Atmos. Chem. Phys. Discuss., 13, 16301–16335, 2013
www.atmos-chem-phys-discuss.net/13/16301/2013/
doi:10.5194/acpd-13-16301-2013

Atmospheric Chemistry and Physics Discussions

Enhancement of atmospheric H_2SO_4/H_2O nucleation: organic oxidation products versus amines

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Received: 10 April 2013 – Accepted: 20 May 2013 – Published: 18 June 2013

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

Abstract

Atmospheric H_2SO_4/H_2O 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 10^7–10^8 molecule cm^{-3} 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_2SO_4 formation starting from SO_2. The oxidant generation is inevitably associated with the formation of a series 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_2SO_4 concentrations higher than $\sim 10^7$ molecule cm^{-3}. A comparison of the results of two different particle counters (50 % cut-off size: about 1.5 nm or 2.5–3 nm) suggested that the early growth process of the nucleated particles was not significantly influenced by the organic oxidation products. An additional, H_2SO_4-independent process of particle (nano-CN) formation was observed in the case of α-pinene and limonene ozonolysis for H_2SO_4 concentrations smaller than $\sim 10^7$ molecule cm^{-3}. Furthermore, the findings confirm the existence of an additional oxidant for SO_2 beside OH radicals, very likely stabilized Criegee Intermediate (sCI). In the case of the ozonolysis of tetramethylethylene, the H_2SO_4 measurements in the absence and presence of an OH radical scavenger were well described by modelling using recently obtained kinetic data for the sCI reactivity in this system. A second set of experiments has been performed in the presence of added amines (trimethylamine, dimethylamine, aniline and pyridine) in the concentration range of a few 10^7–10^{10} molecule cm^{-3}. Here, photolytic OH radical generation was applied for H_2SO_4 production with no addition of other organics. All amines showed a significant nucleation enhancement with increasing efficiency in the order pyridine < aniline < dimethylamine < trimethylamine. This result supports the idea of

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H_2SO_4 cluster stabilization by amines due to strong $H_2SO_4 \leftrightarrow$ amine interactions. On the other hand, this study reveals that for organic oxidation products (in presence of the possible amine background as stated) a distinct H_2SO_4/H_2O nucleation enhancement can be due to increased H_2SO_4 formation caused by additional organic oxidant production (sCI) rather than by stabilization of H_2SO_4 clusters due to $H_2SO_4 \leftrightarrow$ 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. Also the experimental conditions do not cover fully the range of atmospheric observations, e.g., the concentration of precursor vapours represents rather the upper end of the atmospheric range. More experimental work is needed before definite conclusions about the nucleation mechanisms in the atmosphere can be drawn.

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_2SO_4 was ascertained to play a central role in this process (Weber at 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_2SO_4/H_2O (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_2SO_4/ H_2O 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). Amines are consistently identified to be more effective in the en-

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hancement of H_2SO_4/H_2O nucleation compared with ammonia for similar concentration levels. This fact can be explained by increasing interactions of the very strong acid (H_2SO_4) with atmospheric bases for increasing gas-phase basicity according to the proton affinity (base $+H^+ \rightarrow$ base-H^+); ammonia: 854 kJ mol^{-1} versus e.g. dimethylamine: 923 kJ mol^{-1} (Wikipedia, 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) $\times 10^8$ molecule cm^{-3} 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^{12} molecule cm^{-3} 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^{12} molecule cm^{-3} 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_2 capture using amines as the working fluid (Karl et al., 2009). On global scale, however, the annual emission rate of ammonia (55×10^6 tons N) exceeds clearly that for aliphatic amines (0.2×10^6 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 the lower efficiency regarding amines because of the 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_2SO_4) 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

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of a few % from gas-phase ozonolysis of α-pinene. Zhang et al. (2004) investigated the promotion of H_2SO_4/H_2O nucleation by a series of aromatic acids, like benzoic acid, *p*- and *m*-toluic acid. Relatively stable complexes, aromatic acid – H_2SO_4, 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) $\times 10^9$ molecule cm^{-3} of the aromatic acids to the reaction gas. These findings (Zhang et al., 2004) point probably to another nucleation enhancement governed by organic acid – H_2SO_4 interactions. It remains questionable, however, whether the organic acid–H_2SO_4 interactions via hydrogen bridge bonds can be competitive with the very strong H_2SO_4–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.

In this study, H_2SO_4/H_2O nucleation has been investigated either in the presence of organic oxidation products form α-pinene, limonene and other olefins or in the presence of atmospherically relevant amines. The aim of this work is to investigate the possible role of these substances in the process of atmospheric nucleation for close to atmospheric conditions. In order to enhance possible effects, elevated reactant concentrations have been used as well. The results of the ozonolysis experiments originate from the 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.

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2 Experimental

The experimental setup used is 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 ± 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_2 from a calibration gas mixture and $O_3$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_3using a gas monitor (Thermo Environmental Instruments 49C), and SO_2 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_3^-) as the reagent ion. The reagent ions were generated by nitric acid and a ^{241}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 a.m.u (HSO_4^-) and the reagent ion at mass 62 a.m.u (NO_3^-) multiplied by the setup dependent calibration factor. The calibration factor was determined by photolysis of water vapor 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 $^{34}SO_2$ into labeled sulfuric acid yielding finally after ionization ($H^{34}SO_4^-$). The nominal detection limit of the CI-MS instrument is 5×10^4 molecule cm^{-3} for a 5 min integration period.

