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The effect of trimethylamine on atmospheric nucleation involving \( \text{H}_2\text{SO}_4 \)

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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 \( \text{H}_2\text{SO}_4 \). Here, we report laboratory observations that investigate the effect of trimethylamine (TMA) on \( \text{H}_2\text{SO}_4\)-H\(_2\)O nucleation made under aerosol precursor concentrations typically found in the lower troposphere ([\( \text{H}_2\text{SO}_4 \)] \( \approx 10^6 \) cm\(^{-3}\); [TMA] \( \approx 180–1350 \) 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 Log \( J \) vs. Log [\( \text{H}_2\text{SO}_4 \)] and Log \( J \) vs. Log [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 \( \text{H}_2\text{SO}_4 \) 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 interactions (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 \( \text{H}_2\text{SO}_4 \) 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 \( \text{H}_2\text{SO}_4 \) 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
atmosphere with various sources that include animal husbandry, oceans, waste incinerators and cars (Cadle and Mullawa, 1980; Facchini et al., 2008; Schade, 1995). Amines and NH$_3$ in general have similar sources, and the relative abundance of amines vs. NH$_3$ 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 H$_2$SO$_4$ 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 that NH$_3$ 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 NH$_3$ (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 NH$_3$. TMA and NH$_3$ compounds have similar basicities (NH$_3$pK$_a$ = 9.25; TMA$pK_a$ = 10.72) and proton affinities (PA$_{NH_3}$ = 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; NH$_3$ 60 M atm$^{-1}$ at 25 °C (NIST, 2005)). Amines and NH$_3$ can also lower the surface tension above the solution of H$_2$SO$_4$ and H$_2$O and thus can potentially influence the Kelvin effect in homogeneous nucleation (Hyvarinen et al., 2004; Hyvärinen et al., 2005). Like NH$_3$, amines are removed from the atmosphere by reactions with common atmospheric acids such as H$_2$SO$_4$ and HNO$_3$. But unlike NH$_3$, amines are also removed efficiently through rapid oxidation reactions with atmospheric oxidants, such as OH, O$_3$, and NO$_3$ (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 NH$_3$ 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 H$_2$SO$_4$. 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 H$_2$SO$_4$-H$_2$O nucleation under [H$_2$SO$_4$] of $10^6-10^7$ cm$^{-3}$, to compare with NH$_3$-THNn (Benson et al., 2011). Compared to the (Berndt et al., 2010) tert-butylamine study, the aerosol precursor concentrations (H$_2$SO$_4$ and amines) used in the present study were one or three orders of magnitude lower, relevant to the real atmospheric conditions; H$_2$SO$_4$ was also detected directly by a chemical ionization mass spectrometer (CIMS). Particle formation rates as a function of [H$_2$SO$_4$], [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 NH$_3$ on H$_2$SO$_4$ nucleation under conditions relevant to the lower troposphere, as well as growth rates measured with CPC (TSI 3876) at low [H$_2$SO$_4$] 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 SO$_2$, O$_3$, humidified N$_2$ (to control RH), dry N$_2$ gases (vaporized from liquid nitrogen) and TMA, before they entered a temperature controlled fast flow reactor (288 K) where nucleation took place. H$_2$SO$_4$ vapor was produced from the

$$\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3 \quad \text{(R1)}$$

reaction, rate constant $k_1 = 8.8 \times 10^{-13}$ cm$^3$ s$^{-1}$, (Finlayson-Pitts and Pitts, 2000) and was measured with CIMS, using (HNO$_3$)NO$_3^-$ ions as reagent (Eisele and Tanner, 1993; Erupe et al., 2010). Variation in [H$_2$SO$_4$] 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 picomammeter (Keithley 6485) and used to estimate [OH] produced based on (Cantrell et al., 1997; Young et al., 2008). From these [OH], we can estimate [H$_2$SO$_4$] and thus, this method also serves as calibration of H$_2$SO$_4$-CIMS. We also added a second water bath after the UV source, to change RH independently from [OH] (and thus [H$_2$SO$_4$]) (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 a second temperature (288 K). There is another companion paper (Berndt et al., 2010), where we show the effect of NH$_3$ on H$_2$SO$_4$ nucleation under conditions relevant to the lower troposphere, as well as growth rates measured with CPC (TSI 3876) at low [H$_2$SO$_4$] and possible factors which contribute to growth rates.

