor was made by changing the slit width in the UV box using an iris beam splitter, which in turn changed the photon flux in the photolysis tube (Benson et al., 2011). This phototube current was also simultaneously measured by a picoammeter (Keithley 6485) and used to estimate [OH] produced based on (Cantrell et al., 1997; Young et al., 2008). From these [OH], we can estimate [H₂SO₄] and thus, this method also serves as calibration of H₂SO₄-CIMS. We also added a second water bath after the UV source, to change RH independently from [OH] (and thus [H₂SO₄]) (Benson et al., 2011). The nucleation reactor had a diameter of 5.08 cm and a length of 80 cm; and we assumed nucleation time is half of the residence time based on nucleation inversion modeling calculations (Young et al., 2008). The total flow inside the nucleation reactor was maintained at 2–5 liters per minute (lpm), corresponding to a residence time of ~20–50 s.

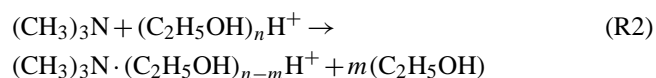
Particle number concentrations were measured using a butanol-based condensation particle counter (CPC, TSI 3776). The cutting sizes of the CPC are 3 nm (100% detection efficiency), 2.3 nm (50%), 2 nm (25–30%) and 1.8 nm (~10%), (http://www.tsi.com/uploadedFiles/Product_Information/Literature/Spec_Sheets/3776_2980346_A4.pdf). As shown in (Benson et al., 2011), the produced particles

were smaller than 2 nm with [H₂SO₄] of 10⁶ to 10⁷ cm⁻³, with the majority smaller than 1.8 nm. The growth rates (~2.6–7.7 nm h⁻¹) estimated from CPC at these low [H₂SO₄] were discussed in detail in (Benson et al., 2011).

To reduce possible impurities of NH₃ in the system, N₂ gases that were used for dilutions and makeup flows were vaporized from liquid nitrogen which has minimal NH₃ (<20 pptv; 1 pptv ≈ 2 × 10⁷ cm⁻³) (Benson et al., 2010; Nowak et al., 2006). All experimental setup was exclusively built with fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon surfaces, since NH₃ adsorption is least effective on these Teflon materials and most effective on the stainless steel material (Benson et al., 2010; Nowak et al., 2007; Yokelson et al., 2003). The impurity NH₃ likely originated from de-ionized water was also determined with CIMS and was below 100 pptv at RH 6–40 % (Benson et al., 2011).

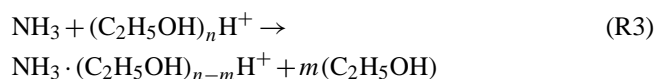
TMA vapor was introduced from a previously calibrated, National Institute of Standard Technology (NIST) traceable disposable permeation tube kept at constant temperature (303 K) in a gas standard generator (Kin-tek 491MB), thereby emitting a uniform known amount of TMA at the ppbv range. Further dilutions were made at the mixing ratio in the range from ~180–1350 pptv. TMA was introduced at 10 cm downstream of SO₂ addition, corresponding to a reaction time of 0.7 s. With this reaction time and [SO₂] of 4 ppmv, 100 % of OH radicals are converted to HSO₃ via Reaction (R1) (hence to H₂SO₄) in the photolysis region, assuming a homogeneous air mixing and negligible CO and hydrocarbons in the system. Moreover, at lower [TMA] level (sub-ppbv or ppbv) used in the current experiments, TMA did not affect the [OH] level to further alter [H₂SO₄]. The possibility that TMA oxidation by OH may form condensable products was further ruled out by running control experiments without adding SO₂. Without SO₂ and with TMA and OH, we did not observe particle formation. The rate constant for the TMA + OH reaction is at the 3.6–6.1 × 10⁻¹¹ cm³ s⁻¹ range (Atkinson, 1986; Koch et al., 1996). It is possible that the TMA + OH oxidation products such as peroxides, alkyl peroxides and imines (Malloy et al., 2009; Murphy, 2007) may be too volatile to form particles in a short time scale (20–50 s) or these oxidation products may not form clusters easily as H₂SO₄ molecules.

