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 in new particle formation processes involving H$_2$SO$_4$. Here, we report laboratory observations that investigate the effect of trimethylamine (TMA) on H$_2$SO$_4$-H$_2$O nucleation made under aerosol precursor concentrations typically found in the lower troposphere ([H$_2$SO$_4$] of $10^6$–$10^7$ cm$^{-3}$; [TMA] of 180–1350 pptv). These results show that the threshold [H$_2$SO$_4$] needed to produce the unity nucleation rate ([H$_2$SO$_4$] of $10^6$–$10^7$ cm$^{-3}$) and the number of precursor molecules in the critical cluster ($n_{H_2SO_4}=4$–$6$; $n_{TMA}=1$) are surprisingly similar to those found in the ammonia (NH$_3$) ternary nucleation study (Benson et al., 2010a). At lower RH, however, enhancement in nucleation rates 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$_2$SO$_4$ nucleation than NH$_3$. Aerosol models should therefore take into account inorganic and organic bases 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 (Kuang et al., 2009). NPF therefore has important climate implications and an understanding of the nucleation (formation of solid or liquid particles from gas phase species) processes involved is vital in reducing the current uncertainty 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 (Kulmala et al., 2004). Although several theories including binary homogeneous nucleation (BHN) and ternary homogeneous nucleation...
(THN) have been proposed to explain nucleation in the atmosphere, most of them come short of reproducing the observed nucleation rates 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; Sipila et al., 2010; Young et al., 2008), field observations (Erupe et al., 2010; Kulmala et al., 2004; Riipinen et al., 2007; Weber et al., 1999) and modeling studies (Antilla et al., 2005; Vehkamäki et al., 2002) have shown that H$_2$SO$_4$ is important in NPF in the atmosphere. However, other species are also needed to explain atmospherically observed nucleation rates (Kulmala et al., 2004). Possible species include NH$_3$ (Ball et al., 1999; Benson et al., 2009, 2010a) and volatile organic compounds (VOCs) such as organic acids (Kavouras et al., 1998; O’Dowd et al., 2002; Zhang et al., 2004), amines (Barsanti et al., 2009; Smith et al., 2010) and 1,3,5-trimethylbenzene (Metzger 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$_2$SO$_4$, more efficiently than NH$_3$ even though amine concentrations are lower than NH$_3$ (Kurtén et al., 2008; Loukonen et al.). 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 that have reported the presence of aminium ions in nanoparticles (Makela et al., 2001; Smith et al., 2008, 2010).

Amines are ubiquitous in the atmosphere with various sources that include animal husbandry, oceans, waste incinerators and cars (Cadle and Mulawa, 1980; Facchini et al., 2008; Schade and Crutzen, 1995). A comprehensive review of a large number of atmospheric amines including their thermodynamic properties has recently been given by (Ge et al., 2010a, b). 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 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 NH$_3$ output (23 300 Gg N yr$^{-1}$) (Schade and Crutzen, 1995). A more recent study has indicated that amines may represent up to 20% of the measured NH$_3$ (Sorooshian et al., 2008). Molecular structurally, amines are classified into primary, secondary, or tertiary categories (Schade and Crutzen, 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 and Crutzen, 1995; Silva et al., 2008).

There are also many similarities in the physical and chemical properties of TMA and NH$_3$, including their strong proton affinities, basicity, and solubility in water. TMA and NH$_3$ compounds have similar basicities (NH$_3$ $pK_a$ = 9.25; TMA $pK_a$ = 9.81) and proton affinities (PA$_{NH_3}$ = 853.6 kJ/mol; PA$_{TMA}$ = 948.9 kJ/mol), while Henry’s law coefficients are somewhat different (TMA $k_H$ = 62 M atm$^{-1}$ at 20°C; NH$_3$ $k_H$ = 9.5 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 et al., 2007; Pitts Jr. et al., 1978). These similarities in sources and physical-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., 2008), make them ideal precursors for aerosol nucleation involving H$_2$SO$_4$ (Kurtén et al., 2008). 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., 2010). 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$_3$-THN (Benson et al., 2010a). Compared to (Berndt et al., 2010), the aerosol precursor concentrations were one or three orders of magnitude lower and H$_2$SO$_4$ was also measured 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 constant temperature (288 K).