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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 to 15 $L min^{-1}$ (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 $L min^{-1}$ (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_2O and CO_2 in total. The water needed for the gas humidifier was taken from an ultrapure water system (Barnstead, resistivity: 17.4 MΩ cm). The Hydrogen 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. The individual olefins and amines diluted with the carrier gas were supplied by a gas metering unit and SO_2 was taken from a 1 ppmv or 10 ppmv calibration mixture in N_2 (Messer).

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_2SO_4 was formed via the reaction of OH radicals with SO_2 using ozone photolysis at a relative humidity of 13 or 25 % for OH radical generation. Ini-

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tial ozone concentrations were in the range of (7.3–7.7) $\times 10^{11}$ molecule cm^{-3} and H_2 (8.2×10^{15} molecule cm^{-3}) was taken to adjust the OH radical concentration needed in the tube to produce an average H_2SO_4 concentration of $\sim 2 \times 10^8$ molecule cm^{-3}. 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_2SO_4 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_2 oxidation processes in this system.

3.1 Simple Mechanism

O_3	+	olefin	$\rightarrow$	yOH + other	(1)
OH	+	olefin	$\rightarrow$	products	(2)
OH	+	H_2	$\rightarrow$	products	(3)
OH	+	SO_2	$\rightarrow$	$\ldots \rightarrow H_2SO_4$	(4)
H_2SO_4			$\rightarrow$	wall	(5)

The needed rate coefficients k_1–k_4 were taken from the literature (unit: cm^3 molecule^{-1} s^{-1}; TME: tetramethylethylene; MCM: 1-methyl-cyclohexene): $k_{1,\mathrm{TME}} = 1.0 \times 10^{-15}$ (Witter et al., 2002); $k_{1,\mathrm{MCH}} = 1.65 \times 10^{-16}$ (Treacy et al., 1997); $k_{1,\alpha\text{-pinene}} = 1.1 \times 10^{-16}$ and $k_{1,\mathrm{limonene}} = 2.5 \times 10^{-16}$ (Witter et al., 2002); $k_{2,\mathrm{TME}} = 1.1 \times 10^{-10}$ (Atkinson, 1986); $k_{2,\mathrm{MCH}} = 9.6 \times 10^{-11}$ (Darnall et al., 1976); $k_{2,\alpha\text{-pinene}} = 5.3 \times 10^{-11}$ (Atkinson, 1986); $k_{2,\mathrm{limonene}} = 1.6 \times 10^{-10}$ (Atkinson et al., 1986); $k_3 = 6.7 \times 10^{-15}$ (DeMore

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et al., 1997) and $k_4 = 1.2 \times 10^{-12}$ (Zellner, 1978). A diffusion controlled process is assumed for the H_2SO_4 wall loss in the flow tube, $k_5 = 3.65 \cdot D(H_2SO_4)/r^2$. The diffusion coefficient $D(H_2SO_4) = 0.075\,cm^2\,s^{-1}$ 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 et al., 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 the recent experimental work from our laboratory, was used for the modelling of simultaneous SO_2 oxidation by OH radicals and the stabilized Criegee Intermediate (sCI), $(CH_3)_2COO$, (Berndt et al., 2012). Pathways (3)–(5) are identical to those given above.

O_3	+	TME	$\rightarrow$	$0.30 \cdot OH$	+	$0.62 \cdot sCI$	+	other	(1, TME)
OH	+	TME	$\rightarrow$	products					(2, TME)
sCI			$\rightarrow$	OH + other					(6)
sCI	+	SO_2	$\rightarrow$	$\ldots \rightarrow H_2SO_4$					(7)

The measured sCI yield of 0.62 at 1 bar air (Berndt et al., 2012) is in a 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

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et al., 2006) for long reaction times in the 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 ± 0.04 from experiments and 0.40 as a result of theoretical calculations. The rate coefficient k_6 is set to 3.0 s^{-1} as recently observed as the total sCI loss rate coefficient (k_{loss}) at a pressure of 1 bar of synthetic air at 293 ± 0.5 K and a relative humidity of 50 % (Berndt et al., 2012). The water-reaction term in the measured k_{loss}, $k_{loss} = k_{dec} + k(sCI + H_2O) \times [H_2O]$, is of less importance due to the very low rate coefficient $k(sCI + H_2O)$ in the order of a few 10^{-19} cm^3 $molecule^{-1}$ s^{-1} (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^3 $molecule^{-1}$ s^{-1} was also taken from our recent kinetic experiment.

4 Results and discussion

4.1 Ozonolyis of olefins without SO_2 addition

First, experiments in the absence of added SO_2 have been performed in order to investigate possible particle formation by the oxidation products of the olefins without relevant H_2SO_4 production. Measured H_2SO_4 concentrations were below 10^6 molecule cm^{-3}. The initial concentrations of α-pinene and limonene varied from close to atmospheric peak concentrations of about (1–3) $\times 10^{10}$ molecule cm^{-3} to 4.4×10^{11} molecule cm^{-3} using nearly constant ozone concentrations of (5.7–6.3) $\times 10^{11}$ molecule cm^{-3}. 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 the PHA-UCPC measurements of about 10 particles or activated "nano-CN" per cm^3 (McMurry et al., 2011) were observed for close to atmospheric peak concentrations of α-pinene and limonene. The signals showed a strong increase with increasing con-

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centration of reacted terpene, see Fig. 1. On the other hand, for a constant amount of reacted terpene, the signal was independent of H_2SO_4 in a wide range of acid concentrations ([H_2SO_4] smaller than $\sim 10^7$ molecule cm^{-3}) as shown later. This fact apparently suggests that H_2SO_4 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 of particle growth). For a more detailed explanation see Lehtipalo et al. (2011). 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). Similar signals from PHA-UCPC measurements were observed during measurements in the nocturnal boreal forest in Hyytiälä (Lehtipalo et al., 2011).

