



# Enhancement of atmospheric H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation: organic oxidation products versus amines

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**Abstract.** Atmospheric H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation influencing effects have been studied in the flow tube IfT-LFT (Institute for Tropospheric Research – Laminar Flow Tube) at 293 ± 0.5 K and a pressure of 1 bar using synthetic air as the carrier gas. The presence of a possible background amine concentration in the order of 10<sup>7</sup>–10<sup>8</sup> molecule cm<sup>−3</sup> throughout the experiments has to be taken into account. In a first set of investigations, ozonolysis of olefins (tetramethylethylene, 1-methyl-cyclohexene, α-pinene and limonene) for close to atmospheric concentrations, served as the source of OH radicals and possibly other oxidants initiating H<sub>2</sub>SO<sub>4</sub> formation starting from SO<sub>2</sub>. The oxidant generation is inevitably associated with the formation of organic oxidation products arising from the parent olefins. These products (first generation mainly) showed no clear effect on the number of nucleated particles within a wide range of experimental conditions for H<sub>2</sub>SO<sub>4</sub> concentrations higher than ∼ 10<sup>7</sup> molecule cm<sup>−3</sup>. Also the early growth process of the nucleated particles was not significantly influenced by the organic oxidation products in line with the expected growth by organic products using literature data. An additional, H<sub>2</sub>SO<sub>4</sub>-independent process of particle (nano-CN) formation was observed in the case of α-pinene and limonene ozonolysis for H<sub>2</sub>SO<sub>4</sub> concentrations smaller than ∼ 10<sup>7</sup> molecule cm<sup>−3</sup>. Furthermore, the findings confirm the appearance of an additional oxidant for SO<sub>2</sub> beside OH radicals, very likely stabilized Criegee Intermediates (sCI). A second set of experiments has been performed in the

presence of added amines in the concentrations range of a few 10<sup>7</sup>–10<sup>10</sup> molecule cm<sup>−3</sup> applying photolytic OH radical generation for H<sub>2</sub>SO<sub>4</sub> production without addition of other organics. All amines showed significant nucleation enhancement with increasing efficiency in the order pyridine < aniline < dimethylamine < trimethylamine. This result supports the idea of H<sub>2</sub>SO<sub>4</sub> cluster stabilization by amines due to strong H<sub>2</sub>SO<sub>4</sub> ↔ amine interactions. On the other hand, this study indicates that for organic oxidation products (in presence of the possible amine background as stated) a distinct H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation enhancement can be due to increased H<sub>2</sub>SO<sub>4</sub> formation caused by additional organic oxidant production (sCI) rather than by stabilization of H<sub>2</sub>SO<sub>4</sub> clusters due to H<sub>2</sub>SO<sub>4</sub> ↔ organics interactions.

## 1 Introduction

For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intense studies in both, field and laboratory. H<sub>2</sub>SO<sub>4</sub> was ascertained to play a central role in this process (Weber et al., 1996; Kulmala et al., 2004, 2006, 2013; Berndt et al., 2004; Riipinen et al., 2007; Sipilä et al., 2010; Kirkby et al., 2011). Large discrepancies between model-predicted nucleation rates for the binary system H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O (Vehkamäki et al., 2002) and much higher atmospheric nucleation data were explained by various supportive participants such as ammonia (Coffman

and Hegg, 1995; Korhonen et al., 1999), organic molecules (Zhang et al., 2004; Metzger et al., 2010) or by ion-mediated nucleation (Lee et al., 2003; Lovejoy et al., 2004).

More recently, the importance of amines for atmospheric H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation has been discovered as a result of quantum-chemical calculations (Kurtén et al., 2008) as well as from laboratory experiments (Berndt et al., 2010; Erupe et al., 2011; Zollner et al., 2012; Almeida et al., 2013). The amines are consistently identified to be more effective in the enhancement of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation compared with ammonia for similar concentration levels. This fact can be explained by increasing interactions of the very strong acid (H<sub>2</sub>SO<sub>4</sub>) with atmospheric bases for increasing gas-phase basicity according to the proton affinity (base + H<sup>+</sup> → base-H<sup>+</sup>); ammonia: 854 kJ mol<sup>-1</sup> versus e.g. dimethylamine: 923 kJ mol<sup>-1</sup> (Jolly, 1991; Kurten et al., 2008; DePalma et al., 2012). Furthermore, the importance of amines for nucleation and growth is also supported by atmospheric measurements showing the occurrence of aminium ions in nanoparticles during nucleation events (Mäkelä et al., 2001; Smith et al., 2010). Amines are ubiquitous in the atmosphere produced by microbial degradation of organic material or released by a series of human activities (Schade and Crutzen, 1995; Ge et al., 2010). Their concentrations cover a wide range. For instance, concentrations of (1–18) × 10<sup>8</sup> molecule cm<sup>-3</sup> for methylamine, dimethylamine, trimethylamine and diethylamine in total have been reported for different weather situations at different sites in Sweden (Grönberg et al., 1992). Total concentrations in the order of 10<sup>12</sup> molecule cm<sup>-3</sup> have been measured close to a dairy farm for a series of amines (diethylamine, butylamine, pyridine, etc.) (Rabaud et al., 2003). Individual concentrations for the three methyl-substituted amines of up to a few 10<sup>12</sup> molecule cm<sup>-3</sup> were detected in an industrial area (Fuselli et al., 1982). Much higher concentrations can be expected in the vicinity of power plants with subsequent CO<sub>2</sub> capture using amines as the working fluid (Karl et al., 2009). On global scale, however, the annual emission rate of ammonia (55 × 10<sup>6</sup> tons N) exceeds clearly that for aliphatic amines (0.2 × 10<sup>6</sup> tons N) and thus, ammonia concentrations can be much higher than the total amine concentrations (Cornell et al., 2003). Therefore, also ammonia can be locally important for the nucleation process compensating its compared to amines lower efficiency by much higher concentration levels.

It is not clear at the moment how organic oxidation products can be incorporated in this nucleation concept based on interactions of a strong acid (H<sub>2</sub>SO<sub>4</sub>) with strong bases (ammonia or amines). Oxidation processes do not produce the basic compounds needed but can yield additional acids or di-acids. For instance, Yu et al. (1999) reported the formation of norpinonic acid, pinonic acid and pinic acid with molar yields of a few % from gas-phase ozonolysis of α-pinene. Zhang et al. (2004) investigated the promotion of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation by a series of aromatic acids, like benzoic acid, p- and m-toluic acid. Relatively stable com-

plexes, H<sub>2</sub>SO<sub>4</sub> – aromatic acid, via hydrogen bridge bonds have been found as a result of theoretical calculations. It was speculated that a lowering of the nucleation barrier could be the consequence of the occurrence of these complexes. Using particle counting techniques suitable for measuring particle sizes as small as 3 nm, an enhancement of the nucleation rate by about one order of magnitude was observed by adding (1–7) × 10<sup>9</sup> molecule cm<sup>-3</sup> of the aromatic acids to the reaction gas. These findings (Zhang et al., 2004) point probably to another nucleation enhancement governed by H<sub>2</sub>SO<sub>4</sub> ↔ aromatic acid interactions. It remains questionable, however, whether the H<sub>2</sub>SO<sub>4</sub> ↔ organic acid interactions via hydrogen bridge bonds can be competitive with the very strong H<sub>2</sub>SO<sub>4</sub> ↔ base (ammonia or amines) interactions. More experiments with respect to this topic for close to atmospheric conditions are needed to get more insight in the nucleation enhancing effects of importance.

Using the same experimental setup, the aim of this work was to quantify for close to atmospheric conditions how both, amines and organic oxidation products, may enhance atmospheric H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation. Such a “comparative study”, bases vs. organic oxidation products, has not been done up to now for all reactants featuring atmospheric concentration levels. In order to enhance possible effects, elevated reactant concentrations have been used as well.

It is to be noted that due to the short residence times and under the conditions prevailing in our flow tube experiments, we have to expect that nearly exclusively organic oxidation products of the first generation are formed. These first generation oxidation products comprise a series of organic acids as low vapour-pressure products, see Yu et al. (1999). However, there are some indications that highly oxidized products may be formed very rapidly as stable first generation products as well. These products have been found first in the course of atmospheric observations by Ehn et al. (2012), and at this stage we cannot rule out their existence in our experiments. Consequently, we define first generation oxidized organics as the “classic” organic acids (and others) plus the potentially present highly oxidized products as detected by Ehn et al. (2012).