2 Experiments

Details about the instruments and the performance of the setup have been described elsewhere (Benson et al., 2008, 2009; Young et al., 2008). We have also included additional descriptions on the experimental setup in (Benson et al., 2010a) and another manuscript (Benson et al., 2010c). Only a brief overview and the details relevant to the current experiments are reported here.

OH radicals were produced by photolyzing water 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$_2$, 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

$$\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3$$

(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 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., 2010c). 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 \( [\text{H}_2\text{SO}_4] \) and thus, this method also serves as calibration of \( \text{H}_2\text{SO}_4 \) CIMS. We also added a second water bath after the UV source, to change RH independently from \([\text{OH}]\) (and thus \([\text{H}_2\text{SO}_4])\) (Benson et al., 2010). 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 \( \sim 20–50 \) s. Particle number concentrations in the size range from 3–170 nm were measured using butanol-based condensation particle counters (CPC, TSI 3776).

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 pptv) (Benson et al., 2010b; Nowak et al., 2006). All experimental setup was exclusively built with fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon, since NH\(_3\) adsorption is least effective on these Teflon materials and most effective on the stainless steel material (Benson et al., 2010b; Nowak et al., 2006; Yokelson et al., 2003). The impurity NH\(_3\) likely originated from de-ionized water, which is unavoidable in nucleation experiments, was also determined with CIMS (Benson et al., 2010b) and was found to be dependent on RH, typically ranging from 20–100 pptv at RH between 6–40% (Benson et al., 2010c).

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 mixing ratios in the range from \( \sim 180–1350 \) pptv and used in the current experiments. TMA was introduced at 10 cm downstream of \( \text{SO}_2 \) addition, corresponding to a reaction time of 0.7 s. With this reaction time and \([\text{SO}_2]\) of 4 ppmv, 100% of OH radicals are converted to HSO\(_3\) via R1 (hence to \( \text{H}_2\text{SO}_4 \)) 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]}
to alter the [H$_2$SO$_4$] level. Possible TMA oxidation by OH to form condensable products was further ruled out by running a control experiment 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 3.6-6.1×10$^{-11}$ cm$^3$ s$^{-1}$ range (Atkinson, 1989; 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 et al., 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., 2010b; Nowak et al., 2006)

$$(\text{CH}_3)_3\text{N} + (\text{C}_2\text{H}_5\text{OH})_n\text{H}^+ \rightarrow (\text{CH}_3)_3\text{N} \cdot (\text{C}_2\text{H}_5\text{OH})_{n-m}\text{H}^+ + m(\text{C}_2\text{H}_5\text{OH})$$

(R2)

Where $m = 1, 2, 3$, etc., and $m$ is also an integer, less of equal to $n$. We have estimated the reaction rate of R3 with trajectory calculations (Viggiano et al., 1982) ($k_2 = 1.23 \times 10^{-9}$ cm$^3$ s$^{-1}$) and the average dipole orientation (ADO) theory (Su and Chesnavich, 1982) ($k_2 = 1.01 \times 10^{-9}$ cm$^3$ s$^{-1}$). Both values are within the same range as the reaction rate, determined experimentally ($k_2 = 1.17 \times 10^{-9}$ cm$^3$ s$^{-1}$) (Keesee and Castleman Jr., 1986). These values are also similar to the reaction rate of the NH$_3$-ethanol system ($k_3 = 1.5 \times 10^{-9}$ cm$^3$ s$^{-1}$) (Nowak et al., 2006):

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

(R3)

As shown in Fig. 1a and b, the product ion signals {[$(\text{CH}_3)_3\text{NH}^+$, mass 60; $(\text{CH}_3)_3\text{N} \cdot (\text{C}_2\text{H}_5\text{OH})\text{H}^+$, mass 106] show that [TMA] produced from the permeation tube was constant and stable.

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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., 2010a). 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 pptv at a temperature of 288 K. These experimental conditions were close to those of (Benson et al., 2010a); but the residence times were different in these two studies, 20–50 s in the current experiments and 190 s in (Benson et al., 2010a). 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 H$_2$SO$_4$ and H$_2$O (Fig. 2a), similarly to NH$_3$ (Benson et al., 2010a).