In our experiment, M-CPC measurements in the case of α-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_2SO_4 particles with diameters down to ~ 1.5 nm (Sipilä et al., 2010; Berndt et al., 2010).

4.2 Ozonolyis of olefins in the presence of added SO_2

Figure 2 shows the raw data from PHA-UCPC particle measurements as a function of the detected H_2SO_4 concentration for six measurement series using constant ozonolysis conditions (constant organic product formation) with varying of SO_2. The H_2SO_4 concentrations have been measured at the IfT-LFT outlet and represent the average steady-state concentration within the flow tube. H_2SO_4 is produced from the oxidation of SO_2 by OH radicals, and most likely by stabilized Criegee Intermediates (sCI), in

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the presence of water vapour. Both oxidants, OH radicals and sCI, are formed in the course of the ozonolysis reaction. Data in the absence of added SO_2 are also shown for the measurements with α-pinene and limonene. The data given in Fig. 2 suggest two different processes driving the particle (nano-CN) formation: (i) for [H_2SO_4] smaller than $\sim 10^7$ molecule cm^{-3}, a H_2SO_4-independent process governed by the products of the ozonolysis reaction as described in the section before, and (ii) a H_2SO_4-dominated process for H_2SO_4 concentration higher than $\sim 10^7$ molecule cm^{-3}. The latter seems to be independent of the chemical nature of the organic oxidation products (products from an acyclic C_6-olefin or cyclic C_7 or C_{10} olefins), as well as 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^{10} molecule cm^{-3} and were enlarged for TME and MCH by a factor of 50 or 10, respectively. Only a small fraction of the olefin, $\sim$ (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 $\sim$ (4–9) $\times 10^8$ molecule cm^{-3} 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_2SO_4] higher than $\sim 10^7$ molecule cm^{-3}. The small differences amongst the various series could be due to the 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) $\times 10^9$ molecule cm^{-3}. In our experiments, the organic acids arising from the terpenes reached only concentrations of a few 10^7 molecule cm^{-3}, according to their formation yields 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 experiment. Furthermore, the results of our study for close to atmospheric conditions do not support the findings by

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Metzger et al. (2010) stating that any organic oxidation products are needed for atmospheric H_2SO_4/H_2O nucleation. On the contrary, the observed nucleation process was rather caused by the strong $H_2SO_4 \leftrightarrow$ amine interactions for background amine concentration in the carrier gas in the order of 10^7–10^8 molecule cm^{-3}. 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_2 (increase of organic oxidation products) or conducting the reaction also in the presence of an OH radical scavenger (H_2), cf. Table 1. The detected H_2SO_4 concentration was identified as the most dominate parameter for particle formation under all circumstances, even in the experiments with the highest terpene concentrations of up to 4.4×10^{11} molecule cm^{-3} (total product concentrations from ozonolysis of a few 10^9 molecule cm^{-3}). In Fig. 3 all results of detection efficiency corrected PHA-CPC and TSI 3025 measurements for [H_2SO_4] higher than $\sim 10^7$ molecule cm^{-3} 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 the 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_2SO_4 profiles within the flow tube caused by the different approaches of SO_2 oxidant formation. The comparison of the results from the PHA-CPC (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-CPC and the TSI 3025 start to merge for H_2SO_4 concentrations higher than 10^8 molecule cm^{-3}. A rough estimate yields a particle growth by pure H_2SO_4 in the flow

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tube of about 0.4–0.6 nm assuming $[H_2SO_4] = (2–3) \times 10^8$ molecule cm^{-3}, an average growth time of 50 s, and a growth rate of 4×10^{-11} cm^3 molecule^{-1} nm s^{-1} (Lehtinen and Kulmala, 2003). This means that H_2SO_4 accounted only for roughly half of the growth in our experiment. Possible other substances, involved in the early growth are probably the amines from the carrier gas background impurities, water vapour and the H_2SO_4 (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 ruled out. Supposing a substantial contribution of organic oxidation products, a growth process with immediate saturation behaviour independent of the kind and the concentration of the parent olefins has to be assumed in order to explain our experimental observations. This scenario is highly speculative at the moment. However, a contribution of amines in the growth process would be 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_2SO_4 formation (other than via OH + SO_2)

In the course of the experiments, also three measurement series have been conducted in the presence of high H_2 concentrations for effective OH radical scavenging. The measured H_2SO_4 concentrations were clearly higher than expected from the reaction of residual OH radicals with SO_2. This fact can be explained by additional oxidation of SO_2 by organic ozonolysis products, very likely by stabilized Criegee Intermediates (sCI). Recently, we discovered the atmospheric relevance of this pathway (Mauldin et al., 2012). Figure 4 shows the results of H_2SO_4 formation from TME ozonolysis in the presence and absence of H_2. 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_2 (open circles), and for both, OH radicals and sCI as oxidants for SO_2 (open stars), are given. The used chemical schemes including the kinetic pa-