Furthermore, for longer time scales and under atmospheric conditions, higher generation reaction products may affect the nucleation and growth processes additionally not ascertainable in our experiment.

The results of the ozonolysis experiments originate from a 2009 campaign where a PHA-UCPC (pulse height analysing ultrafine condensation particle counter, Weber et al., 1995), and, only for a certain time period, a M-CPC (mixing-type condensation particle counter, Vanhanen, 2009) were available for high sensitivity particle measurements. A PSM (particle size magnifier, Vanhanen et al., 2011) came into operation in the later investigations with amine additions.

## 2 Experimental

The experimental setup used was already explained in detail elsewhere (Berndt et al., 2010). Therefore, here only a brief description is given. The experiments have been conducted in the atmospheric pressure flow-tube (Institute for Tropospheric Research – Laminar Flow Tube, IFT-LFT) (i.d. 8 cm; length 505 cm) at a temperature of  $293 \pm 0.5$  K using synthetic air as the carrier gas. The first flow-tube section (56 cm) contains the inlet system for gas input (humid air premixed with the olefins or the amines from a gas metering unit, SO<sub>2</sub> from a calibration gas mixture and O<sub>3</sub> from an ozone generator UVP OG-2). A second section (344 cm) is surrounded by 8 UV lamps (Hg-lamps made of quartz-glass PN235 with a cut-off wavelength of 210 nm). The sampling outlets are attached at the non-irradiated end section (105 cm). The relative humidity was measured by means of a humidity sensor (Vaisala), O<sub>3</sub> using a gas monitor (Thermo Environmental Instruments 49C), and SO<sub>2</sub> by a gas monitor (Thermo Environmental Instruments 49C). The concentrations of the olefins were detected with the help of a quadrupole proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH) (Lindinger et al., 1998).

Sulfuric acid was measured at the IFT-LFT outlet by means of a Chemical Ionization Mass spectrometer, CI-MS (Eisele and Tanner, 1993; Mauldin et al., 1998; Petäjä et al., 2009) using (NO<sub>3</sub><sup>-</sup>) as the reagent ion. The reagent ions were generated by nitric acid and a <sup>241</sup>Am alpha source and mixed in a drift tube utilizing concentric sheath and sample flows together with electrostatic lenses. The sulfuric acid concentration is determined by the ratio between the signals at mass 97 amu (HSO<sub>4</sub><sup>-</sup>) and the reagent ion at mass 62 amu (NO<sub>3</sub><sup>-</sup>) multiplied by the setup dependent calibration factor. The calibration factor was determined by photolysis of water vapour with a mercury lamp to generate a defined amount of OH radicals in front of the inlet (e.g. Mauldin et al., 2001). The produced OH radicals subsequently convert isotopically labeled <sup>34</sup>SO<sub>2</sub> into labeled sulfuric acid yielding finally after ionization (H<sup>34</sup>SO<sub>4</sub><sup>-</sup>). The nominal detection limit of the CI-MS instrument is  $5 \times 10^4$  molecule cm<sup>-3</sup> for a 5 min integration period.

Particle total number measurements have been carried out using a butanol-based UCPC (TSI 3025) with a 50 % cut-off size of about 2.5–3 nm. Furthermore, for high sensitivity particle number measurements down to a diameter of about 1.5 nm, a tuned-up pulse height analysing ultrafine condensation particle counter, PHA-UCPC, (Weber et al., 1995), a mixing-type CPC, M-CPC (Vanhanen, 2009), as well as a PSM (particle size magnifier, Vanhanen et al., 2011) came into operation. M-CPC represented the prototype of the later available PSM. More detailed information regarding the operating parameters of the PHA-UCPC is given in Sipilä et al. (2008, 2009).

The total gas flow rate was set at 15 L min<sup>-1</sup> (STP) in the ozonolysis experiments resulting in a bulk residence time of 94 s. In the case of photolysis experiments with amine additions, a flow rate of 30 L min<sup>-1</sup> (STP) was chosen corresponding to a residence time of 32 s in the irradiated middle section. All gas flows were set by means of calibrated gas flow controllers (MKS 1259/1179).

A purification device (GateKeeper CE-500KF-O-4R, AERONEX) was applied for further purification of the commercial synthetic air (99.999 vol %, Air Products). Stated output gas impurity from GateKeeper is < 500 ppt for NMHCs, H<sub>2</sub>O and CO<sub>2</sub> in total. The water needed for the gas humidifier was taken from an ultrapure water system (Barnstead, resistivity: 17.4 MΩ cm). The H<sub>2</sub> used as the OH radical scavenger had a stated purity of 99.9999 vol % (Air Liquide). Tetramethylethylene (> 99 %, Fluka), 1-methyl-cyclohexene (99 %, Fluka), α-pinene (99 %, Fluka), limonene (99 %, Fluka), trimethylamine (99 %, Aldrich), dimethylamine (99 %, Aldrich), aniline (99.5 %, Sigma), and pyridine (99.8 %, Fluka) were used without further purification. SO<sub>2</sub> was taken from a 1 ppmv or 10 ppmv calibration mixture in N<sub>2</sub> (Messer).

Well defined, diluted samples of the individual olefins and amines were produced using a gas metering unit based on absolute pressure measurements. These olefin/amine samples were further diluted with the carrier gas at the entrance of the flow tube to establish the final tube concentration.

In Table 1 the gas composition for the reactants during different ozonolysis experiments is given. All olefin ozonolysis experiments have been conducted at a relative humidity of 22 %. In the case of nucleation experiments with added amines (absence of added olefins), H<sub>2</sub>SO<sub>4</sub> was formed via the reaction of OH radicals with SO<sub>2</sub> using ozone photolysis at a relative humidity of 13 or 25 % for OH radical generation. Initial ozone concentrations were in the range of  $(7.3\text{--}7.7) \times 10^{11}$  molecule cm<sup>-3</sup> and H<sub>2</sub> ( $8.2 \times 10^{15}$  molecule cm<sup>-3</sup>) was taken for adjusting the OH radical concentration needed in the tube to produce an average H<sub>2</sub>SO<sub>4</sub> concentration of  $\sim 2 \times 10^8$  molecule cm<sup>-3</sup>. More detailed information regarding photolysis experiments is given in Berndt et al. (2010).

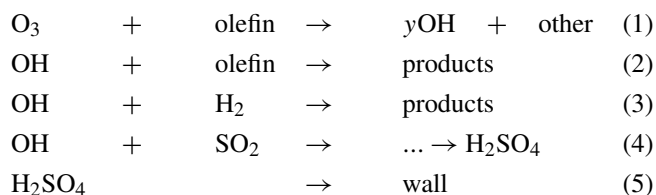
## 3 Modelling of chemical processes

The conversion of the olefins, as well as resulting H<sub>2</sub>SO<sub>4</sub> formation in the flow tube, were determined using model calculations. First, a simplified reaction scheme with special attention to the olefin conversion was applied. In the next step, a detailed reaction mechanism including Criegee Intermediate reactions allowed for a more precise description of the SO<sub>2</sub> oxidation processes in this system.

**Table 1.** Reactant concentrations used in ozonolysis experiments in synthetic air, RH = 22 %, bulk residence time = 94 s.

