

# Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of $\alpha$ -pinene

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Received: 17 December 2009 – Published in Atmos. Chem. Phys. Discuss.: 5 February 2010

Revised: 28 June 2010 – Accepted: 12 July 2010 – Published: 3 August 2010

**Abstract.** The ozonolysis of  $\alpha$ -pinene has been investigated under dry and humid conditions in the temperature range of 243–303 K. The results provided new insight into the role of water and temperature in the degradation mechanism of  $\alpha$ -pinene and in the formation of secondary organic aerosols (SOA). The SOA yields were higher at humid conditions than at dry conditions. The water induced gain was largest for the lowest temperatures investigated (243 and 253 K). The increase in the SOA yields was dominated by water (and temperature) effects on the organic product distribution, whilst physical uptake of water was negligible. This will be demonstrated for the example of pinonaldehyde (PA) which was formed as a major product in the humid experiments with total molar yields of  $0.30 \pm 0.06$  at 303 K and  $0.15 \pm 0.03$  at 243 K. In the dry experiments the molar yields of PA were only  $0.07 \pm 0.02$  at 303 K and  $0.02 \pm 0.02$  at 253 K. The observed partitioning of PA as a function of the SOA mass present at 303 K limited the effective vapour pressure of pure PA  $p_{\text{PA}}^0$  to the range of 0.01–0.001 Pa, 3–4 orders of magnitude lower than literature values. The corresponding mass partitioning coefficient was determined to  $K_{\text{PA}} = 0.005 \pm 0.004 \text{ m}^3 \mu\text{g}^{-1}$  and the total mass yield  $\alpha_{\text{PA total}} = 0.37 \pm 0.08$ . At 303 K PA preferably stayed in the gas-phase, whereas at 253 K and 243 K it exclusively partitioned into the particulate phase. PA could thus account at

least for half of the water induced gain in SOA mass at 253 K. The corresponding effect was negligible at 303 K because the PA preferably remained in the gas-phase.

The yield of OH radicals, which were produced in the ozonolysis, was indirectly determined by means of the yield of cyclohexanone formed in the reaction of OH radicals with cyclohexane. OH yields of the  $\alpha$ -pinene ozonolysis were determined to  $0.67 \pm 0.17$  for humid and  $0.54 \pm 0.13$  for dry conditions at 303 K, indicating a water dependent path of OH radical formation. For 253 and 243 K OH yields could be estimated to 0.5 with no significant difference between the dry and humid experiments. This is the first clear indication for OH radical formation by  $\alpha$ -pinene ozonolysis at such low temperatures.

## 1 Introduction

Ozonolysis of large unsaturated compounds, such as monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ) has been and still is of concern when it comes to formation of atmospheric secondary organic aerosols (SOA) (Hallquist et al., 2009; Kanakidou et al., 2005; Went, 1960). In addition, gas-phase chemistry of alkenes in general and monoterpenes in particular have been the subject of several studies as has been summarized previously (Atkinson and Arey, 2003; Calvert et al., 2000). From previous studies it is now obvious that the topic of ozonolysis of terpenes has several aspects that merit further



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investigation (Donahue et al., 2005; Kanakidou et al., 2005). In this respect both the gas and the particle phase have to be considered for acquiring more firm conclusions on the chemical degradation mechanism for monoterpenes (Jenkin, 2004). The environmental concerns related to particles are today focused on climate and health issues (Pöschl, 2005). Regarding climate, the Earth radiation budget is influenced directly, by particle light scattering and absorption, and indirectly by cloud formation interactions e.g. IPCC (2007). The health effect of particles has been known for long but is complex and can depend on particle size and composition e.g. Brunekreef and Forsberg (2005); Schwarze et al. (2006); Sioutas et al. (2005). In addition to the particulate phase the environmental effects of the products remaining in the gas phase are responsible for enhanced ground level ozone formation and the production of noxious organic compounds, such as organic peroxides and nitrates (Wayne, 1991). For future projections, the magnitude of all these effects and their interactions will depend on climate variables such as temperature, relative humidity and mixing state of the atmosphere that are all predicted to change in the future, e.g. Liao et al. (2006). In the present study the focus is to explore the temperature and humidity dependences of the ozonolysis of one of the most abundant monoterpenes, i.e.  $\alpha$ -pinene.

In the degradation of unsaturated compounds by ozone, water has been suggested to influence both gas and particle phase composition and distributions e.g. Bonn et al. (2002); Jonsson et al. (2006); Ma et al. (2007); von Hessberg et al. (2009); Wegener et al. (2007). One of the identified major products from  $\alpha$ -pinene oxidation is pinonaldehyde. This compound has been identified both in laboratory studies and in field measurements e.g. Calogirou et al. (1999); Hatakeyama et al. (1989); Kavouras et al. (1998); Pio et al. (2001); Yokouchi and Ambe (1985); Yu et al. (1999b). It is a semivolatile compound with sufficient vapour pressure to be present mostly in the gas phase at room temperature, but at low temperatures it can contribute to the condensed phase (Cahill et al., 2006; Hallquist et al., 1997; Plewka et al., 2006). The mechanism forming pinonaldehyde from the ozonolysis of  $\alpha$ -pinene is still under discussion (Johnson and Marston, 2008). Pinonaldehyde has been detected under dry and humid reaction conditions. The reaction of the stabilized Criegee Intermediate (SCI) with water (reaction Scheme 1) has been suggested to yield pinonaldehyde under humid conditions (Alvarado et al., 1998).