An examination of the slope, which according to (Kashchiev, 1982; McGraw and Zhang, 2008), can be interpreted as the number of molecules of H$_2$SO$_4$ in the critical cluster ($n_{H_2SO_4}$) reveals similarities between TMA and NH$_3$ on H$_2$SO$_4$ nucleation. In the absence of TMA, $n_{H_2SO_4}$ was between 4–6 and generally increased as the RH decreased, similarly to our previous laboratory studies of homogeneous nucleation (Benson et al., 2008; Benson et al., 2009; Young et al., 2008). The [H$_2$SO$_4$] needed to produce the unity nucleation rate (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. (2010a), 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 (Berndt et al., 2010) and (Benson et al., 2010c), it has little effect on the cutoff of [H$_2$SO$_4$] needed to produce the unity nucleation rate at least for the TMA case. The numbers of H$_2$SO$_4$ molecules in the critical cluster were also slightly reduced by 1-2 in the presence of TMA. This reduction in $n_{H_2SO_4}$ is also very similar to the NH$_3$ ternary homogeneous nucleation case (Benson et al., 2009, 2010a).

Figure 2b shows results for log $J$ vs. log [TMA] for $J$ values between 250-6300 cm$^{-3}$ s$^{-1}$ and [TMA] in the range 180–1350 pptv. The total flow rate in the nu-
The number of TMA molecules in the critical cluster ($n_{\text{TMA}}$) obtained from the slope is approximately one, for $[\text{H}_2\text{SO}_4]$ at the $10^7$ cm$^{-3}$ range and 25% RH. This is again strikingly similar to the NH$_3$-THN result, $n_{\text{NH}_3} \approx 1$, from (Benson et al., 2010a) which utilized $[\text{H}_2\text{SO}_4]$ of $10^6$–$10^7$ cm$^{-3}$ and from (Berndt et al., 2010) which used $[\text{H}_2\text{SO}_4]$ of $8 \times 10^8$ cm$^{-3}$.

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 $[\text{H}_2\text{SO}_4]$ and [TMA]. This ratio, defined as the enhancement factor (EF), was found to be exponentially dependent on $[\text{H}_2\text{SO}_4]$, with higher values at lower $[\text{H}_2\text{SO}_4]$ (Fig. 3a). These EF values (2–35) were somewhat higher than those found in NH$_3$-THN experiments (Benson et al., 2010a) under similar $[\text{H}_2\text{SO}_4]$, but generally lower than the values in (Benson et al., 2009) at higher $[\text{H}_2\text{SO}_4]$. The difference in EF between TMA multicomponent nucleation and NH$_3$-THN could be due to residence times and different $[\text{H}_2\text{SO}_4]$. 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., 2010c). In the TMA multicomponent nucleation, additional NH$_3$ impurities may also exist from the TMA permeation tube, as TMA compounds are usually synthesized industrially from NH$_3$. For these reasons, it is difficult to have NH$_3$-free homogeneous nucleation experiments, and therefore the particle nucleation enhancement reported here and in (Benson et al., 2009, 2010a) are somewhat an underestimation. Nevertheless, in the actual atmosphere, NH$_3$ and amines are usually from the same sources.
(as in the permeation tube). 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 concentration. But as shown in (Benson et al., 2010a), 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-butylamine enhances nucleation up to two orders of magnitude more than NH$_3$, at amine concentrations at the ppbv or tenth ppbv level. This EF is at the same order as that seen in the NH$_3$ study (Benson et al., 2009) at similar 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 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 et al., 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, 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 nucleation (Benson et al., 2008, 2009, 2010a; 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, 2010a; Young et al., 2008), in the presence of TMA the RH effect diminishes at higher RH, consistent with atmos-
spheric 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, 2010a; Berndt et al., 2005; Erupe et al., 2010; Kulmala et al., 2004; McMurry et al., 2005; Sipila et al., 2010; Young et al., 2008). Our experiments show the values of $n_{\text{H}_2\text{SO}_4}$ between 4–6, with and without TMA. This is somewhat different from atmospheric observations of the power dependency of $J$ to [H$_2$SO$_4$], leading to 1–2 molecules in the critical cluster (Erupe et al., 2010; Kulmala et al., 2004). 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 $n_{\text{H}_2\text{SO}_4}$ 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, the former does not follow the assumption of classical nucleation theories (Kashchiev, 1982; McGraw and Zhang, 2008), whereas the latter does. From these reasons, a direct comparison of slopes taken in the laboratory and derived from field studies is not straightforward.