		O <sub>3</sub> (molecule cm <sup>-3</sup> )	olefin (molecule cm <sup>-3</sup> )	SO <sub>2</sub> (molecule cm <sup>-3</sup> )	H <sub>2</sub> (molecule cm <sup>-3</sup> )
1	TME varied, SO <sub>2</sub> fix	6.1 × 10 <sup>11</sup>	(1.25–75) × 10 <sup>10</sup>	3.07 × 10 <sup>10</sup>	–
2	TME varied, SO <sub>2</sub> fix, H <sub>2</sub>	6.08 × 10 <sup>11</sup>	(1.5–75) × 10 <sup>10</sup>	3.07 × 10 <sup>10</sup>	1.6 × 10 <sup>17</sup>
3	TME (high) fix, SO <sub>2</sub> varied	6.08 × 10 <sup>11</sup>	7.5 × 10 <sup>11</sup>	(4.6–62) × 10 <sup>9</sup>	–
4	TME (low) fix, SO <sub>2</sub> varied	6.08 × 10 <sup>11</sup>	1.5 × 10 <sup>10</sup>	(3.8–17) × 10 <sup>10</sup>	–
5	MCH varied, SO <sub>2</sub> fix	6.03 × 10 <sup>11</sup>	(6.0–40) × 10 <sup>10</sup>	5.37 × 10 <sup>11</sup>	–
6	MCH (high) fix, SO <sub>2</sub> varied	6.11 × 10 <sup>11</sup>	4.0 × 10 <sup>11</sup>	(1.8–18) × 10 <sup>11</sup>	–
7	MCH (low) fix, SO <sub>2</sub> varied	6.03 × 10 <sup>11</sup>	4.0 × 10 <sup>10</sup>	(7.2–18) × 10 <sup>11</sup>	–
8	limonene varied, no SO <sub>2</sub>	6.1 × 10 <sup>11</sup>	(9.7–440) × 10 <sup>9</sup>	–	–
9	limonene varied, SO <sub>2</sub> fix	6.08 × 10 <sup>11</sup>	(2.8–28) × 10 <sup>10</sup>	3.6 × 10 <sup>11</sup>	–
10	limonene varied, SO <sub>2</sub> fix, H <sub>2</sub>	6.3 × 10 <sup>11</sup>	(6.0–44) × 10 <sup>10</sup>	3.6 × 10 <sup>11</sup>	2.4 × 10 <sup>17</sup>
11	limonene fix, SO <sub>2</sub> varied	6.3 × 10 <sup>11</sup>	6.0 × 10 <sup>10</sup>	(3.6–18) × 10 <sup>11</sup>	–
12	α-pinene varied, no SO <sub>2</sub>	(5.7–6.3) × 10 <sup>11</sup>	(2.8–44) × 10 <sup>10</sup>	–	–
13	α-pinene varied, SO <sub>2</sub> fix	6.3 × 10 <sup>11</sup>	(8.0–44) × 10 <sup>10</sup>	3.6 × 10 <sup>11</sup>	–
14	α-pinene varied, SO <sub>2</sub> fix, H <sub>2</sub>	6.3 × 10 <sup>11</sup>	(1.6–4.4) × 10 <sup>11</sup>	3.6 × 10 <sup>11</sup>	2.4 × 10 <sup>17</sup>
15	α-pinene fix, SO <sub>2</sub> varied	6.3 × 10 <sup>11</sup>	4.0 × 10 <sup>10</sup>	(2.7–18) × 10 <sup>11</sup>	–

### 3.1 Simple mechanism

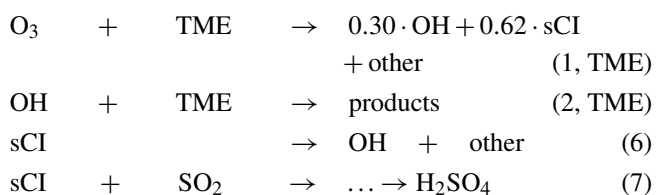


The needed rate coefficients  $k_1$ – $k_4$  were taken from the literature (unit: cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; TME: tetramethylethylene; MCH: 1-methyl-cyclohexene):  $k_{1,\text{TME}} = 1.0 \times 10^{-15}$  (Witter et al., 2002);  $k_{1,\text{MCH}} = 1.65 \times 10^{-16}$  (Treacy et al., 1997);  $k_{1,\alpha\text{-pinene}} = 1.1 \times 10^{-16}$  and  $k_{1,\text{limonene}} = 2.5 \times 10^{-16}$  (Witter et al., 2002);  $k_{2,\text{TME}} = 1.1 \times 10^{-10}$  (Atkinson, 1986);  $k_{2,\text{MCH}} = 9.6 \times 10^{-11}$  (Darnall et al., 1976);  $k_{2,\alpha\text{-pinene}} = 5.3 \times 10^{-11}$  (Atkinson, 1986);  $k_{2,\text{limonene}} = 1.6 \times 10^{-10}$  (Atkinson et al., 1986);  $k_3 = 6.7 \times 10^{-15}$  (DeMore et al., 1997) and  $k_4 = 1.2 \times 10^{-12}$  (Zellner, 1978). A diffusion controlled process is assumed for the H<sub>2</sub>SO<sub>4</sub> wall loss in the flow tube,  $k_5 = 3.65 \cdot D(\text{H}_2\text{SO}_4)/r^2$ . The diffusion coefficient  $D(\text{H}_2\text{SO}_4) = 0.075 \text{ cm}^2 \text{ s}^{-1}$  was taken from the experimental work by Hanson and Eisele (2000). For the OH radical yields  $y$  in pathway (1) the following values have been applied: 0.92 for TME (Berndt and Böge, 2006), 0.90 for MCH (Atkinson et al., 1995), 0.91 for α-pinene (Siese et al., 2001) and 0.86 for limonene (Atkinson et al., 1992). The data for the individual OH radical yields from the different olefins originate from chamber studies or from flow-tube investigations with reaction times of minutes or longer. Therefore, these OH yields comprise the prompt OH radical formation from the excited Criegee Intermediates (time scale of less than a millisecond) as well as from the thermal channel

of stabilized Criegee Intermediates (time scale of seconds) (e.g. Kroll et al., 2001).

### 3.2 Detailed mechanism for TME ozonolysis (stabilized Criegee Intermediate involved)

A more detailed reaction mechanism for TME ozonolysis, based on recent experimental work from our laboratory, was used for modelling of simultaneous SO<sub>2</sub> oxidation by OH radicals as well as by the stabilized Criegee Intermediate (sCI), (CH<sub>3</sub>)<sub>2</sub>COO, (Berndt et al., 2012). Pathways (3)–(5) are identical to those given above.



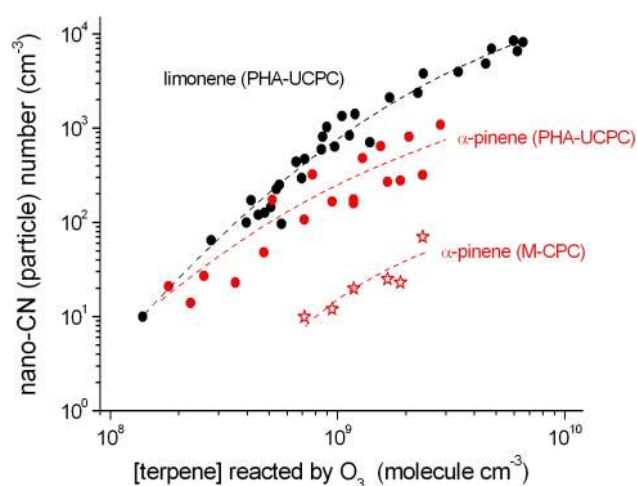
The measured sCI yield of 0.62 at 1 bar air (Berndt et al., 2012) is in very good agreement with previous results (Drozd et al., 2011). A prompt OH radical yield of 0.30 in pathway (1,TME) was assumed in order to fulfil a total OH radical yield of 0.92 (Berndt et al., 2006) for long reaction times in absence of bimolecular reactions of sCI (OH radical yield of unity from sCI decomposition). For comparison, Kroll et al. (2001) reported for a pressure of 100 Torr a prompt OH radical yield of  $0.21 \pm 0.04$  from experiments and 0.40 as a result of theoretical calculations. The rate coefficient  $k_6$  is set to  $3.0 \text{ s}^{-1}$  as recently observed as the total sCI loss rate coefficient ( $k_{\text{loss}}$ ) at a pressure of 1 bar of synthetic air at  $293 \pm 0.5 \text{ K}$  and a relative humidity of 50 % (Berndt et al., 2012). The water-reaction term in the measured  $k_{\text{loss}}$ ,  $k_{\text{loss}} = k_{\text{dec}} + k(\text{sCI} + \text{H}_2\text{O}) \cdot [\text{H}_2\text{O}]$ , is of less importance due to the very low rate coefficient  $k(\text{sCI} + \text{H}_2\text{O})$

in the order of a few  $10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Anglada et al., 2002; Ryzhkov and Ariya, 2004). Therefore, the explicit reaction of sCI with water vapour was neglected. The value  $k_7 = 7.7 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was also taken from our recent kinetic experiment.