However, previous studies have presented positive, negative and neutral dependence of pinonaldehyde production on water concentration (Baker et al., 2001; Berndt et al., 2003; Bonn et al., 2002; Warscheid and Hoffmann, 2001). These discrepancies may be explained by experimental conditions and will be discussed later with respect to the results presented here. Another product channel from the water reaction with one of the two possible SCI, is giving pinonic acid and water. Ma et al. (2007) showed a water dependence on pinonic acid where the water effect disappears upon

addition of acetic acid acting as an effective SCI scavenger (Ma et al., 2007). This is in line with a water dependent route for pinonaldehyde since the water reaction is suggested to give either pinonaldehyde and  $\text{H}_2\text{O}_2$  or pinonic acid and  $\text{H}_2\text{O}$ . Another issue in water dependent routes from the oxidation of unsaturated compounds is the production of OH radicals from the ozonolysis. The yield of OH radicals can be large and previous studies have reported yields between 0.68–0.91 for  $\alpha$ -pinene (Atkinson and Arey, 2003; Berndt et al., 2003). For the OH production two possible reaction pathways have received attention in the literature (Anglada et al., 2002; Hasson et al., 2003; Zhang and Zhang, 2005). One is the production directly from rearrangement and decomposition of the excited CI, while the other is the water reaction with SCI producing hydroxy hydroperoxides that subsequently decompose, yielding OH radicals.

The production route to OH via excited CI should not depend on water in contrast to the production from the hydroxy hydroperoxide. For the ozonolysis of terpenes, previous experiments show that there is no water dependence regarding the OH yields (Aschmann et al., 2002; Atkinson et al., 1992; Berndt et al., 2003). However, if all OH would be produced from the non water dependent channel, via the excited CI, the water dependent channels yielding pinonaldehyde and pinonic acid would be limited to less than 0.32 to 0.09, depending on reported yields of OH. It should be noted that there is some indication that not all OH is produced directly from the ozonolysis but from secondary chemistry, such as any produced  $\text{HO}_2$  reacting with available  $\text{O}_3$  e.g. Atkinson et al. (2004); Jenkin 2004). In addition, the water dependent OH production was reinvestigated for small alkenes and in that study, a positive dependence on OH formation was obtained (Wegener et al., 2007). When it comes to aerosol production Jonsson et al. (2006) revised the water dependence on SOA formation from selected terpenes, which illustrates its complex dependence on experimental conditions (Jonsson et al., 2006). In addition, the aerosol formation and its water dependence is coupled to details in the radical chemistry, e.g. the OH radical yield (Jonsson et al., 2008b).

Another key issue, in addition to water dependence in the ozonolysis of terpenes, is the temperature dependence (Heald et al., 2008). At low temperatures, the partitioning of semivolatile compounds and the chemical degradation will be different compared to room temperatures both influencing SOA formation. So far the number of temperature dependent studies is limited (Jonsson et al., 2008a; Pathak et al., 2007; Saathoff et al., 2009; von Hessberg et al., 2009) and most information is from studies close to room temperature (Berndt et al., 2003; Cocker et al., 2001; Griffin et al., 1999; Hoffmann et al., 1997; Hoppel et al., 2001; Iinuma et al., 2004; Johnson and Marston, 2008; Northcross and Jang, 2007; Presto and Donahue, 2006; Shilling et al., 2008). For  $\alpha$ -pinene, Pathak et al. (2007) presented a temperature dependence of the aerosol mass fraction AMF (i.e. a yield) in the range 273–313 K. They determined the AMF

at a reference temperature (288 K) and ramped it to higher temperatures in order to distinguish between changes in the degradation mechanism and partitioning. The partitioning increased with decreasing temperature as expected. However, the overall temperature dependence of the AMF between 288 K and 313 K was more or less neutral. This implies that the negative dependence of the partitioning on the temperature is counteracted by a positive dependence of the chemical mechanism. Obviously, in that temperature range the formation of less volatile products is favoured which enhance the AMF. Between 273 K and 288 K they reported increasing AMF with decreasing temperature.

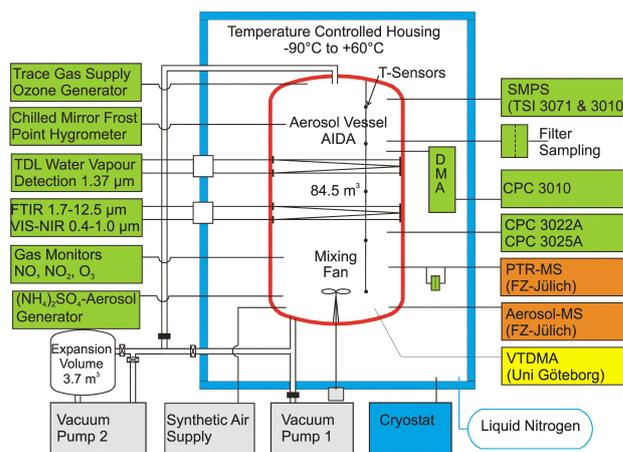
The results presented in this paper were obtained in a number of experiments using the AIDA simulation chamber dedicated to low temperature. A summary of all measurements and the temperature dependence of the SOA yields from the ozonolysis of  $\alpha$ -pinene and limonene are described by Saathoff et al. (2009). That paper also provides parameters specifically useful for aerosol yield calculations in atmospheric models. The temperature dependence on the kinetics of  $\alpha$ -pinene with ozone and the volatility of produced SOA are presented in Tillmann et al. (2009) and Jonsson et al. (2007), respectively.