It is commonly believed that species other than H$_2$SO$_4$ and H$_2$O are needed to explain aerosol nucleation in the atmosphere (Erupe et al., 2010; Weber et al., 1998), but the identity of the third species which can efficiently enhance nucleation of H$_2$SO$_4$ is unknown. While NH$_3$ can contribute to H$_2$SO$_4$-H$_2$O binary nucleation (Ball et al., 1999; Benson et al., 2009, 2010a; Weber et al., 1998), organic compounds, such as trimethylbenzene (Metzger et al., 2010), toluic acid (Zhang et al., 2004), and cis-pinonic acid
(Zhang et al., 2009) can also enhance aerosol nucleation. Our results of multicomponent nucleation involving TMA provides direct insights into the possible role of amines, in line with some recent studies which showed that amines could play more important roles in H$_2$SO$_4$-H$_2$O nucleation (Berndt et al., 2010; Kurtén et al., 2008; Loukonen et al., 2010).

5 Conclusions

To our knowledge, we have provided the first comprehensive laboratory investigation of trimethylamine multicomponent aerosol nucleation, as a function of aerosol precursor concentrations. Under [H$_2$SO$_4$] and [TMA] conditions relevant to the lower troposphere, we show that TMA can enhance H$_2$SO$_4$-H$_2$O nucleation and the cutoff [H$_2$SO$_4$] needed for nucleation is surprisingly similar to that in NH$_3$-THN (Benson et al., 2010a). The number of molecules of H$_2$SO$_4$ in the critical cluster ranges from 4–6, whereas in the presence of TMA, they are slightly reduced to 4–5, depending on RH. Only one molecule of TMA appears to be present in the critical cluster, similar to NH$_3$ in ternary nucleation. Our results show that TMA enhances nucleation, but the enhancement effect is 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 thus they co-exist near the source region. Our results, together with (Ball et al., 1999; Benson et al., 2009, 2010a; 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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Fig. 1. (a) CIMS-measured TMA (black solid line and filled circles) and background NH\textsubscript{3} originated from Kintek (blue dotted line and crosses). This figure shows that the production of TMA from the permeation tube is steady with time, but NH\textsubscript{3} impurities also exist from TMA. (b) A mass spectrum before and after adding 480 pptv TMA. After addition of TMA, TMA ion peaks [(\text{CH}_3)_3\text{NH}^+, \text{mass 60 amu}; (\text{CH}_3)_3\text{N}-(\text{C}_2\text{H}_5\text{OH})\text{H}^+, \text{mass 106}] were clearly observed. Also, NH\textsubscript{3} peaks [(\text{NH}_3):3(\text{C}_2\text{H}_5\text{OH})\text{H}^+, \text{mass 64}; \text{NH}_4^+, \text{mass 18}] increased, indicating that there were some NH\textsubscript{3} 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 NH\textsubscript{3} impurities in the system (including those from TMA and de-ionized water).
Fig. 2. (a) The measured Log J vs. Log [H$_2$SO$_4$] 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 [H$_2$SO$_4$] was from 5 x 10$^6$-1 x 10$^8$ cm$^{-3}$. Solid lines indicate linear fitting of the data. The slope of the linear fittings (n$_{H_2SO_4}$) was 4–6 before adding TMA and 4–5 after adding TMA. At higher RH, the difference in n$_{H_2SO_4}$ before and after adding TMA was negligible. (b) Log J vs. Log [TMA] (180–1350 pptv). The number of TMA molecules in the critical cluster (n$_{TMA}$) was estimated to be ~1 from the slope of the linear fitting (solid line). The flow rate in the reactor was 5 lpm translating to ~20 s residence time.
Fig. 3. (a) The measured EF as a function of [H$_2$SO$_4$] (in the range of 5×10$^6$–6×10$^7$ 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 [H$_2$SO$_4$]=1×10$^7$ cm$^{-3}$ and RH = 25%.