## 4 Results and discussion

### 4.1 Ozonolysis of olefins without SO<sub>2</sub> addition

First, experiments in absence of added SO<sub>2</sub> have been performed in order to investigate possible particle formation by the oxidation products of the olefins without relevant H<sub>2</sub>SO<sub>4</sub> production. Measured H<sub>2</sub>SO<sub>4</sub> concentrations were below  $10^6$  molecule cm<sup>-3</sup>. The initial concentrations of  $\alpha$ -pinene and limonene varied from close to atmospheric peak concentrations of about  $(1\text{--}3) \times 10^{10}$  molecule cm<sup>-3</sup> to  $4.4 \times 10^{11}$  molecule cm<sup>-3</sup> using nearly constant ozone concentrations of  $(5.7\text{--}6.3) \times 10^{11}$  molecule cm<sup>-3</sup>. Particle formation was followed by means of PHA-UCPC and in few cases using the M-CPC for comparison. The findings for the terpenes are given in Fig. 1 as a function of reacted olefin by the ozone reaction, pathway (1). The amount of converted olefin was obtained by modelling, see Sect. 3.1. Signals from PHA-UCPC measurements of about 10 particles or activated “nano-CN” per cm<sup>3</sup> (McMurry et al., 2011) were observed for close to atmospheric peak concentrations of  $\alpha$ -pinene and limonene. The signals showed a strong increase with increasing concentration of reacted terpene, see Fig. 1. On the other hand, for a constant amount of reacted terpene, the signal was independent of H<sub>2</sub>SO<sub>4</sub> in a wide range of the acid concentration ( $[\text{H}_2\text{SO}_4]$  smaller than  $\sim 10^7$  molecule cm<sup>-3</sup>) as shown later. This fact apparently suggests that H<sub>2</sub>SO<sub>4</sub> was not necessarily needed for the appearance of these signals. However, the analysis of the PHA-UCPC measurements revealed that the observed signals appeared all in the same channel range (i.e. same size) with no shift for rising concentrations of the reacted terpene (i.e. no clear indication for particle growth). Only a distinct increase of the signal height was visible for increasing amounts of reacted terpenes. This finding was already discussed in a separate paper by Lehtipalo et al. (2011). There, in Fig. 5, the average PHA-UCPC count rates per channel are depicted for the ozonolysis experiments with limonene,  $[\text{limonene}] = (0\text{--}4.4) \times 10^{11}$  molecule cm<sup>-3</sup>. It can be concluded that probably oxidation products of the olefins (large molecules or clusters) were detected and counted as particles by the PHA-UCPC. Possible candidates for such large molecules from terpene oxidation are highly oxidized products recently detected by Ehn et al. (2012). There are some indications from different recent experiments that these highly oxidized products may be formed very rapidly as stable first generation products. Therefore, we cannot rule out that they are also present under our experimental conditions.

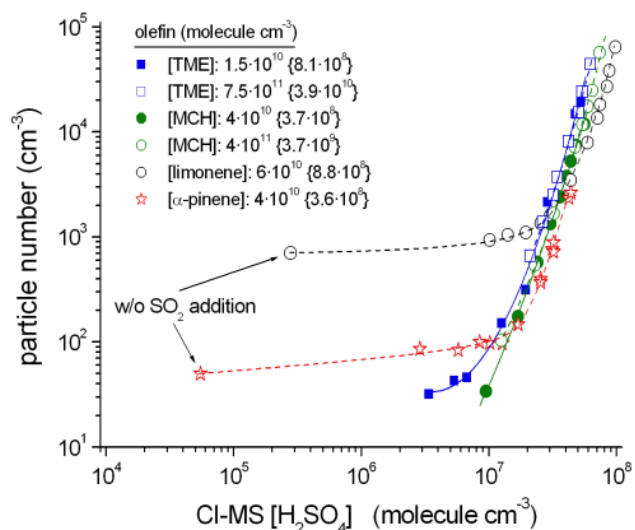


**Fig. 1.** Measured particle numbers (PHA-UCPC and M-CPC) as a function of converted terpene by the ozone reaction. The H<sub>2</sub>SO<sub>4</sub> concentrations were below  $10^6$  molecule cm<sup>-3</sup>. The reactant concentrations are given in Table 1, measurement series 9 and 12.

In our experiment, M-CPC measurements in the case of  $\alpha$ -pinene ozonolysis showed more than one order of magnitude lower particle numbers compared to simultaneously performed PHA-UCPC measurements, see Fig. 1. This fact can be due to the different activation conditions in both instruments (Sipilä et al., 2009; Vanhanen et al., 2011). It is to be noted, that nearly identical detection efficiency for both instruments was found in the case of H<sub>2</sub>SO<sub>4</sub> particles with diameters down to  $\sim 1.5$  nm (Sipilä et al., 2010; Berndt et al., 2010).

### 4.2 Ozonolysis of olefins in the presence of added SO<sub>2</sub>

Figure 2 shows the raw data from PHA-UCPC particle measurements as a function of the detected H<sub>2</sub>SO<sub>4</sub> concentration for six measurement series using constant ozonolysis conditions (constant organic product formation) by variation of SO<sub>2</sub>. The H<sub>2</sub>SO<sub>4</sub> concentrations have been measured at the IfT-LFT outlet and represent the average steady-state concentration within the flow tube. H<sub>2</sub>SO<sub>4</sub> is produced from the oxidation of SO<sub>2</sub> by OH radicals, and most likely by stabilized Criegee Intermediates (sCI), in the presence of water vapour. Both oxidants, OH radicals and sCI, are formed in the course of the ozonolysis reaction. Data in absence of added SO<sub>2</sub> are also shown for the measurements with  $\alpha$ -pinene and limonene. The data given in Fig. 2 suggest two different processes driving the particle (nano-CN) formation: (i) for  $[\text{H}_2\text{SO}_4]$  smaller than  $\sim 10^7$  molecule cm<sup>-3</sup>, a H<sub>2</sub>SO<sub>4</sub>-independent process governed by the products of the ozonolysis reaction as described in the section before, and (ii) a H<sub>2</sub>SO<sub>4</sub>-dominated process for H<sub>2</sub>SO<sub>4</sub> concentration higher than  $\sim 10^7$  molecule cm<sup>-3</sup>. The latter seems to be independent of the chemical nature of the organic oxidation products



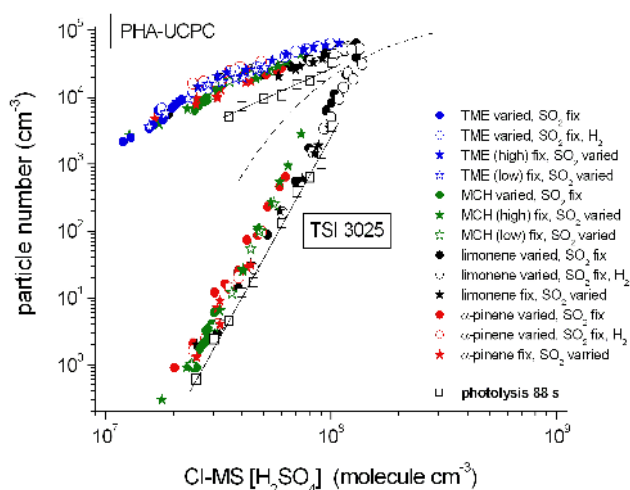
**Fig. 2.** Raw particle numbers from PHA-UCPC measurements in dependence on measured H<sub>2</sub>SO<sub>4</sub> concentration by variation of SO<sub>2</sub> for constant ozonolysis conditions. Initial olefin concentrations are given along with the converted olefin by ozone (in brackets), measurement series 3, 4, 6, 7, 11 and 15. The data for very low H<sub>2</sub>SO<sub>4</sub> concentrations (< 10<sup>6</sup> molecule cm<sup>-3</sup>) were obtained without SO<sub>2</sub> addition.