The focus of this paper is on the interplay of humidity and temperature in the formation and partitioning of pinonaldehyde in relation to other simultaneous observations such as aerosol water content, OH radical and SOA production. The use of a Proton Transfer Reaction-Mass Spectrometer (PTR-MS) and Aerosol Mass Spectrometer (AMS) enabled high time resolution in selected molar or mass yield observations. The presented results are used to further improve the understanding of the mechanism of the ozonolysis of  $\alpha$ -pinene with emphasis on its dependence on water and temperature.

## 2 Experimental

Multiple experiments of the ozonolysis of  $\alpha$ -pinene were performed at temperatures of 243 K, 253 K, 273 K, and 303 K under dry and humid conditions. The experiments were performed in the AIDA aerosol and cloud simulation chamber of Forschungszentrum Karlsruhe (FZK) (Fig. 1). The AIDA chamber is a cylindrical aluminium vessel of 84.5 m<sup>3</sup> volume. It is mounted in a thermally insulating chamber with walls of 200 mm polyurethane foam. The reactor can be thermostated in a temperature range of 183–333 K. The facility is surrounded by working platforms which render access to various reactor flanges for sampling. The AIDA chamber, the analytical techniques used and the experimental procedures are described in detail elsewhere (Saathoff et al., 2003, 2009). Below we only describe the measurements of specific importance for the work presented here.

$\alpha$ -Pinene and its oxidation products were measured at a time resolution of 5 min using a high sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS, IONICON,



**Fig. 1.** AIDA chamber with instrumentation. For this study data provided by a Scanning Mobility Particle Sizer (SMPS), a Proton-Transfer-Reaction-Mass Spectrometer (PTR-MS), and an Aerosol Mass Spectrometer (AMS) were used. Further supporting instruments were condensational particle counters (CPC), a differential mobility analyzer (DMA), a tuneable diode laser system (TDL), a fourier transform infrared (FTIR) spectrometer, a volatility tandem mobility analyzer (VTDMA) and a frost point mirror hygrometer as well as gas monitors for NO, NO<sub>2</sub> and O<sub>3</sub>. The temperature in the chamber was varied between 243 K and 303 K.

Innsbruck, Austria). This technique is extensively described in the literature, e.g. Lindinger et al. (1998) and only some important aspects of the measurements are described here. In a drift tube held at an  $E/N$  ratio of 124 Td ( $E$  being the electric field strength and  $N$  the buffer gas number density; 1 Td =  $10^{-17}$  cm<sup>2</sup> V molecule<sup>-1</sup>) chemical ionization of VOC is achieved by proton transfer from  $H_3O^+ \cdot (H_2O)_n$  ( $n=0, 1, 2$ ), the so called primary ions. The protonation results in a  $m/z$  signal of  $M+1$ , with  $M$  being the molecular mass of the VOC besides some fragment ions. All  $m/z$  signals were normalized to the signal intensity of the primary ions to account for differences in the proton transfer capacity between the different experiments.

The PTR-MS was calibrated for  $\alpha$ -pinene, cyclohexanone and verbenone, the latter served as a substitute for the commercially unavailable oxidation product pinonaldehyde. The calibration was performed by using diffusion sources operated in the low ppb mixing ratio range (Gautrois and Koppmann, 1999). All data signals were background corrected using dry synthetic air. A gas standard was routinely measured with the PTR-MS to check for constant operating conditions during calibration and measurements. The  $m/z$  signals evaluated were 137 and 138 for  $\alpha$ -pinene, corrected for an interference from pinonaldehyde;  $m/z$  170, 169, 152, 151, 137 (minor contribution), 124, 123, 108 and 107 for pinonaldehyde and  $m/z$  100 and 99 for cyclohexanone. The  $1\sigma$  uncertainty of the calibration of the  $\alpha$ -pinene and cyclohexanone measurements are 7% and 10%, respectively. The uncertainty of

the pinonaldehyde measurement is estimated to be 25% accounting for the use of verbenone as a substitute for the calibration. The PTR-MS was connected to the chamber via a 6 mm PFA line (4 mm inner diameter) extending 40 cm into the chamber. The sampling line had a filter held at chamber temperature to remove and collect the aerosol particles formed from the  $\alpha$ -pinene/ozone reaction. The filter mount was made of Silco-steel and housed a Teflon filter with a nominal pore size of 200 nm (PTFE, 47 mm in diameter, Sartorius). Optionally, the filter could be bypassed to transfer the vapour and the particulate phase through a 1/8" PFA tubing heated to 323 K. The inlet and the reaction chamber of the PTR-MS were also kept at 323 K. The sample flow was 0.3 slm. The bypassing option of the filter was used in selected experiments in order to measure a total of oxidation products, including semivolatiles which reside in the particle phase at the chamber conditions but evaporate at the temperature of the sample line (323 K). Using this option gave means to e.g. determine the total yields of pinonaldehyde at low temperatures.