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rameters are described in Sect. 3.1 and 3.2. The comparison of measured H_2SO_4 concentrations with modelling results considering only OH radicals as the SO_2 oxidant shows clearly that an additional pathway for SO_2 oxidations has to exist. A very good agreement between measurement and modelling is achieved assuming additional SO_2 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_2OO) towards SO_2 than incorporated in our modelling. Using simply this higher rate coefficient in the calculations, $k_7 = 3.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, the modelling results overestimated the measured H_2SO_4 concentrations by a factor of up to 35. However, for a given ratio k_6/k_7, the calculated H_2SO_4 concentrations for the chosen conditions are very sensitive regarding this ratio, and less sensitive regarding the absolute values of the individual rate coefficients k_6 and k_7. As a result of our kinetic measurements $k_6/k_7 = 3.9 \times 10^{12}$ molecule cm^{-3} and $k_6 = 3.0$ s^{-1} have been determined (Berndt et al., 2012). The rate coefficient k_6 is identical with k_{loss} for a negligible sCI + water reaction. Assuming again $k_7 = 3.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Welz et al., 2012), $k_6 = 152$ s^{-1} follows in order to retain $k_6/k_7 = 3.9 \times 10^{12}$ molecule cm^{-3} as needed for an appropriate description of the measurements, see Fig. 4. Kroll et al. (2001) stated for acetone oxide, $(CH_3)_2COO$, $k_6 = 6.4 \pm 0.9$ s^{-1} from time-dependent measurements at 100 Torr and $k_6 = 3.5$ s^{-1} resulting from theoretical considerations. These data for k_6 are in reasonable agreement with our $k_6 = 3.0$ s^{-1}, supporting also the lower value $k_7 = 7.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the reaction of sCI with SO_2. 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_2, the measurements show clearly that, in addition to the SO_2 oxidation by OH radicals, another process forming H_2SO_4 from SO_2, exists. The additional H_2SO_4 formation step (most likely by sCI) can account for a substantial fraction of the total H_2SO_4 production in the atmosphere, cf. Mauldin et al. (2012). Thus, products of olefin ozonolysis (sCI) can support atmospheric nucleation in terms of an enhancement in

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H_2SO_4 formation. The results of this study suggest that this indirect nucleation promoting effect via amplified H_2SO_4 formation outbalances probably any direct participation of organic oxidation products in the H_2SO_4/ H_2O nucleation process.

4.4 Experiments with amine additions

The measurements with amine additions were conducted with a total gas flow of 30 L min^{-1} (STP) resulting in a relatively short residence time of 32 s in the irradiated IfT-LFT middle section. For these flow conditions, after a waiting time of about 1 h (to equilibrate gas and walls) the measured NH_3 concentrations at the flow-tube inlet and the outlet were found to be nearly identical (Berndt et al., 2010). A similar behaviour was also expected in the experiments with amine additions. Here, no reliable measurement technique for amine concentrations in the considered range (a few 10^7–10^{10} molecule cm^{-3}) was available. The stated amine concentrations are those at the flow-tube entrance as provided by a gas metering unit after further dilution with the carrier gas. In each experiment, after switching on the diluted amine flow, it took about 1 h or more, before stable particle numbers were measureable, similar to the behaviour observed in the former study with NH_3. 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 entrance amine 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 $[H_2SO_4] = 2 \times 10^8$ molecule cm^{-3}.

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Measurements without amine addition are given at the x-axis at 10^7 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 H_2SO_4/H_2O nucleation (Berndt et al., 2010; Erupe et al., 2011; Zollner et al., 2012). Some kind of saturation behaviour for the number of formed particles can be seen at a relative humidity of 13 % for dimethylamine concentrations $\geq 5 \times 10^9$ 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 $\geq$ ca.1.5 nm were measured with a diethyleneglycol flow of 0.5 L min^{-1} and for particles with a diameter $\geq$ 2.0–2.5 nm a flow of 0.2 L min^{-1} was taken (Vanhanen et al., 2011). The comparison of the PSM measurements for 1.5 nm particles (diameter $\geq$ ca.1.5 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 1.1×10^9 molecule cm^{-3}. The distribution at RH = 25 % showed no rise with increasing diethyleneglycol flow for flow rates $\geq$ 0.5 L min^{-1}. At RH = 13 %, for higher diethyleneglycol flows of around 1.0 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 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 the increasing water vapour content as mentioned before.

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The results for nucleation enhancement by trimethylamine, dimethylamine, aniline and pyridine detected at RH = 13 % and for $[H_2SO_4] = 2 \times 10^8$ molecule cm^{-3} are depicted in Fig. 7 (PSM measurements for a diameter ≥ 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 upper limits. 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 $+H^+ \rightarrow$ base-H^+) characterizes the strength of the $H_2SO_4 \leftrightarrow$ amine interactions. The corresponding values of the proton affinity are (unit: kJ mol^{-1}); trimethylamine: 942, dimethylamine: 923, aniline: 877, pyridine: 924 (Wikipedia, 2012). Decreasing enhancement factors, in the order trimethylamine, dimethylamine and aniline, can be explained by the decreasing proton affinity and subsequently by lowering of the $H_2SO_4 \leftrightarrow$ 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 in the nucleation process beside the thermodynamic features. 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_2SO_4/H_2O nucleation.

Zollner at al. (2012) observed for a methylamine addition with a mixing ratio of 3 pptv (7.4×10^7 molecule cm^{-3}), and a H_2SO_4 concentration of $\sim 3 \times 10^9$ molecule cm^{-3}, an enhancement factor of 2×10^4, 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 at 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 amine additions, an amine or base background equivalent to 10^7 molecule cm^{-3} of trimethy-

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lamine or 10^8 molecule cm^{-3} of aniline can be assumed. In performed model calculations, a background concentration of 10^7–10^8 molecule cm^{-3} dimethylamine was needed for explaining the measured H_2SO_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 H_2SO_4/H_2O nucleation enhancement by amines with concentrations similar those found in the atmosphere, e.g. (1–18) $\times 10^8$ molecule cm^{-3}, as measured for methylamine, dimethylamine, trimethylamine and diethylamine in total (Grönberg et al., 1992). The strong $H_2SO_4 \leftrightarrow$ amine (acid $\leftrightarrow$ base) interactions seem to be more effective for the process of new particle formation than any $H_2SO_4 \leftrightarrow$ organics interactions.