(products from an acyclic C<sub>6</sub>-olefin or cyclic C<sub>7</sub> or C<sub>10</sub> olefins), as well as of their concentration levels in the considered range (in Fig. 2 shown for TME and MCH ozonolysis). The initial olefin concentrations were in the order of a few 10<sup>10</sup> molecule cm<sup>-3</sup> and were enlarged for TME and MCH by a factor of 50 or 10, respectively. Only a small fraction of the olefin, ~ (1–5) %, has been converted by ozone due to the relatively low reactivity and the short residence time in the flow tube of 94 s. Resulting total product concentrations from ozonolysis (at the flow-tube outlet) were in the range ~ (4–9) × 10<sup>8</sup> molecule cm<sup>-3</sup> or respectively higher for TME and MCH experiments with the higher olefin concentrations. From the measurements it is obvious that the organic oxidation products in this concentration range (mainly from first generation) have no measurable influence on the nucleation process for [H<sub>2</sub>SO<sub>4</sub>] higher than ~ 10<sup>7</sup> molecule cm<sup>-3</sup>. The small differences amongst the various series could be due to experimental uncertainties, especially from the PHA-UCPC measurements. Zhang et al. (2004) observed a clear nucleation enhancement in the presence of aromatic acids in the concentration range of (1–7) × 10<sup>9</sup> molecule cm<sup>-3</sup>. In our experiments, the organic acids arising from the terpenes reached only concentrations of a few 10<sup>7</sup> molecule cm<sup>-3</sup>, according to their formation yields as given in the literature (Yu et al., 1999). Thus, the absence of a clear promoting effect of organic acids on nucleation in our experiment can be caused by significantly lower organic acid concentration compared to the study by Zhang et al. (2004), or by the fact that no aromatic acids were formed in our experi-

ment. Furthermore, the results of our study for close to atmospheric conditions do not support the findings by Metzger et al. (2010) stating that any organic oxidation products are needed for atmospheric H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation. On the contrary, the observed nucleation process was rather caused by the strong H<sub>2</sub>SO<sub>4</sub> ↔ amine interactions for background amine concentration in the carrier gas in the order of 10<sup>7</sup>–10<sup>8</sup> molecule cm<sup>-3</sup>. The disagreement between our results and Metzger et al. (2010) might be due this strong effect of background amines on nucleation, pushing back a possible contribution of organic oxidation products in the nucleation process. The effects of amines being present in the carrier gas will be described below.

In the course of the measurement campaign the reaction parameters of the olefin ozonolysis were modified in a relatively wide range, increasing the olefin concentrations for constant SO<sub>2</sub> (increase of organic oxidation products) or conducting the reaction also in the presence of an OH radical scavenger (H<sub>2</sub>), cf. Table 1. The detected H<sub>2</sub>SO<sub>4</sub> concentration was identified as the most dominant parameter for particle formation under all circumstances, even in the experiments with the highest terpene concentrations of up to 4.4 × 10<sup>11</sup> molecule cm<sup>-3</sup> (total product concentrations from ozonolysis of a few 10<sup>9</sup> molecule cm<sup>-3</sup>). In Fig. 3 all results of detection efficiency corrected PHA-UCPC and TSI 3025 measurements for [H<sub>2</sub>SO<sub>4</sub>] higher than ~ 10<sup>7</sup> molecule cm<sup>-3</sup> are depicted. The results of the olefin ozonolysis series among each other showed again no clear differences for both particle counters. For comparison, the findings from ozone photolysis in absence of added organics (residence time of 88 s) are also given. Generally, the detected particle numbers from the olefin ozonolysis experiments were higher by a factor of 2–5 compared to those from the photolysis experiments. This fact can be due to the different H<sub>2</sub>SO<sub>4</sub> profiles within the flow tube caused by the different approaches of SO<sub>2</sub> oxidant formation. The comparison of the results from the PHA-UCPC (50 % cut-off size: about 1.5 nm) and the TSI 3025 (50 % cut-off size: about 2.5–3 nm) reveals that the early growth of the particles from about 1.5 nm to about 2.5–3 nm was little influenced by the organic oxidation products. The measured particle numbers from the PHA-UCPC and the TSI 3025 start to merge for H<sub>2</sub>SO<sub>4</sub> concentrations higher than 10<sup>8</sup> molecule cm<sup>-3</sup>. A rough estimate yields a particle growth by pure H<sub>2</sub>SO<sub>4</sub> in the flow tube of about 0.4–0.6 nm assuming [H<sub>2</sub>SO<sub>4</sub>] = (2–3) × 10<sup>8</sup> molecule cm<sup>-3</sup>, an average growth time of 50 s, and a growth rate of 4 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> nm s<sup>-1</sup> (Lehtinen and Kulmala, 2003). That means that H<sub>2</sub>SO<sub>4</sub> accounted only for roughly half of the growth in our experiment. Possible substances, also involved in the early growth are probably the amines from the carrier gas background impurities, water vapour and the H<sub>2</sub>SO<sub>4</sub> (amine) dimers (not detected at the monomer channel of the CI-MS) as described by Petäjä et al. (2011). A possible contribution of any organic oxidation products in the early growth process cannot be totally





**Fig. 3.** Measurements of the particle numbers by PHA-UCPC (corrected) and TSI 3025 as a function of the H<sub>2</sub>SO<sub>4</sub> concentration. The dashed line separates the data from both particle counters. The reactant concentrations are given in Table 1, measurement series 1–7, 9–11 and 13–15. Measurement data from ozone photolysis experiments (full lines) in absence of added organics are shown for comparison.

ruled out, but is expected to be very small considering the growth rates given in the literature. Riccobono et al. (2012) reported from a H<sub>2</sub>SO<sub>4</sub>/α-pinene system an initial growth rate of about 2 nm h<sup>−1</sup> for 1.5–2 nm particles caused by organic oxidation products for a α-pinene conversion rate of 1–6 ppt s<sup>−1</sup>, (2.5–15) × 10<sup>7</sup> molecule cm<sup>−3</sup> s<sup>−1</sup>. The α-pinene conversion rate stands as a proxy for the formation rate of organic products participating in the growth process. For our α-pinene reaction rate of (0.2–2.9) × 10<sup>7</sup> molecule cm<sup>−3</sup> s<sup>−1</sup> we can assume the reported growth rate of 2 nm h<sup>−1</sup> for small particles as an upper limit. For a 50 s growth time a diameter increase of 0.028 nm (upper limit) follows, which is very small and impossible to detect.

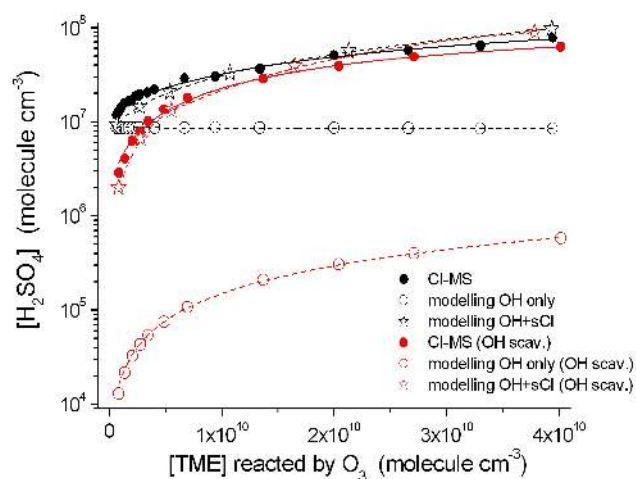
It is impossible to give a clear statement regarding the chemical nature of the substances involved in the growth process beside H<sub>2</sub>SO<sub>4</sub>. However, a contribution of amines in the growth process would be at least qualitatively in line with observations from a field study where aminium ions were detected as a substantial fraction of measured ions from 8–10 nm particles (Smith et al., 2010).