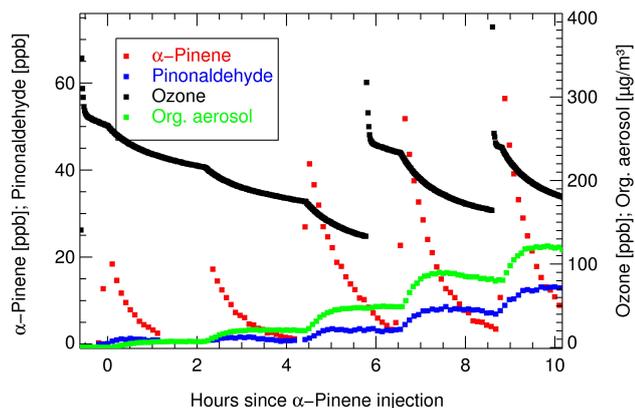
An aerosol mass spectrometer (Aerodyne Q-AMS) was operated to measure the aerosol chemical composition. The AMS was connected to the AIDA chamber via a short thermostated stainless steel tube in order to minimise losses in the sampling line. The AMS working principles and modes of operation are explained in detail elsewhere (Jayne et al., 2000; Jimenez et al., 2003). For the extraction of chemically resolved mass concentrations of individual species the AMS raw data are typically evaluated with standard assumptions as described by Allan et al. (2004). In brief this approach makes use of the reproducibility of mass spectral patterns of typical inorganic aerosol components such as ammonium, sulfate and nitrate. Subtracting from a measured mass spectrum the contributions of inorganic constituents and the contribution of gas phase sample, which is exclusively composed of  $N_2$ ,  $O_2$ , and gases with mixing ratios in the ppm range, one obtains the mass spectrum of the organic aerosol. Due to the non selective ionization with electron impact at 70 eV used in the AMS and the high fragmentation induced, further identification of individual molecules in a complex organic component is not possible. Nevertheless the total organic content can be measured sensitively, quantitatively, and with high time resolution. Measurements of particulate water with the AMS are subject to a number of possible interferences. The ions used for water measurements are at mass to charge ratios  $m/z$  18 ( $H_2O^+$ ), 17 ( $OH^+$ ), and 16 ( $O^+$ ). Possible interferences from other ions at these masses such as  $NH_2^+$  at  $m/z$  16 and  $NH_3^+$  at  $m/z$  17 can be accounted for. The same is true for  $O^+$  from gas phase  $O_2$ . Remaining possible interferences arise from gas phase water, sulfate and organics. The gas phase water signal is a function of the absolute humidity and was determined by measurements of particle free air from the freshly prepared chamber for each experiment. Since no sulfate was detected in the experiments this generally possible interference was not applicable for the chamber

experiments. The remaining possible interference is the production of  $H_2O^+$  during the ionization of organic oxygenated material. The contribution of organics to the signal of  $m/z$  18 was derived from the experiment at 303 K and 0% RH under the assumption that no water is present in the particle phase. We derived a  $(m/z\ 18)/(m/z\ 44)$  ratio of 0.69 with  $m/z$  44 being a representative for oxidized organics. Note that the standard ratio applied for ambient AMS measurements equals 1. With this adjustment to the fragmentation pattern the particulate water mass concentration in the dry experiments at 303 K and 253 K is 0–1  $\mu g\ m^{-3}$  independently of the total mass loading in the different sections of the experiment. The ratio  $(m/z\ 18)/(m/z\ 44)=0.69$  was used for all experiments assuming that the overall fragmentation patterns of the organic aerosol components with respect to  $m/z$  18 and 44 are independent of temperature, RH and mass loading. This may be an oversimplification of the system. Nevertheless by comparing within one temperature and at similar mass loadings it is possible to semiquantitatively detect particulate water by this approach.

Capillary Electrophoresis (CE, Agilent Technologies, Santa Clara, CA, USA) coupled to an Electrospray Ion Trap Mass Spectrometry (ESI-ITMS, Esquire 3000 plus, Bruker, Germany) was used for quantification of pinonic acid in the particle phase sampled with Teflon filters and quartz backup filters. A detailed description of the CE/ESI-ITMS method can be found elsewhere (Iinuma et al., 2004). The identification of pinonic acid was based on the comparison of a migration time and the  $m/z$  values of a detected  $[M-H]^-$  ion to that of an authentic standard. Calibration was performed before a series of sample analysis. A linear regression coefficient for pinonic acid standard was better than 0.99.

Particle number size distributions were obtained using a scanning mobility particle sizer (DMA 3071, TSI) and a condensation particle counter (CPC 3010, TSI) where the sampling took place via stainless steel tubes ranging 35 cm into the AIDA chamber. For the purpose of this study the volume concentrations estimated from the mobility measurements were converted to mass concentrations of SOA using a density of 1.25  $g/cm^3$  (Saathoff et al., 2009).