5 Summary

H_2SO_4/ H_2O nucleation influencing effects were 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 and a bulk residence time of 94 or 32 s.

The first set of experiments was performed in the presence of organic oxidation products arising from the ozonolysis of olefins (tetramethylethylene, 1-methyl-cyclohexene, α-pinene and limonene) for close to atmospheric concentrations. Ozonolysis served also as the source of OH radicals and possibly other oxidants initiating H_2SO_4 formation starting from 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 $[H_2SO_4]$ higher than $\sim 10^7$ 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

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to atmospheric reactant concentrations was not significantly influenced by the organic oxidation products under our conditions (background amine concentration of the order of 10^7–10^8 molecules cm^{-3}). A rough estimate yields a particle growth by pure H_2SO_4 of about 0.4–0.6 nm for a growth time of 50 s ($[H_2SO_4] = (2–3) \times 10^8$ 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 H_2SO_4 (amine) dimers or larger clusters. A possible contribution of any organic oxidation products, however, cannot be totally ruled out.

For H_2SO_4 concentrations smaller than $\sim 10^7$ molecule cm^{-3}, an additional, H_2SO_4-independent process of particle (nano-CN) formation was observed in the case of the ozonolysis of α-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 existence of an additional oxidant for SO_2 beside the OH radicals, very likely stabilized Criegee Intermediates (sCI), has been confirmed. In the case of the ozonolysis of TME, the H_2SO_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 10^7–10^{10} molecule cm^{-3} using photolytic OH radical generation for the formation of H_2SO_4. 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 $H_2SO_4 \leftrightarrow$ 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 pos-

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sible amine or base background equivalent to 10^7 molecule cm^{-3} of trimethylamine or 10^8 molecule cm^{-3} of aniline.

The results of this study support the strong H_2SO_4/H_2O nucleation enhancement by amines, at least in presence of amines in the concentration range of few 10^7 molecule cm^{-3} or above. The strong $H_2SO_4 \leftrightarrow$ amine (acid $\leftrightarrow$ base) interactions appear to be much more effective for the process of new particle formation than any $H_2SO_4 \leftrightarrow$ organics interactions. The additional H_2SO_4 formation step (most likely via sCI) can account for a substantial fraction of the total H_2SO_4 production in the atmosphere, cf. Mauldin et al. (2012). Thus, products of olefin ozonolysis (sCI) could possibly support atmospheric nucleation in terms of an enhancement of H_2SO_4 formation rather than by stabilization of H_2SO_4 clusters due to $H_2SO_4 \leftrightarrow$ organics interactions. Nevertheless, further work is required before the definite conclusions about the nucleation mechanisms in the atmosphere can be drawn.

Acknowledgements. The authors thank K. Pielok, Th. Conrath and A. Rohmer for technical assistance. This work has been funded by the European Research Council Project No. 227463-ATMNUCLE. The support from the Academy of Finland Centre of Excellence program and related projects (Nos. 1118615 and 1127372) is also gratefully acknowledged. Financial support in part by EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interactions) No 036833-2 is acknowledged.

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

		O_3 (molecule cm^{-3})	olefin (molecule cm^{-3})	SO_2 (molecule cm^{-3})	H_2 (molecule cm^{-3})
1	TME varied, SO_2 fix	6.1×10^{11}	$(1.25–75) \times 10^{10}$	3.07×10^{10}	–
2	TME varied, SO_2 fix, H_2	6.08×10^{11}	$(1.5–75) \times 10^{10}$	3.07×10^{10}	1.6×10^{17}
3	TME (high) fix, SO_2 varied	6.08×10^{11}	7.5×10^{11}	$(4.6–62) \times 10^{9}$	–
4	TME (low) fix, SO_2 varied	6.08×10^{11}	1.5×10^{10}	$(3.8–17) \times 10^{10}$	–
5	MCH varied, SO_2 fix	6.03×10^{11}	$(6.0–40) \times 10^{10}$	5.37×10^{11}	–
6	MCH (high) fix, SO_2 varied	6.11×10^{11}	4.0×10^{11}	$(1.8–18) \times 10^{11}$	–
7	MCH (low) fix, SO_2 varied	6.03×10^{11}	4.0×10^{10}	$(7.2–18) \times 10^{11}$	–
8	limonene varied, no SO_2	6.1×10^{11}	$(9.7–440) \times 10^{9}$	–	–
9	limonene varied, SO_2 fix	6.08×10^{11}	$(2.8–28) \times 10^{10}$	3.6×10^{11}	–
10	limonene varied, SO_2 fix, H_2	6.3×10^{11}	$(6.0–44) \times 10^{10}$	3.6×10^{11}	2.4×10^{17}
11	limonene fix, SO_2 varied	6.3×10^{11}	6.0×10^{10}	$(3.6–18) \times 10^{11}$	–
12	α-pinene varied, no SO_2	$(5.7–6.3) \times 10^{11}$	$(2.8–44) \times 10^{10}$	–	–
13	α-pinene varied, SO_2 fix	6.3×10^{11}	$(8.0–44) \times 10^{10}$	3.6×10^{11}	–
14	α-pinene varied, SO_2 fix, H_2	6.3×10^{11}	$(1.6–4.4) \times 10^{11}$	3.6×10^{11}	2.4×10^{17}
15	α-pinene fix, SO_2 varied	6.3×10^{11}	4.0×10^{10}	$(2.7–18) \times 10^{11}$	–