#### 4.3 Additional H<sub>2</sub>SO<sub>4</sub> formation (other than via OH + SO<sub>2</sub>)

In the course of the experiments, also three measurement series have been conducted in the presence of high H<sub>2</sub> concentrations for effective OH radical scavenging. The measured H<sub>2</sub>SO<sub>4</sub> concentrations were clearly higher than expected from the reaction of residual OH radicals with SO<sub>2</sub>. This fact can be explained by additional oxidation of SO<sub>2</sub>

by organic ozonolysis products, very likely by stabilized Criegee Intermediates (sCI). Recently, the atmospheric relevance of this pathway was discovered (Mauldin et al., 2012). Figure 4 shows the results of H<sub>2</sub>SO<sub>4</sub> formation from TME ozonolysis in the presence and absence of H<sub>2</sub>. The findings for α-pinene and limonene, which feature analogous reactions, have been already discussed by Mauldin et al. (2012). Beside the measurements (full circles), also the results from modelling considering OH radicals as the only oxidant for SO<sub>2</sub> (open circles), and for both, OH radicals and sCI as oxidants for SO<sub>2</sub> (open stars), are given. The used chemical schemes including the kinetic parameters are described in Sects. 3.1 and 3.2. The comparison of measured H<sub>2</sub>SO<sub>4</sub> concentrations with modelling results considering only OH radicals as the SO<sub>2</sub> oxidant shows clearly that an additional pathway for SO<sub>2</sub> oxidations has to exist. A very good agreement between measurement and modelling is achieved assuming additional SO<sub>2</sub> oxidation by sCI based on kinetic parameters from an independent study, cf. Sect. 3.2. It is to be noted, that Welz et al. (2012) reported recently a much higher reactivity of sCI (here CH<sub>2</sub>OO) towards SO<sub>2</sub> than incorporated in our modelling. Using simply this higher rate coefficient in the calculations,  $k_7 = 3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (instead of  $k_7 = 7.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), the modelling results overestimated the measured H<sub>2</sub>SO<sub>4</sub> concentrations by a factor of up to 35. However, the calculated H<sub>2</sub>SO<sub>4</sub> concentrations for the chosen conditions are very sensitive regarding the ratio  $k_6/k_7$ , and less sensitive regarding the absolute values of the individual rate coefficients  $k_6$  and  $k_7$  for a given ratio  $k_6/k_7$ . As a result of our kinetic measurements  $k_6/k_7 = 3.9 \times 10^{12} \text{ molecule cm}^{-3}$  and  $k_6 = 3.0 \text{ s}^{-1}$  have been determined (Berndt et al., 2012). The rate coefficient  $k_6$  is identical with  $k_{\text{loss}}$  for a negligible sCI + water reaction. Assuming again  $k_7 = 3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Welz et al., 2012),  $k_6 = 152 \text{ s}^{-1}$  follows in order to retain  $k_6/k_7 = 3.9 \times 10^{12} \text{ molecule cm}^{-3}$  as needed for an appropriate description of the measurements, see Fig. 4. Kroll et al. (2001) stated for acetone oxide, (CH<sub>3</sub>)<sub>2</sub>COO,  $k_6 = 6.4 \pm 0.9 \text{ s}^{-1}$  from time-dependent measurements at 100 Torr and  $k_6 = 3.5 \text{ s}^{-1}$  resulting from theoretical considerations. These data for  $k_6$  are in reasonable agreement with our  $k_6 = 3.0 \text{ s}^{-1}$ , supporting also the lower value  $k_7 = 7.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of sCI with SO<sub>2</sub>. Nevertheless, much more work is needed for a more reliable understanding of the sCI reactivity.

Despite the current debate regarding the absolute values of the rate coefficient for sCI + SO<sub>2</sub>, the measurements show clearly that, in addition to the SO<sub>2</sub> oxidation by OH radicals, another process forming H<sub>2</sub>SO<sub>4</sub> from SO<sub>2</sub> exists. The additional H<sub>2</sub>SO<sub>4</sub> formation step (most likely by sCI) can account for a substantial fraction of the total H<sub>2</sub>SO<sub>4</sub> production in the atmosphere, see Mauldin et al. (2012). Thus, products of olefin ozonolysis (sCI) can support atmospheric nucleation in terms of an enhancement of H<sub>2</sub>SO<sub>4</sub> formation. The results of this study suggest that this indirect nucleation promoting



**Fig. 4.** Measured  $\text{H}_2\text{SO}_4$  concentrations from TME ozonolysis experiments as a function of reacted TME by ozone in the presence (full circles, red) and absence (full circles, black) of  $\text{H}_2$  as an OH radical scavenger. Reactant concentrations are given in Table 1, measurement series 1 and 2. The measurements are compared with modelling results considering only OH radicals as the oxidant for  $\text{SO}_2$  (open circles) or for OH radicals and sCl as oxidants for  $\text{SO}_2$  (open stars).

effect via amplified  $\text{H}_2\text{SO}_4$  formation outbalances probably any direct participation of organic oxidation products in the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleation process.

#### 4.4 Experiments with amine additions

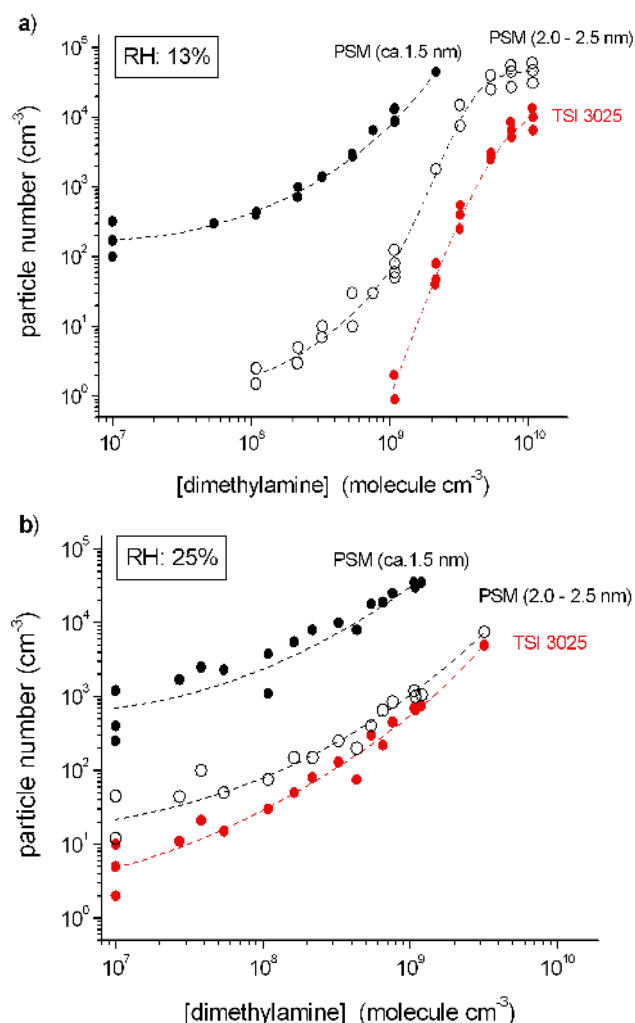
The measurements with amine additions were conducted with a total gas flow of  $30 \text{ L min}^{-1}$  (STP) resulting in a relatively short residence time of 32 s in the irradiated IFT-LFT middle section. The individual amines were taken from well defined, diluted samples from a gas metering unit based on absolute pressure measurements. After further dilution with the carrier gas at the entrance of the flow the final tube concentration of the amines was established. The same procedure has been done for  $\text{NH}_3$ . In the case of  $\text{NH}_3$  we were able to measure the resulting  $\text{NH}_3$  concentration at the flow-tube inlet and outlet by means of a sensitive  $\text{NH}_3$  detector, see Berndt et al. (2010). After an equilibration time of about one hour stable  $\text{NH}_3$  concentration were detected at the inlet and outlet being very close to the expected concentration as calculated from the diluted gas sample. For the amines we assumed the same behaviour as measured for  $\text{NH}_3$ . The measurements showed that also in the case of amine additions about one hour was needed to adjust stable nucleation conditions (constant particle numbers) in the tube. Stable amine concentrations in the nucleation zone can be expected under these conditions (the particle number was found to be very sensitive regarding amine concentrations). Nevertheless, there is no direct measurement of the amine concentration in the nucleation zone, and therefore the given values

of the amine concentrations (calculated entrance concentrations) have to be considered only as upper limits. It should be noted, that clear memory effects were observed after switching off the amine flow as well. Hence, to ensure reproducibility, between the experiments (and over night), the whole system was purged with pure carrier gas. In addition, the flow-tube walls have been washed with high purity water before changing the kind of the amine applied in the experiment.