Ozone was generated by a silent discharge generator (Semozon 030.2, Sorbios) in concentrations of about 3% in a 5 SLM flow of pure oxygen (99.998%, Linde). The obtained concentration was measured by UV absorption with a commercial monitor (O3-41M, Environment) giving a time resolution of 1 min. The  $\alpha$ -pinene (99%, Aldrich) was evaporated up to pressures of  $\sim 4$  hPa into a 1 L glass bulb and either diluted or flushed directly into the chamber with 10 SLM synthetic air for 3 minutes. Cyclohexane (99.5%, Merck), 500 ppm, was used as an OH scavenger to suppress the degradation of the  $\alpha$ -pinene by OH radicals generated by its ozonolysis (Atkinson et al., 1992). Before an experiment the evacuated AIDA chamber was filled with dry or humidified synthetic air (low hydrocarbon grade, Basi). In the next step



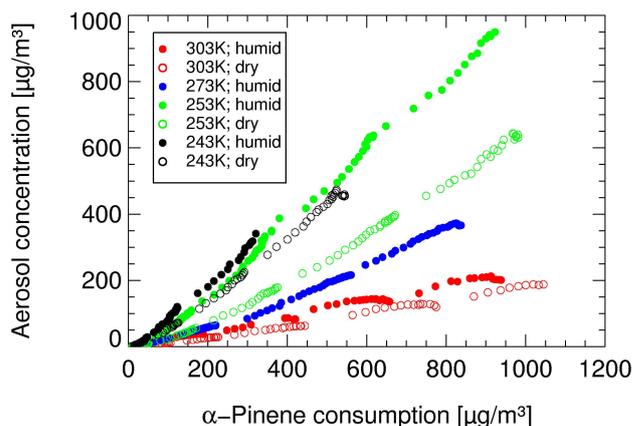
**Fig. 2.** Typical experiment performed in a sequence of single additions of  $\alpha$ -pinene and ozone to the chamber. The experiment was conducted at dry conditions, a temperature of 303 K and with 500 ppm cyclohexane added as OH-scavenger. Data were analysed for the whole experiment in order to get average quantities for the given temperature and the humidity. Data were analysed for each section in order to get gas-phase yields and partitioning as a function of the particle mass load.

cyclohexane and ozone were added followed by the sequential injections of  $\alpha$ -pinene. Mixing within the AIDA chamber was achieved by a fan within less than 5 min. The subsequent additions of  $\alpha$ -pinene gave an incremental increase of SOA mass (and of oxidation products) covering a range of several hundred  $\mu\text{g m}^{-3}$  (Fig. 2). In later stages ozone was refilled to keep it in 3–10 fold excess. Consequently, each experiment (at one  $T$  and RH) consisted of a sequence of sub-experiments as a result of the subsequent additions of  $\alpha$ -pinene, which are denoted experiment sections. From section to section the total consumption of  $\alpha$ -pinene increases and therewith the concentration of the particle mass.

### 3 Results and discussion

#### 3.1 SOA mass

The SOA concentration produced from  $\alpha$ -pinene ozonolysis was measured at several temperatures in the presence and absence of water vapour. Figure 3 shows the *observed* SOA mass concentrations as a function of the consumed  $\alpha$ -pinene mass concentrations. This type of plot is called a growth function. If the SOA mass is corrected for wall loss, the slope in each point of the growth curve gives the actual mass fractional yield. The SOA growth functions in Fig. 3 are classified by temperature (colour) and RH (open: dry and filled symbols: humid). Curvature and discontinuities in the growth curves arise from the sequential procedure of the experiments as explained in the experimental section and are shown in Fig. 2. By comparing the respective humid and dry experiments separately, it is evident that at decreasing



**Fig. 3.** Growth curves for the  $\alpha$ -pinene ozonolysis for different temperatures and at low (open symbols) and high relative humidity (filled symbols). Curvature and discontinuities are caused by the section character of the experiments as shown in Fig. 2.  $\alpha$ -Pinene was measured by PTRMS, aerosol concentration was derived from SMPS-data.

temperatures more SOA mass is produced from the same amount of precursors reacted. The details on the temperature dependence of SOA yields including a thorough aerosol model analysis are presented in a separate paper (Saathoff et al., 2009). For the present paper one concludes that more SOA mass was produced from the same amount of  $\alpha$ -pinene in the humid cases as compared to dry conditions. As shown in Fig. 3 this is most pronounced in the experiments at lower temperatures, whereas at 303 K the SOA mass produced under dry and humid conditions are only slightly different. The smaller effect of humidity at 243 K in comparison to 253 K may partly be due to the fact that in the dry case the absolute humidity was about 40 ppm ( $\text{RH} \approx 10\%$ ), somewhat higher than in the dry cases at 253 K and 303 K ( $\leq 10$  ppm, compare Table 1a). In addition, with decreasing temperatures an increasing fraction of compounds which are semivolatile at room temperature are likely to contribute to SOA mass irrespectively of the humidity. Moreover, lower temperatures may disable reaction channels and thus shift product branching ratios. The higher SOA yield in the presence of water could in general be the result of water dependent channels which produce low vapour pressure products or due to an increasing absorption of water at increasing RH. Both possibilities are discussed in the following.

#### 3.2 Water absorption

Regarding the SOA concentrations determined from measured size distributions (SMPS data) the water effect could also be attributed to physical partitioning of water into the aerosol particles as opposed to any direct influence on the chemical degradation. AMS measurements provide information that enables estimates on the relative contribution of

**Table 1.** Molar Yields of Pinonaldehyde.

A) Average yields of pinonaldehyde as function of humidity and temperature							
Exp. No. <sup>a</sup>	<i>T</i> [K]	Relative humidity [%]	Water [ppm]	Gas phase molar yield of PA <sup>f</sup>	$\chi^2$ of the linear fit	<i>N</i> <sup>b</sup>	Total Molar Yield of PA <sup>c,f</sup>
SOA05-1	303.2	44–43	18 590–18 170	0.196±0.001	181	203	
SOA05-13	303.2	48–41	20 258–17 430	0.191±0.002	75	89	0.30±0.06
SOA05-2	303.3	0.02	10	0.069±0.002	70	87	0.07±0.002
SOA06-6	273.0	74–71	4450–4227	0.044±0.001	16	106	n.d.
SOA05-8	253.0	69–66	854–819	≤ 0.01	3	86	n.d.
SOA05-7	252.9	0.17	2	≤ 0.01	1.9	105	0.02±0.01
SOA05-9	243.1	72–70	365–355	≤ 0.01	0.1	47	0.15±0.02
SOA05-10	243.1	8	40	≤ 0.01	0.4	71	n.d.