We have used the TMA concentrations, provided by the permeation tube, in this study. Occasionally, TMA in the nucleation reactor was also verified using a CIMS, utilizing a detection scheme shown below, which is similar to that used for NH₃ (Benson et al., 2010; Nowak et al., 2006)



where $m = 1, 2, 3, \dots$ etc., and m is also an integer which is less or equal to n . We have estimated the reaction rate of Reaction (R3) with trajectory calculations (Viggiano et al., 1982)

(1.23 × 10⁻⁹ cm³ s⁻¹) and the average dipole orientation (ADO) theory (Baulch et al., 1982) (1.01 × 10⁻⁹ cm³ s⁻¹). Both values are within the same range as the reaction rate, determined experimentally (1.17 × 10⁻⁹ cm³ s⁻¹) (Keese, 1986 #1379). These values are also similar to the reaction rate of the NH₃-ethanol system ($k_4 = 1.5 \times 10^{-9}$ cm³ s⁻¹) (Nowak et al., 2002), as expected:



As shown in Fig. 1a and b, the product ion signals [(CH₃)₃NH⁺, mass 60; (CH₃)₃N · (C₂H₅OH)H⁺, mass 106] show that [TMA] produced from the permeation tube was constant and stable. The possible impurities [TMA] in the nucleation tube were estimated to roughly <~85 ppbv at low RH (<10 %) conditions, but more systematic investigations are required in future studies. Due to such impurities of NH₃ (<100 pptv) and amines (e.g., TMA <85 pptv) in the system, the experiments performed without adding TMA should be considered as a pseudo BHN system.

3 Results

One of the objectives of the present study was to compare the effects of TMA on H₂SO₄ nucleation with the NH₃ effects reported in (Benson et al., 2011). And, our experimental results show that TMA acts very similarly to NH₃. Figure 2a shows the results of Log J vs. Log [H₂SO₄] for RH between 12–41 %, [H₂SO₄] between 3 × 10⁶–4 × 10⁷ cm⁻³ and [TMA] of 480 pptv at a temperature of 288 K. These experimental conditions were close to those of (Benson et al., 2011); but the residence times were different in these two studies, 20–50 s in the current experiments and 190 s in (Benson et al., 2011). In the presence of 480 pptv TMA, J was higher than in the absence of TMA, within the RH range studied (12–41 %), demonstrating that TMA indeed enhances nucleation of H₂SO₄ and H₂O (Fig. 2a), similarly to NH₃ (Benson et al., 2011).

In the absence of TMA, the slope of Log J vs. Log [H₂SO₄] was between 4–6 and generally increased as the RH decreased, similarly to our previous laboratory studies of homogeneous nucleation (Benson et al., 2008, 2009; Young et al., 2008). Since the particle measurements with CPC have size dependent detection efficiencies and the formed particles also grow by condensation in addition to nucleation, the observed slope of Log J vs. Log [H₂SO₄] included both nucleation and condensation effects and condensation growth made the slope appear higher than the actual values. The [H₂SO₄] needed to produce the unity J (that is, threshold [H₂SO₄] for nucleation) was about 4 × 10⁶ cm⁻³. This is also similar to (Benson et al., 2011), despite the residence times being up to a factor of 5 lower in the present study. Thus, whereas residence time is important in nucleation as discussed in (Benson et al., 2011; Berndt et al., 2010), it