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 [H$_2$SO$_4$] of 10$^6$ to 10$^7$ cm$^{-3}$, with the majority smaller than 1.8 nm. The growth rates ($\sim$2.6–7.7 nm h$^{-1}$) estimated from CPC at these low [H$_2$SO$_4$] were discussed in detail in (Benson et al., 2011).

To reduce possible impurities of NH$_3$ in the system, N$_2$ gases that were used for dilutions and makeup flows were vaporized from liquid nitrogen which has minimal NH$_3$ ($<20$ ppptv; 1 ppptv $\approx 2 \times 10^{-7}$ 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 NH$_3$ 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 NH$_3$ likely originating from de-ionized water was also determined with CIMS and was below 100 ppptv 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 $\sim$180–1350 ppptv. TMA was introduced at 10 cm downstream of SO$_2$ addition, corresponding to a reaction time of 0.7 s. With this reaction time and [SO$_2$] of 4 ppmv. 100% of OH radicals are converted to HSO$_4^-$ via Reaction (R1) (hence to H$_2$SO$_4$) 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 [H$_2$SO$_4$]. The possibility that TMA oxidation by OH may form condensable products was further ruled out by running control experiments without adding SO$_2$. Without SO$_2$ 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 $\times$ 10$^{-11}$ cm$^3$ s$^{-1}$ range (Atkinson, 1986; Koch et al., 1996). It is possible that the TMA + OH oxidation products such as peroxides, alkyl peroxydes 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 H$_2$SO$_4$ 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 NH$_3$ (Benson et al., 2010; Nowak et al., 2006)

\[
(\text{CH}_3)_3\text{N} + (\text{C}_2\text{H}_5\text{OH})_n\text{H}^+ \rightarrow (R2)\]

where $m = 1, 2, 3, \ldots$ etc., and $m$ is also an integer which is less of equal to $n$. We have estimated the reaction rate of Reaction (R3) with trajectory calculations (Viggiano et al., 1982) (1.23 $\times$ 10$^{-9}$ cm$^3$ s$^{-1}$) and the average dipole orientation (ADO) theory (Baulch et al., 1982) (1.01 $\times$ 10$^{-9}$ cm$^3$ s$^{-1}$).

Both values are within the same range as the reaction rate, determined experimentally (1.17 $\times$ 10$^{-9}$ cm$^3$ s$^{-1}$) (Keesee, 1986 #1379). These values are also similar to the reaction rate of the NH$_3$-ethanol system ($k_4 = 1.5 \times 10^{-9}$ cm$^3$ s$^{-1}$) (Nowak et al., 2002), as expected:

\[
\text{NH}_3 + (\text{C}_2\text{H}_5\text{OH})_n\text{H}^+ \rightarrow \text{(R3)}
\]

\[
\text{NH}_3 \cdot (\text{C}_2\text{H}_5\text{OH})_{n-m}\text{H}^+ + m(\text{C}_2\text{H}_5\text{OH})
\]

As shown in Fig. 1a and b, the product ion signals [(CH$_3$)$_3$NH$^+$, mass 60; (CH$_3$)$_3$N(---H$_2$OH)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 $\sim$85 ppbv at low RH ($<10\%$) conditions, but more systematic investigations are required in future studies. Due to such impurities of NH$_3$ ($<100$ ppptv) and amines (e.g., TMA $<$85 ppptv) 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 H$_2$SO$_4$ nucleation with the NH$_3$ effects reported in (Benson et al., 2011). And, our experimental results show that TMA acts very similarly to NH$_3$. Figure 2a shows the results of Log J vs. Log [H$_2$SO$_4$] for RH between 12–41%, [H$_2$SO$_4$] between 3 $\times$ 10$^6$ – 4 $\times$ 10$^7$ cm$^{-3}$ and [TMA] of 480 ppptv 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 ppptv TMA, J was higher than in the absence of TMA, within the RH range studied (12–41%), demonstrating that TMA indeed enhances nucleation of H$_2$SO$_4$ and H$_2$O (Fig. 2a), similarly to NH$_3$ (Benson et al., 2011).