B) Section yields of pinonaldehyde as a function of organic mass load <i>M</i> <sub>org</sub> at 303 K and 44% relative humidity from experiments SOA05-1 and SOA05-13					
Section	Gas phase molar yield of PA <sup>f</sup>	r of linear fit <sup>d</sup>	<i>N</i> <sup>b</sup>	<i>M</i> <sub>org</sub> [ $\mu\text{g m}^{-3}$ ] <sup>e</sup>	
SOA05-1					
1	0.29±0.03	−0.89	16	11.3	
2	0.26±0.13	−0.82	6	20.5	
3	0.19±0.02	−0.95	28	45.0	
SOA05-13					
1	0.28±0.02	−0.74	17	16.3	
2	poor correlation	−0.25	19	33.8	
3	0.41±0.11	−0.69	10	68.8	
4	0.18±0.02	−0.91	19	113.8	
5	0.15±0.02	−0.83	15	171.3	

<sup>a</sup> Further information on the experimental conditions of the individual experiments is given by Saathoff et al. (2009).

<sup>b</sup> Number of data points regarded.

<sup>c</sup> The term total molar yield comprise the sum of aerosol and gas phase yield.

<sup>d</sup> Correlation coefficient.

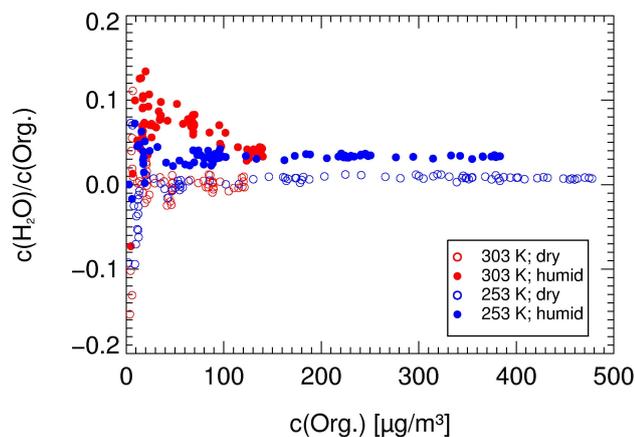
<sup>e</sup> Maximum amount of organic aerosol mass present in that experimental section ( $\rho = 1.25 \text{ g cm}^{-3}$ ).

<sup>f</sup> Provided errors are the  $1\sigma$ -precisions.

n.d.: not determined.

organics and liquid water to the observed increase in SOA production. Figure 4, presents AMS data on the mass ratio of water to organics (w/org) as function of the mass load of SOA at 303 K and 253 K under dry (open symbol) and humid conditions (filled symbol). The scatter of the data at SOA mass loads  $<30 \mu\text{g m}^{-3}$  arises from division of two small numbers with substantial errors at small aerosol concentrations. For SOA mass loads  $>30 \mu\text{g m}^{-3}$  it is evident from the data presented in Fig. 4 that particulate water is detectable in the humid cases, while it is zero under dry conditions. Moreover, at low SOA loads the water fraction seems to be larger at 303 K but decays with increasing SOA concentration. This decrease of the water fraction can be understood from the fact that the aerosol mass load in the AIDA was increased stepwise to more than  $150 \mu\text{g m}^{-3}$  and thus increasing amounts of less-polar semivolatiles absorb into the aerosol particles. At low temperature (253 K) a constant water to organic ratio of 0.03 is observed. Hence, the relative composition of the SOA does not change with increasing

aerosol mass load. This is in accordance with the assumption that most of the compounds which are semivolatile at 303 K (e.g. pinonaldehyde) partition at 253 K into the particulate phase even at small particle mass loads. The observed water content of the aerosol can be compared to independently determined hygroscopic growth factors (HGF) of SOA generated from the oxidation of  $\alpha$ -pinene. The HGF is the ratio of the diameter of the particle in equilibrium at a certain relative humidity to the diameter of a corresponding dry particle. Varutbangkul et al. (2006) determined the HGF of  $\alpha$ -pinene SOA to be 1.02 at 293 K and 50% R.H., corresponding to a volume fraction of water of 6.1%. Applying a density of  $1.25 \text{ g cm}^{-3}$  to the organic fraction results in a mass fraction of water of 0.05, which is in accordance with the water to organic ratio of 0.1–0.03 at 303 K and 44% RH measured in the present study. Consequently, at 303 K water uptake could account for the slightly higher increase in SOA mass under humid conditions shown in Fig. 3. At 253 K and 68% RH the SOA mass production increased the most in comparison