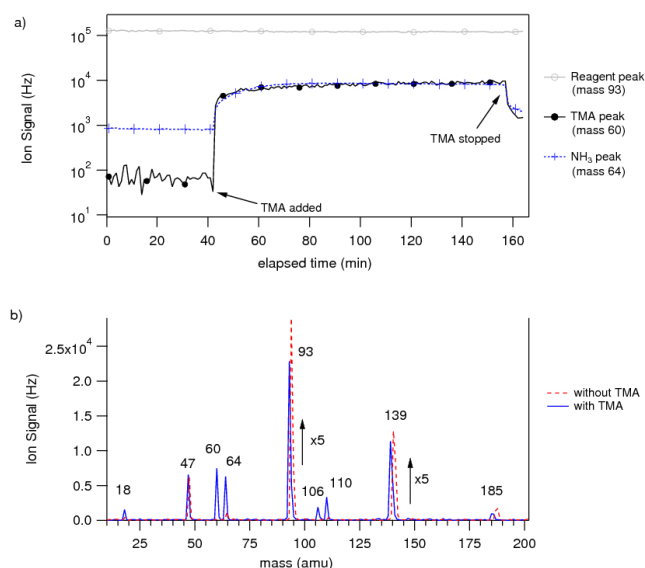


Fig. 1. (a) CIMS-measured TMA (black solid line and filled circles) and background NH₃ originated from the TMA permeation tube (blue dotted line and crosses). This figure shows that the production of TMA from the permeation tube is steady with time, but NH₃ impurities also exist from TMA. (b) A mass spectrum before and after adding 480 pptv TMA. After addition of TMA, TMA ion peaks [(CH₃)₃NH⁺, mass 60 amu; (CH₃)₃N · (C₂H₅OH)H⁺, mass 106] were clearly observed. Also, NH₃ peaks [(NH₃ · (C₂H₅OH)H⁺, mass 64; NH₄⁺, mass 18] increased, indicating that there were some NH₃ impurities from the TMA source. The spectrum without TMA is right-shifted 2 % and mass 93 and 139 are scaled down (5 times) for clarity. We have estimated up to 400 pptv of NH₃ impurities in the system (including those from TMA and de-ionized water).

has little effect on the cutoff of [H₂SO₄] needed to produce the unity J , at least for the TMA case. The slope of Log J vs. Log [H₂SO₄] also slightly reduced by 1–2 in the presence of TMA. This reduction in the slope of Log J vs. Log [H₂SO₄] is also very similar to the NH₃ ternary homogeneous nucleation case (Benson et al., 2009, 2011).

Figure 2b shows results for log J vs. log [TMA] for J values between 12–41 cm⁻³ s⁻¹ and [TMA] in the range 180–1350 pptv. The total flow rate in the nucleation reactor was ~5 lpm corresponding to a residence time of 20 s. The slope of Log J vs. Log [TMA] was 0.7, for [H₂SO₄] at the 10⁷ cm⁻³ range and 25 % RH. This is again similar to the NH₃-THN result, where the slope of log J vs. log [NH₃] was nearly 1 (Benson et al., 2011).

The effect of TMA in particle number concentration was quantitatively characterized by comparing the ratios of particle number concentration with and without TMA as a function of both [H₂SO₄] and [TMA]. This ratio, defined as the enhancement factor (EF), was found to be dependent on [H₂SO₄], with higher values at lower [H₂SO₄] (Fig. 3a). These EF values (2–35) were somewhat higher than those found in NH₃-THN experiments (Benson et al., 2011) un-