In the absence of TMA, the slope of Log J vs. Log [H$_2$SO$_4$] 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 [H$_2$SO$_4$] included both nucleation and condensation effects and condensation growth made the slope appear higher than the actual values. The [H$_2$SO$_4$] needed to produce the unity J (that is, threshold [H$_2$SO$_4$] for nucleation) was about 4 $\times$ 10$^6$ 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
has little effect on the cutoff of [H$_2$SO$_4$] needed to produce the unity $J$, at least for the TMA case. The slope of Log $J$ vs. Log [H$_2$SO$_4$] also slightly reduced by 1–2 in the presence of TMA. This reduction in the slope of Log $J$ vs. Log [H$_2$SO$_4$] is also very similar to the NH$_3$ 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 $\sim$5 lpm corresponding to a residence time of 20 s. The slope of Log $J$ vs. Log [TMA] was 0.7, for [H$_2$SO$_4$] at the 10$^7$ cm$^{-3}$ range and 25% RH. This is again similar to the NH$_3$-THN result, where the slope of log $J$ vs. log [NH$_3$] was nearly 1 (Benson et al., 2011).

The effect of TMA to particle number concentration was quantitatively characterized by comparing the ratios of particle number concentration with and without TMA as a function of both [H$_2$SO$_4$] and [TMA]. This ratio, defined as the enhancement factor (EF), was found to be dependent on [H$_2$SO$_4$], with higher values at lower [H$_2$SO$_4$] (Fig. 3a). These EF values (2–35) were somewhat higher than those found in NH$_3$-THN experiments (Benson et al., 2011) under similar [H$_2$SO$_4$], but generally lower than the values in (Benson et al., 2009) at higher [H$_2$SO$_4$]. The difference in EF between TMA multicomponent nucleation and NH$_3$-THN could be due to residence times and likely due to the higher basicity of TMA than NH$_3$. 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
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 NH$_3$ from the humidified air (Benson et al., 2011). In the TMA multicomponent nucleation, additional NH$_3$ impurities may also exist in the TMA permeation tube, as TMA compounds are usually synthesized industrially from NH$_3$ (Ullmann et al., 1996). For these reasons, it is difficult to have NH$_3$-free homogeneous nucleation experiments, and therefore the particle nucleation enhancement reported here and in our NH$_3$-THN studies (Benson et al., 2009, 2011) are somewhat an underestimation. Nevertheless, in the actual atmosphere, NH$_3$ and amines are also usually from the same sources. Under the experimental conditions reported here, we have estimated 400 pptv NH$_3$ (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 [NH$_3$] (1.2–2.6 ppbv) and under similar [H$_2$SO$_4$] (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 NH$_3$ and hence can form neutral and ionic clusters more efficiently with H$_2$SO$_4$ compared to NH$_3$ (Kurtén et al., 2008).

A recent study (Berndt et al., 2010) has shown that a primary amine, tert-buty lamine enhances nucleation up to two orders of magnitude more than NH$_3$, at amine concentrations of ppbv or tenth ppbv. This EF is at the same order as that seen in the NH$_3$ study (Benson et al., 2009) at similarly high concentrations of H$_2$SO$_4$ and NH$_3$. Our results, using much lower [H$_2$SO$_4$] and approximately the same concentrations of TMA, however, show that TMA enhances nucleation at 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-buty lamine 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 NH$_3$ are different, as NH$_3$ 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 NH$_3$.

Our observations show that TMA enhances particle nucleation, but H$_2$SO$_4$ 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 NH$_3$-H$_2$SO$_4$-H$_2$O 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 $[\text{H}_2\text{SO}_4]$ 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 $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ are also needed to explain aerosol nucleation in the atmosphere, but the identity of the third species which can efficiently enhance nucleation of $\text{H}_2\text{SO}_4$ is unknown. While NH$_3$ can contribute to $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ 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 $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ 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 $[\text{H}_2\text{SO}_4]$ and [TMA] conditions relevant to the lower troposphere, we show that TMA can enhance $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ nucleation but the cutoff $[\text{H}_2\text{SO}_4]$ needed for nucleation was surprisingly similar to that in NH$_3$-THN (Benson et al., 2011). The slope of Log $J$ vs. Log $[\text{H}_2\text{SO}_4]$ 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 NH$_3$ 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 NH$_3$. 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 (NH$_3$ and amines such as TMA and tert-butylamine) on nucleation should be taken into account together to improve nucleation theories.

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