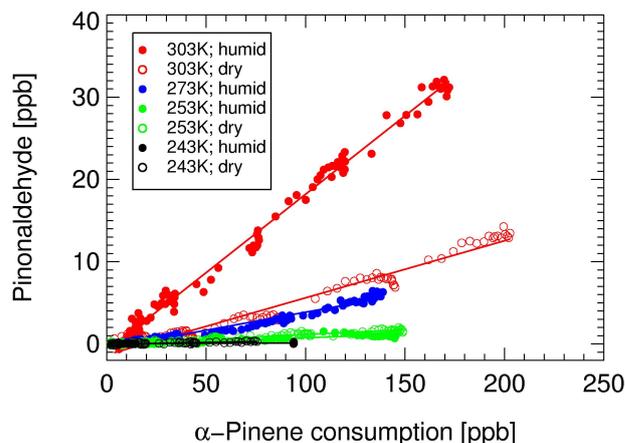
**Fig. 4.** Mass ratio of water to organics (w/org) as function of the mass load of SOA at 303 K and 253 K (colour) under dry (open symbols) and humid conditions (filled symbols) as derived by AMS.

to the corresponding dry experiment and even for this case the water to organic mass ratio was only 0.03. In conclusion, the physical water uptake of the aerosol at that temperature contributes only minor to the SOA mass under humid conditions. The influence of water and temperature on the degradation path of  $\alpha$ -pinene dominates the increase of SOA mass.

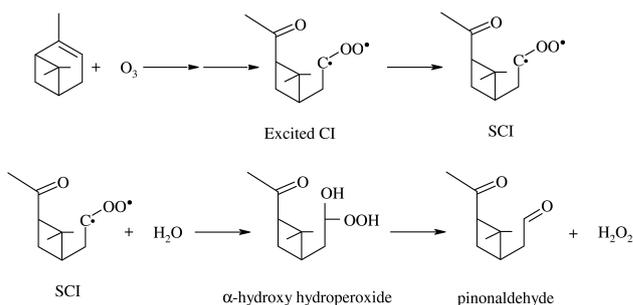
### 3.3 Pinonaldehyde

Water dependent reaction channels in the production of non- or semivolatile products may contribute to the observed increased SOA formation under humid conditions. As shown by reaction Scheme 1 pinonaldehyde (PA) is proposed to be produced from SCI reacting with water and consequently may exhibit a water dependence. PA is regarded as a semivolatile compound with a significant vapour pressure at ambient temperatures (Hallquist et al., 1997). However, PA may contribute to the condensed phase at lower temperatures and can serve as an indicator for other less volatile compounds formed by the water reaction with the SCI, e.g. pinonic acid (Ma et al., 2007).

In order to derive gas-phase molar yields, the observed PA mixing ratios were plotted vs. the consumption of  $\alpha$ -pinene, as is shown in Fig. 5. Overall linear relationships were established for the respective conditions, i.e. temperature (different colours) and humidity (filled and open symbols). The slopes corresponding to those relationships are the average gas-phase molar yields ( $Y_{PA}$ ) of PA for the respective RH and temperature. The PA yields obtained are summarised in Table 1a with the corresponding number of data points ( $N$ ) and the  $\chi^2$  value of the linear fit. For the experiments at 303 K, the PA yield is a factor of 3 higher for humid conditions,  $Y_{PA}=0.191\pm 0.002$ , compared to dry conditions,  $Y_{PA}=0.069\pm 0.002$ . For the humid cases the average gas-phase molar yields decrease rapidly with decreasing temper-

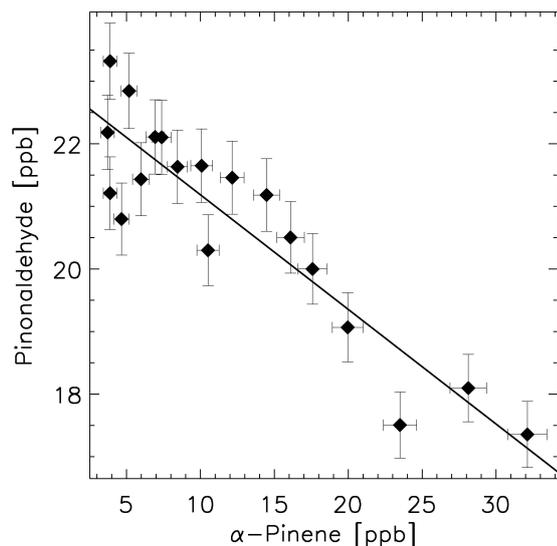


**Fig. 5.** Pinonaldehyde mixing ratios measured in the gas phase vs. the consumed  $\alpha$ -pinene for the temperature (colour coded lines and points) and humidity regimes (open symbols: dry and filled symbols: humid conditions). The data points present standard measurements with particle filter in-line and OH scavenger as described in the experimental section.