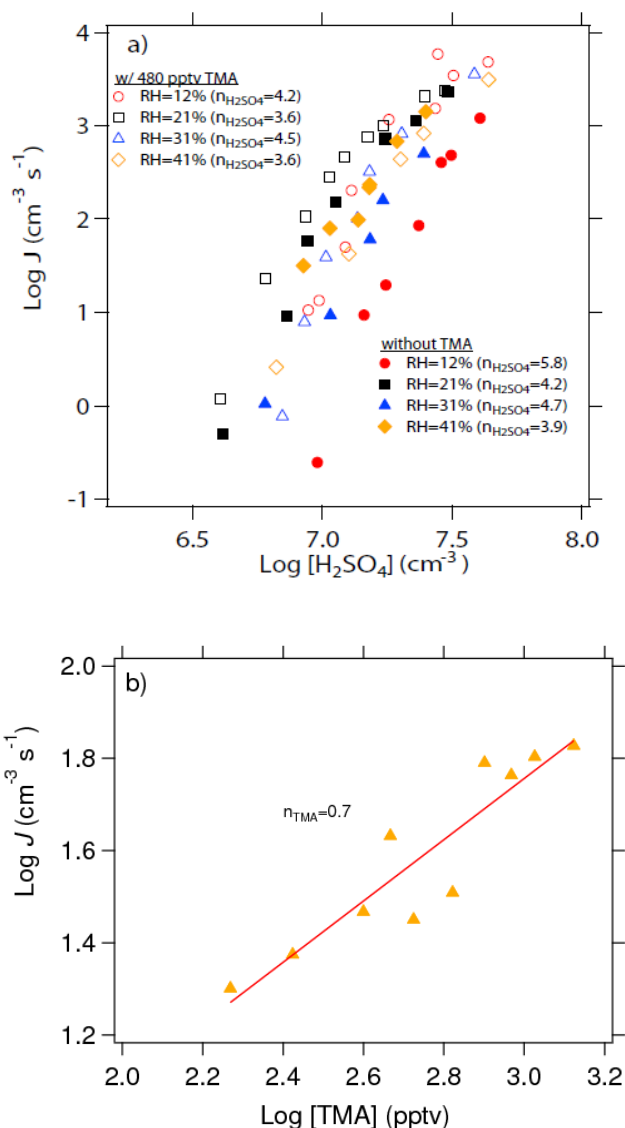


Fig. 2. (a) The measured Log J vs. Log [H₂SO₄] at RH of 12–41 % without (filled symbols) and with TMA (480 pptv) (open symbols). The total flow in the reactor was maintained at 2 lpm, corresponding to residence time of ~50 s. The range of [H₂SO₄] was from 5 × 10⁶–1 × 10⁸ cm⁻³. For clarity, linear fitting lines of the data are not included here. The slope of the linear fittings (n_{H₂SO₄}) was 4–6 before adding TMA and 4–5 after adding TMA of 480 pptv. (b) Log J vs. Log [TMA] (180–1350 pptv). The flow rate in the reactor was 5 lpm translating to ~20 s residence time. The solid line shows the linear fitting of the data and n_{TMA} indicates the slope.

der similar [H₂SO₄], but generally lower than the values in (Benson et al., 2009) at higher [H₂SO₄]. The difference in EF between TMA multicomponent nucleation and NH₃-THN could be due to residence times and likely due to the higher basicity of TMA than NH₃. The relationship between EF and [TMA] is presented in Fig. 3b. There was also a linear relationship between EF and TMA for [TMA] in the range