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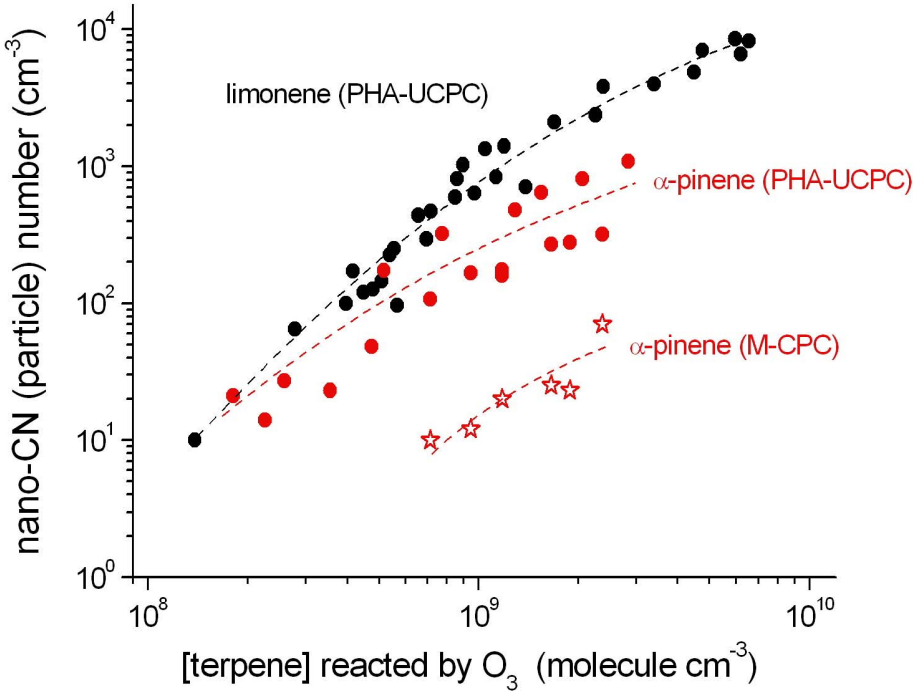

Fig. 1. Measured particle numbers (PHA-UCPC and M-CPC) as a function of converted terpene by the ozone reaction. The H_2SO_4 concentrations were below 10^6 molecule cm^{-3}. The reactant concentrations are given in Table 1, measurement series 9 and 12.

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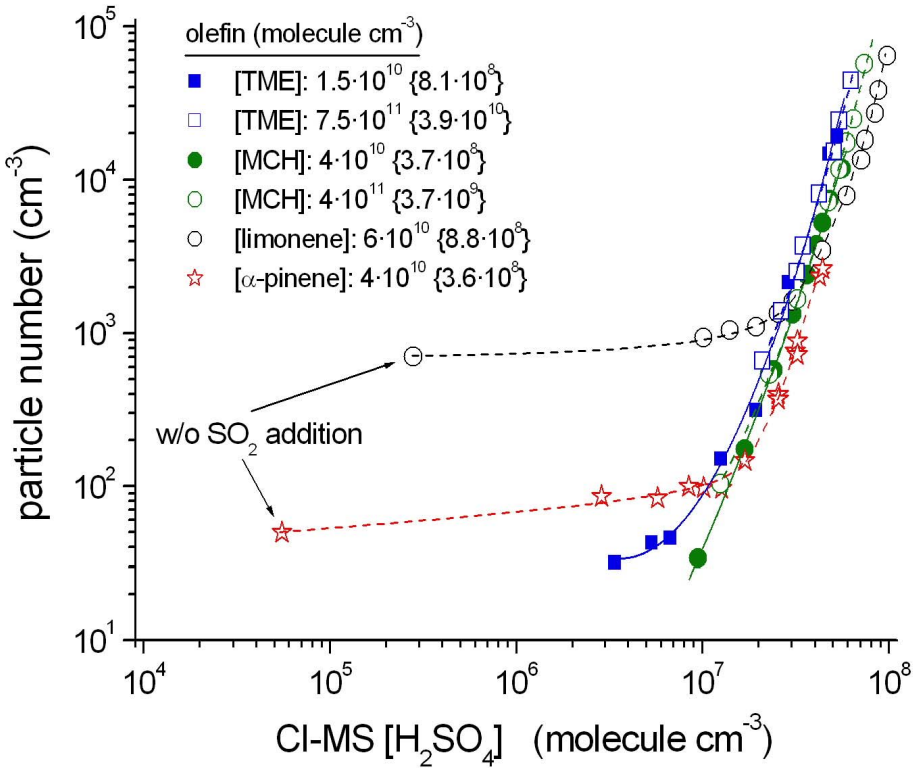

Fig. 2. Raw particle numbers from PHA-UCPC measurements in dependence on measured H_2SO_4 concentration by variation of SO_2 for constant ozonolysis conditions. Initial olefin concentrations are given along with the converted olefin by ozone (in brackets), measurement series 3, 4, 6, 7, 11 and 15, cf. Table 1. The data for very low H_2SO_4 concentrations ($< 10^6$ molecule cm^{-3}) were obtained without SO_2 addition.