In Fig. 5a and b the results of the particle measurements at relative humidity of 13 and 25 %, performed by means of PSM (two different cut-off sizes) and by TSI 3025 are depicted as a function of added dimethylamine for  $[\text{H}_2\text{SO}_4] = 2 \times 10^8 \text{ molecule cm}^{-3}$ . Measurements without amine addition are given at the x axis at  $10^7 \text{ molecule cm}^{-3}$ . All measurement traces showed a very strong increase of the particle number with increasing dimethylamine additions. This behaviour is at least qualitatively in line with observations from other laboratory studies describing the effect of amine additions on  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleation (Berndt et al., 2010; Erupe et al., 2011; Zollner et al., 2012; Almeida et al., 2013). Some kind of saturation behaviour for the number of formed particles can be seen at a relative humidity of 13 % for dimethylamine concentrations  $\geq 5 \times 10^9 \text{ molecule cm}^{-3}$ . For the higher humidity of 25 %, this effect is not visible caused by missing measurements for high dimethylamine concentrations. Particles with a diameter  $\geq \text{ca. } 1.5 \text{ nm}$  were measured with a diethyleneglycol flow of  $0.5 \text{ L min}^{-1}$  and for particles with a diameter  $\geq 2.0\text{--}2.5 \text{ nm}$  a flow of  $0.2 \text{ L min}^{-1}$  was taken (Vanhanen et al., 2011). The comparison of the PSM measurements for  $1.5 \text{ nm}$  particles (diameter  $\geq \text{ca. } 1.5 \text{ nm}$ ) points to an increase of the nucleation rate with increasing humidity. It is not clear at the moment whether this effect is merely due to the increasing water vapour concentration. We cannot rule out that, with increasing water vapour, more background amines were flushed in the flow tube. Furthermore, changing activation conditions in the counter with changing relative humidity can also cause this effect, at least partly. In Fig. 6 cumulative size distributions as measured by PSM (scanning the diethyleneglycol flow in the instrument) are shown for both relative humidities considered, and a dimethylamine concentration of  $1.1 \times 10^9 \text{ molecule cm}^{-3}$ . The size distribution at  $\text{RH} = 25 \%$  showed no rise with increasing diethyleneglycol flow for flow rates  $\geq 0.5 \text{ L min}^{-1}$ . At  $\text{RH} = 13 \%$ , for higher diethyleneglycol flows of around  $1.0 \text{ L min}^{-1}$  (higher detection efficiency for smaller particles) only a small increase of the measured number by a factor of two, as compared to the standard measurements at  $0.5 \text{ L min}^{-1}$ , was detected. This observation provides the guarantee that the PSM did not detect any other clusters or large molecules even for high super-saturations. A more detailed interpretation of the cumulative distributions appears to be difficult due to the possible issues connected with increasing water vapour content as mentioned before.

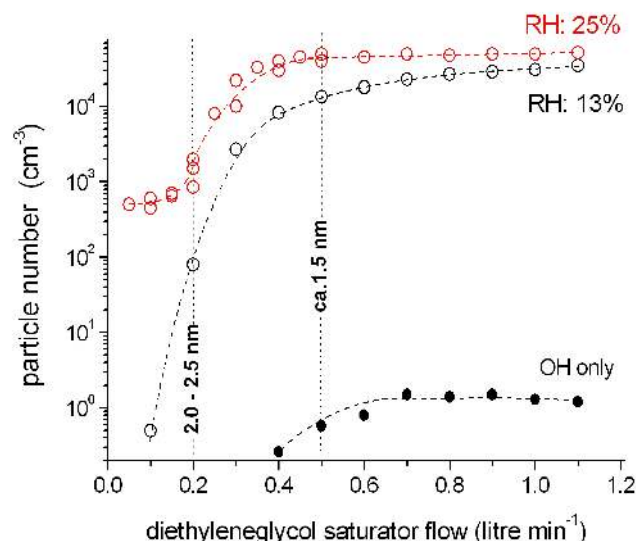
The results for nucleation enhancement by trimethylamine, dimethylamine, aniline and pyridine detected at





**Fig. 5.** Particle numbers as a functions of added dimethylamine concentration at a relative humidity of 13 % (a) and 25 % (b), [H<sub>2</sub>SO<sub>4</sub>] =  $2 \times 10^8$  molecule cm<sup>-3</sup>. Measurements have been done by PSM with a diethyleneglycol flow of 0.5 L min<sup>-1</sup> (50 % cut-off size: about 1.5 nm), a diethyleneglycol flow of 0.2 L min<sup>-1</sup> (50 % cut-off size: about 2.0–2.5 nm), and by TSI 3025 (50 % cut-off size: about 2.5–3.0 nm). Measurements without amine addition are given at the x axis at 10<sup>7</sup> molecule cm<sup>-3</sup>.

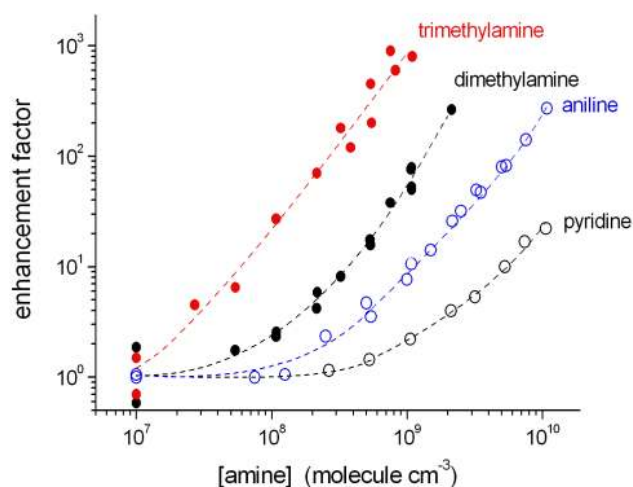
RH = 13 % and for [H<sub>2</sub>SO<sub>4</sub>] =  $2 \times 10^8$  molecule cm<sup>-3</sup> are depicted in Fig. 7 (PSM measurements for a diameter  $\geq$  ca. 1.5 nm). The data are normalized by the particle number observed in the absence of amine additions. It is to be noted, that a part of the observed enhancement can be due to enhanced growth by the amine additions unless all particles have been counted with the chosen PSM settings in each case. Therefore, the given enhancement factors should be treated as an upper limit. All amines show a nucleation promoting behaviour whereas the strength of enhancement is strongly substance specific. The gas-phase basicity according to the proton affinity (base + H<sup>+</sup>  $\rightarrow$  base-H<sup>+</sup>) characterizes



**Fig. 6.** Cumulative size distributions from PSM measurements (by scanning the diethyleneglycol flow) for a dimethylamine concentration of  $1.1 \times 10^9$  molecule cm<sup>-3</sup> at a relative humidity of 13 and 25 %. The data for “OH only” have been obtained under conditions with OH radical formation in the absence of added amine and SO<sub>2</sub> representing a background measurement. Dotted lines show the diethyleneglycol flow settings as used in the measurements for particles with a diameter  $\geq$  ca. 1.5 nm or particles with a diameter  $\geq$  2.0–2.5 nm.

the strength of the H<sub>2</sub>SO<sub>4</sub>  $\leftrightarrow$  amine interactions. The corresponding values of the proton affinity are (unit: kJ mol<sup>-1</sup>); trimethylamine: 942, dimethylamine: 923, aniline: 877, pyridine: 924 (Jolly, 1991). Decreasing enhancement factors, in the order trimethylamine, dimethylamine and aniline, can be explained by decreasing proton affinity and subsequently by lowering of H<sub>2</sub>SO<sub>4</sub>  $\leftrightarrow$  amine interactions. For pyridine a similar behaviour was expected as observed for dimethylamine due to the nearly identical proton affinity. However, pyridine was much less effective in nucleation enhancement than thought. Obviously, the molecule structure of the base has also fundamental impact on the nucleation process beside the thermodynamic feature (Kurten et al., 2008; DePalma et al., 2012). More comprehensive measurement series with a couple of other bases are needed for a better mechanistic understanding for the most important steps of the base (amine) promoted H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation.