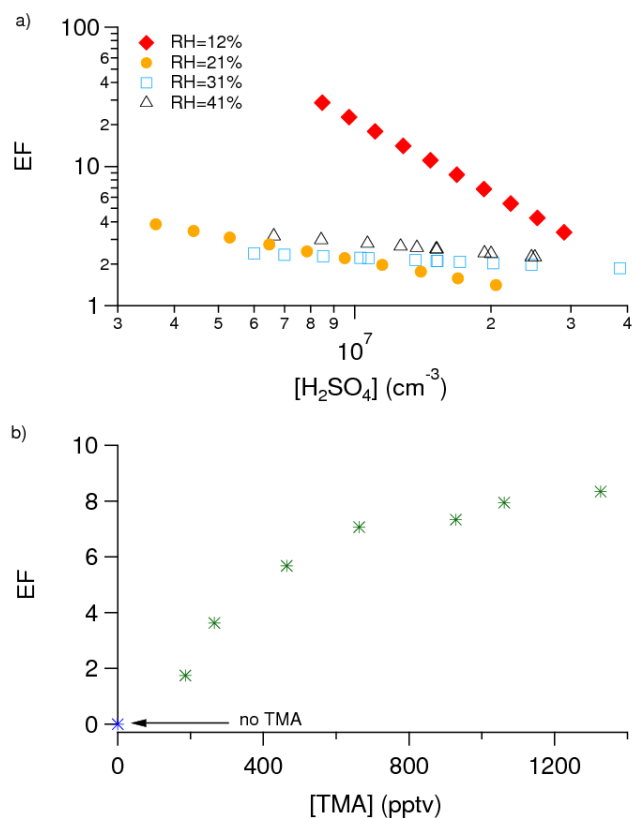


Fig. 3. (a) The measured EF as a function of [H₂SO₄] (in the range of $5 \times 10^6 - 6 \times 10^7 \text{ cm}^{-3}$) at RH = 12 % (red diamonds), 21 % (orange circles), 31 % (light blue squares), and 41 % (black triangles). (b) EF as a function of [TMA] (180–1350 pptv) at [H₂SO₄] = $1 \times 10^7 \text{ cm}^{-3}$ and RH = 25 %.

of 180–1350 pptv. However at higher [TMA], the slope appeared to decrease in similar manner to (Berndt et al., 2010), likely because particle concentrations would have saturated at this level in CPC.

4 Discussion

While we consider experiments without TMA to be BHN, strictly speaking they are pseudo-BHN because of the presence of NH₃ from the humidified air (Benson et al., 2011). In the TMA multicomponent nucleation, additional NH₃ impurities may also exist in the TMA permeation tube, as TMA compounds are usually synthesized industrially from NH₃ (Ullmann et al., 1996). For these reasons, it is difficult to have NH₃-free homogeneous nucleation experiments, and therefore the particle nucleation enhancement reported here and in our NH₃-THN studies (Benson et al., 2009, 2011) are somewhat an underestimation. Nevertheless, in the actual atmosphere, NH₃ and amines are also usually from the same sources. Under the experimental conditions reported here, we have estimated 400 pptv NH₃ (upper limit) in the

flow reactor from de-ionized water and TMA together. This is a substantial amount which can enhance particle number concentrations. But as shown in (Benson et al., 2011), at higher [NH₃] (1.2–2.6 ppbv) and under similar [H₂SO₄] (10^7 cm^{-3}), RH (12 %) and residence time (60 s), the resultant EF (<2) was an order of magnitude lower than the EF from TMA reported here. This higher EF is thus definitely attributed to TMA, which is a stronger base than NH₃ and hence can form neutral and ionic clusters more efficiently with H₂SO₄ compared to NH₃ (Kurtén et al., 2008).

A recent study (Berndt et al., 2010) has shown that a primary amine, tert-butylamine enhances nucleation up to two orders of magnitude more than NH₃, at amine concentrations of ppbv or tenth ppbv. This EF is at the same order as that seen in the NH₃ study (Benson et al., 2009) at similarly high concentrations of H₂SO₄ and NH₃. Our results, using much lower [H₂SO₄] and approximately the same concentrations of TMA, however, show that TMA enhances nucleation at about an order of magnitude lower than in (Berndt et al., 2010). The plausible explanation of this difference is the structure (primary amine, and therefore less steric hindrance) and the higher molecular weight of tert-butylamine than TMA. Laboratory studies have shown that the particle formation potential of amines can vary depending on the molecular structure and experimental conditions (Murphy, 2007).