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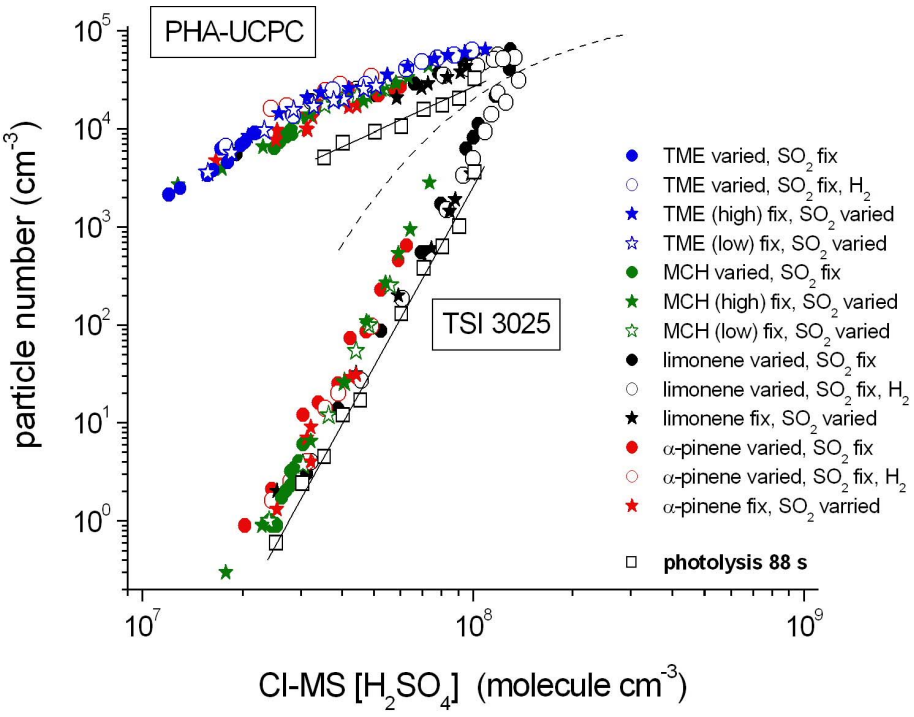

Fig. 3. Measurements of the particle numbers by PHA-UCPC (corrected) and TSI 3025 as a function of the H_2SO_4 concentration. The reactant concentrations are given in Table 1, measurement series 1–7, 9–11 and 13–15. Data from ozone photolysis experiments in the absence of added organics are shown for comparison.

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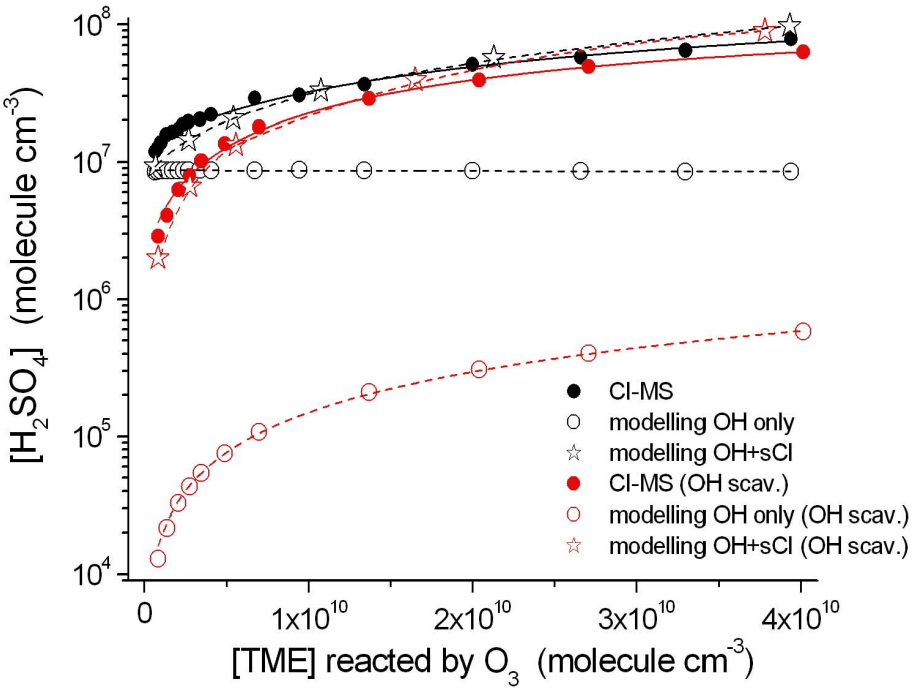

Fig. 4. Measured H_2SO_4 concentrations from TME ozonolysis experiments as a function of reacted TME by ozone in the presence (full circles, red) and absence (full circles, black) of H_2 as an OH radical scavenger. Reactant concentrations are given in Table 1, measurement series 1 and 2. The measurements are compared with modelling results considering only OH radicals as the oxidant for SO_2 (open circles) or for OH radicals and sCI as oxidants for SO_2 (open stars).

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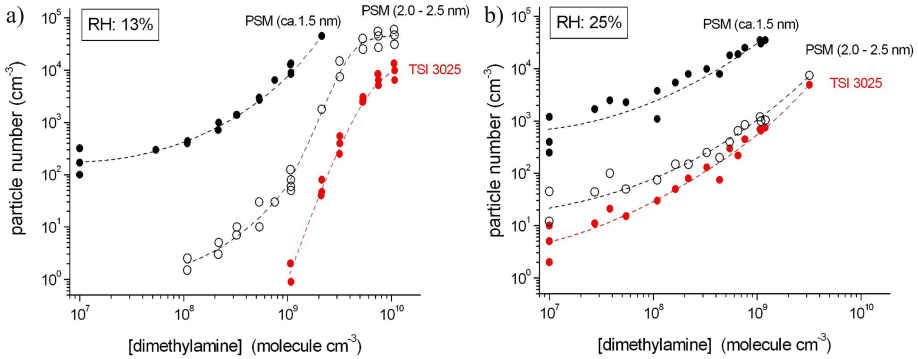

Fig. 5. (a, b): Particle numbers as a function of added dimethylamine concentration at a relative humidity of 13 % **(a)** and 25 % **(b)**, $[H_2SO_4] = 2 \times 10^8$ molecule cm^{-3}. Measurements have been done by PSM with a diethyleneglycol flow of 0.5 L min^{-1} (50 % cut-off size: about 1.5 nm), a diethyleneglycol flow of 0.2 L min^{-1} (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 10^7 molecule cm^{-3}.