Zollner et al. (2012) observed for a methylamine addition with a mixing ratio of 3 pptv ( $7.4 \times 10^7$  molecule cm<sup>-3</sup>), and a H<sub>2</sub>SO<sub>4</sub> concentration of  $\sim 3 \times 10^9$  molecule cm<sup>-3</sup>, an enhancement factor of  $2 \times 10^4$ , much higher than our values for comparable amine additions. This fact indicates that our carrier gas was possibly contaminated with higher amine levels compared to the background being present in the experiments by Zollner et al. (2012). The runs given in Fig. 7 were taken to get a rough estimate regarding our possible amine background. As a result of extrapolation to a “zero” effect of the



**Fig. 7.** Enhancement factors,  $N_{\text{amine added}}/N_{\text{w/o amine addition}}$ , for trimethylamine, dimethylamine, aniline and pyridine detected at  $\text{RH} = 13\%$  for  $[\text{H}_2\text{SO}_4] = 2 \times 10^8 \text{ molecule cm}^{-3}$ , PSM measurements for a diameter  $\geq \text{ca. } 1.5 \text{ nm}$ .

amine additions, an amine or base background equivalent to  $10^7 \text{ molecule cm}^{-3}$  of trimethylamine or  $10^8 \text{ molecule cm}^{-3}$  of aniline can be assumed. A possible source for the amine background is the water used in the humidifier. We tested different water qualities and also the acidification of the humidifier water as described by Ball et al. (1999), but without a change or “improvement” regarding the possible amine background. Here, the detected particle formation from a standard nucleation experiment (constant reactant concentrations) served as the parameter evaluating the possible amine background. Also the substitution of the carrier gas source (with subsequent purification using GateKeeper) did not change the situation. The source of the amine background is still unsolved.

In performed model calculations, a background concentration of  $10^7\text{--}10^8 \text{ molecule cm}^{-3}$  dimethylamine was needed for explaining the measured  $\text{H}_2\text{SO}_4$  dimer concentrations in our experiment (Petäjä et al., 2011). It is to be noted, that a similar, possible amine background level has to be assumed also for our former studies (e.g. Sipilä et al., 2010; Berndt et al., 2010). Different amine background concentrations can cause the wide range of nucleation rates observed in various experiments beside the issues connected with different growth times and the efficiency of particle detection.

Finally, the results of this study support the strong  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleation enhancement by amines with concentrations similar to those found in the atmosphere, e.g.  $(1\text{--}18) \times 10^8 \text{ molecule cm}^{-3}$ , as measured for methylamine, dimethylamine, trimethylamine and diethylamine in total (Grönberg et al., 1992). The strong  $\text{H}_2\text{SO}_4 \leftrightarrow \text{amine}$  (acid  $\leftrightarrow$  base) interactions seem to be more effective for the process of new particle formation than any  $\text{H}_2\text{SO}_4 \leftrightarrow \text{organics}$  interactions.

## 5 Summary

$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleation influencing effects were studied in the flow tube IfT-LFT (Institute for Tropospheric Research – Laminar Flow Tube) at  $293 \pm 0.5 \text{ K}$  and a pressure of 1 bar using synthetic air as the carrier gas and a bulk residence time of 94 or 32 s. The aim of this work was to quantify how both, amines and organic oxidation products, may enhance atmospheric  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleation for close to atmospheric conditions. Such a “comparative study”, bases vs. organic oxidation products, performed in the same experimental setup is not given in the literature up to now.

The first set of experiments has been performed in the presence of organic oxidation products arising from the ozonolysis of olefins (tetramethylethylene, 1-methylcyclohexene,  $\alpha$ -pinene and limonene) for close to atmospheric concentrations. Ozonolysis served also as the source of OH radicals and possibly other oxidants initiating  $\text{H}_2\text{SO}_4$  formation starting from  $\text{SO}_2$ . These organic oxidation products (first generation mainly) showed no clear effect on the number of nucleated particles within a wide range of experimental conditions for  $[\text{H}_2\text{SO}_4]$  higher than  $\sim 10^7 \text{ molecule cm}^{-3}$ . The comparison of the results of two different particle counters (50 % cut-off size: about 1.5 nm or 2.5–3 nm) point to the fact that the early growth process of the nucleated particles for close to atmospheric reactant concentrations was not significantly influenced by the organic oxidation products under our conditions (background amine concentration of the order of  $10^7\text{--}10^8 \text{ molecules cm}^{-3}$ ). This finding is in line with the expected growth rate by organics for our conditions as deduced from literature data, see Riccobono et al. (2012). A rough estimate yields a particle growth by pure  $\text{H}_2\text{SO}_4$  of about 0.4–0.6 nm for a growth time of 50 s ( $[\text{H}_2\text{SO}_4] = (2\text{--}3) \times 10^8 \text{ molecule cm}^{-3}$ ) accounted for roughly half of the growth in the experiment. Possible substances, also involved in the early growth are amines, water vapour and  $\text{H}_2\text{SO}_4$  (amine) dimers or larger clusters.

For  $\text{H}_2\text{SO}_4$  concentrations smaller than  $\sim 10^7 \text{ molecule cm}^{-3}$ , an additional,  $\text{H}_2\text{SO}_4$ -independent process of particle (nano-CN) formation was observed in the case of the ozonolysis of  $\alpha$ -pinene and limonene. From the analysis of the PHA-UCPC signals it can be concluded that probably oxidation products of the terpenes (large molecules or clusters) were detected. Such substances could be highly oxidized products as recently discovered by Ehn et al. (2012).

The appearance of an additional oxidant for  $\text{SO}_2$  beside OH radicals, very likely stabilized Criegee Intermediates (sCI), has been confirmed. In the case of the ozonolysis of TME, the  $\text{H}_2\text{SO}_4$  measurements in the presence and absence of an OH radical scavenger were well described by modelling using recently obtained kinetic data for the sCI reactivity.

A second set of experiments has been performed in the presence of added amines (trimethylamine, dimethylamine, aniline and pyridine) in the concentrations range of a few

10<sup>7</sup>–10<sup>10</sup> molecule cm<sup>−3</sup> using photolytic OH radical generation for the formation of H<sub>2</sub>SO<sub>4</sub>. All amines showed a strong nucleation enhancing effect. Decreasing enhancement factors, in the order trimethylamine, dimethylamine and aniline, can be explained by decreasing proton affinity and subsequently by lowering of H<sub>2</sub>SO<sub>4</sub> ↔ amine interactions. However, pyridine was much less effective in nucleation enhancement than expected according to its proton affinity. This fact indicates the impact of the molecule structure of the base on the nucleation process. The extrapolation of the obtained enhancement factors to a “zero” effect of the amine addition points to a possible amine or base background equivalent to 10<sup>7</sup> molecule cm<sup>−3</sup> of trimethylamine or 10<sup>8</sup> molecule cm<sup>−3</sup> of aniline.

The results of this study support the strong H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O nucleation enhancement by amines, at least in presence of amines in the concentration range of few 10<sup>7</sup> molecule cm<sup>−3</sup> or above. The strong H<sub>2</sub>SO<sub>4</sub> ↔ amine (acid ↔ base) interactions appear to be much more effective for the process of new particle formation than any H<sub>2</sub>SO<sub>4</sub> ↔ organics interactions. The additional H<sub>2</sub>SO<sub>4</sub> formation step (most likely via sCI) can account for a substantial fraction of the total H<sub>2</sub>SO<sub>4</sub> production in the atmosphere, see Mauldin et al. (2012). Thus, products of olefin ozonolysis (sCI) could possibly support atmospheric nucleation in terms of an enhancement of H<sub>2</sub>SO<sub>4</sub> formation rather than by stabilization of H<sub>2</sub>SO<sub>4</sub> clusters due to H<sub>2</sub>SO<sub>4</sub> ↔ organics interactions.

However, because the molecular composition of nucleating clusters was not measured, the role of any background substances, unavoidably present in any system, to experimental data remains unclear. More experimental work is needed before definite conclusions about the nucleation mechanisms in the atmosphere can be drawn.

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