The role of RH found in atmospheric observations often contradicts that from laboratory experiments (Laaksonen et al., 2008). In atmospheric observations RH appears to diminish nucleation (Hamed et al., 2011), for example, as shown by much lower NPF frequencies in summer (<~10 %) than in spring and fall (both >~40 %) (Bonn and Moortgat, 2003; Erupe et al., 2010; Kulmala et al., 2004), while laboratory experiments indicate that RH enhances (Benson et al., 2008, 2009, 2011; Young et al., 2008). In the current experiments, while an increase in RH appears to enhance BHN rates like in previous laboratory studies (Benson et al., 2008, 2009; Young et al., 2008), in the presence of TMA the RH effect diminishes at higher RH, consistent with atmospheric observations. Quantum chemical study of dimethylamine has indicated that hydrations of dimethylamine and NH₃ are different, as NH₃ clusters hydrate more efficiently at higher RH than dimethylamine (Loukonen et al., 2010). This could in part explain the different RH dependence of nucleation involving TMA and NH₃.

Our observations show that TMA enhances particle nucleation, but H₂SO₄ appears to be still the key nucleation precursor even in the presence of high concentrations of TMA (up to 1.5 ppbv), consistent with previous observations (Benson et al., 2008, 2009, 2011; Berndt et al., 2005; McMurry et al., 2005; Sipilä et al., 2010; Young et al., 2008). Currently, there are no field studies of amines in a similar manner to the NH₃-H₂SO₄-H₂O ternary nucleation studies in Atlanta, GA (McMurry et al., 2005) and Kent, OH (Erupe et al., 2010) to test the laboratory experiments. There is also caveat when

comparing the slopes of Log J vs. Log [H₂SO₄] values taken from laboratory studies and from field observations, because the former is taken under a constant temperature and constant saturations ratios of water (that is, RH) and of other possible ternary species, but the latter is derived from the ensemble data taken at various RH and temperatures and in the presence of many different chemical species of different saturation ratios. That is, careful laboratory experiments fulfill the assumptions inherent in the 1st nucleation theorem (Kashchiev, 1982; McGraw and Zhang, 2008), but field experiments typically do not follow such assumptions. From these reasons, a direct comparison of slopes taken in the laboratory and derived from field studies is not straightforward.

In some atmospheric conditions, species other than H₂SO₄ and H₂O are also needed to explain aerosol nucleation in the atmosphere, but the identity of the third species which can efficiently enhance nucleation of H₂SO₄ is unknown. While NH₃ can contribute to H₂SO₄-H₂O binary nucleation (Ball et al., 1999; Benson et al., 2009, 2011; Weber et al., 1998), organic compounds, such as trimethylbenzene (Metzger et al., 2010) and toluic acid (Zhang et al., 2004) can also enhance aerosol nucleation. Our results of multicomponent nucleation involving TMA provide direct insights into the possible role of amines, in line with some recent studies which showed that amines could play more important roles in H₂SO₄-H₂O nucleation (Berndt et al., 2010; Kurtén et al., 2008; Loukonen et al., 2010).

5 Conclusions

To our knowledge, we provide the first comprehensive laboratory investigation of multicomponent aerosol nucleation involving TMA, as a function of aerosol precursor concentrations. Under [H₂SO₄] and [TMA] conditions relevant to the lower troposphere, we show that TMA can enhance H₂SO₄-H₂O nucleation but the cutoff [H₂SO₄] needed for nucleation was surprisingly similar to that in NH₃-THN (Benson et al., 2011). The slope of Log J vs. Log [H₂SO₄] was 4–6 in the absence of TMA, whereas in the presence of TMA, the slope was slightly reduced to 4–5, depending on RH. The slope of Log J vs. Log [TMA] was only one, similar to NH₃ in ternary nucleation. Our results show that TMA enhances nucleation, but the EF was rather moderate, at the conditions relevant to the lower troposphere, also similar to NH₃. Amines can contribute significantly to the total budget of atmospheric bases both in continental and marine environments, and in most of atmospheric regions their sources are similar and they co-exist near the source region. Our results, together with (Ball et al., 1999; Benson et al., 2009, 2011; Berndt et al., 2010), strongly imply that the effects of inorganic and organic base gases (NH₃ and amines such as TMA and tert-butylamine) on nucleation should be taken into account together to improve nucleation theories.

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