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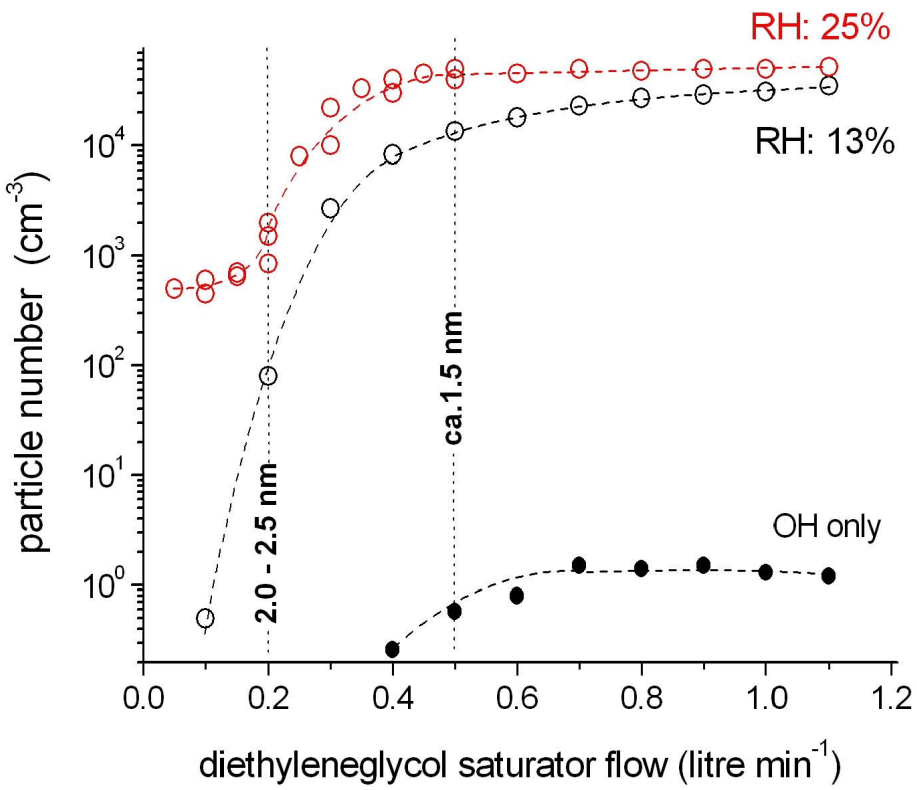

Fig. 6. Cumulative size distributions from PSM measurements (by scanning the diethyleneglycol flow) for a dimethylamine concentration of 1.1×10^9 molecule cm^{-3} at a relative humidity of 13 and 25 %. The data for "OH only" have been obtained under conditions with OH radical formation in the absence of added amine and SO_2 representing a background measurement. Dotted lines show the diethyleneglycol flow settings as used in the measurements for particles with a diameter ≥ ca. 1.5 nm or particles with a diameter ≥ 2.0–2.5 nm.

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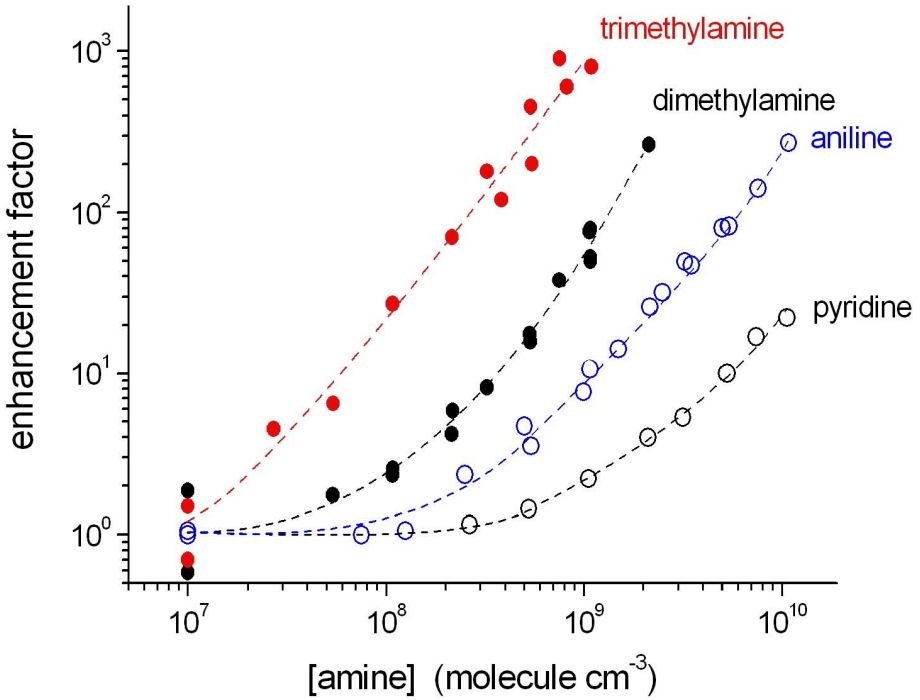

Fig. 7. Enhancement factors, $N_{\text{amine added}}/N_{\text{w/o amine addition}}$, for trimethylamine, dimethylamine, aniline and pyridine detected at RH = 13 % for $[H_2SO_4] = 2 \times 10^8$ molecule cm^{-3}, PSM measurements for a diameter ≥ ca.1.5 nm.

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