**Scheme 1.** Water dependent reaction path for the formation of pinonaldehyde in the ozonolysis of  $\alpha$ -pinene.

atures, from 0.19 to below detection limit. At  $T \leq 253$  K less than 1 ppb PA is found in the gas phase for both humid and dry conditions, and gas-phase yields are  $\leq 0.01$ . The temperature effect on the gas phase molar yield of PA could be caused by a temperature dependent branching in the reaction mechanism or a pronounced partitioning of the semivolatile PA towards the particulate phase. Gas-to-particle partitioning of organic semivolatile species is dependent on temperature but also on the actual available particle mass (mostly to the organic fraction). Under warm conditions the gas-phase concentrations of PA were high enough to enable analysis of the gas phase molar yield for each section of the experiments, therewith the gas phase yields were obtained as a function of the SOA mass load (in extension to the average molar yield presented in Table 1a and Fig. 5). For each section molar yields for PA were derived using the relative measurements of PA and  $\alpha$ -pinene, i.e. the observed PA mixing ratio is plotted vs. the mixing ratio of  $\alpha$ -pinene as shown for example in Fig. 6. The modulus of the slope in Fig. 6 directly

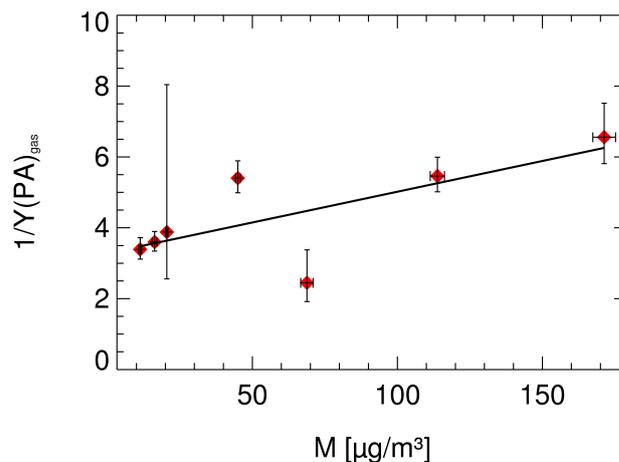


**Fig. 6.** Determination of the molar yield of pinonaldehyde from PTR-MS gas-phase measurement within a section of an experiment. The negative of the slope gives the approximate gas-phase molar yield. The respective fit parameters are given in Table 1b.

provides the molar yield of PA. The correlation between the mixing ratio of  $\alpha$ -pinene and the product PA are close to linear with a tendency to level off somewhat for large turnovers, i.e. long reaction times. However, the overall effect is small within each section and was neglected in the evaluation procedure. The derived gas-phase molar yields of all sections at 303 K are given in Table 1b. It should be noted that wall losses for PA were determined from a long term observation of PA after complete consumption of  $\alpha$ -pinene at 303 K and 44% RH. Within 15 h the PA mixing ratio decreased with a wall loss rate of only  $130 \text{ ppt h}^{-1}$  and was therefore neglected in the calculation of the molar yields. From the sectional yields measured at 303 K an overall decrease in gas-phase molar yields was noted with increasing particle load providing means to estimate PA partitioning and corresponding vapour pressure. Any absorption of a semivolatile compound can be described by use of a partitioning coefficient  $K_i$  as given by Eq. (1) (Seinfeld and Pandis, 1998):

$$K_i = \frac{Y_{i,\text{aerosol}}}{Y_{i,\text{gas}} M_{\text{org}}} = \frac{RT}{\overline{MW}_{\text{om}} \gamma_i p_i^0} \quad (1)$$

Therein  $Y_{i,\text{aerosol}}$  and  $Y_{i,\text{gas}}$  are the molar yields of compound  $i$  in the aerosol and in the gas phase, respectively.  $M_{\text{org}}$  denotes the organic mass concentration of the aerosol,  $\overline{MW}_{\text{om}}$  is the mean molecular mass of the aerosol constituents,  $R$  the ideal gas constant,  $T$  the temperature,  $\gamma_i$  the activity coefficient and  $p_i^0$  is the saturation vapour pressure of compound  $i$ . If  $Y_{i,\text{aerosol}}$  is expressed by  $Y_{i,\text{gas}}$  and  $Y_{i,\text{total}}$ , wherein  $Y_{i,\text{total}}$  denotes the total molar yield of compound  $i$ , Eq. (1) can



**Fig. 7.** Gas-phase molar yield as function of the organic aerosol mass concentration at 303 K and humid conditions. The linear fit to the data assumes a constant activity coefficient of pinonaldehyde  $\gamma_{\text{PA}}$  over the range of observation. From the slope and the intercept of the regression line overall yield  $\alpha_{\text{PA}}$  and vapour pressure  $p_{\text{PA}}^0$  of pure pinonaldehyde are derived as described in the text.

be transformed, such that  $1/Y_{i,\text{gas}}$  is a linear function of the available particle mass concentration  $M_{\text{org}}$ :

$$\frac{1}{Y_{i,\text{gas}}} = \frac{RT}{\overline{MW}_{\text{om}} \gamma_i p_i^0 Y_{i,\text{total}}} \cdot M_{\text{org}} + \frac{1}{Y_{i,\text{total}}} \quad (2)$$

Figure 7 shows the relationship of  $1/Y_{\text{PA,gas}}$  vs.  $M_{\text{org}}$  applying the sectional yield data recorded in Table 1b. Using this linear relationship one can extract further physical properties for PA and its partitioning. In order to derive a total molecular yield  $Y_{\text{PA,total}}$  from the intercept we have to know the average molecular weight  $\overline{MW}_{\text{om}}$  of the products. A value of  $180 \text{ g mol}^{-1}$  was calculated from the weighted average molecular masses of the aerosol components detected from the ozonolysis of  $\alpha$ -pinene as presented by Yu et al. (1999a). Using  $180 \text{ g mol}^{-1}$  for  $\overline{MW}_{\text{om}}$  we derive a total molecular yield  $Y_{\text{PA,total}}$  of  $0.30 \pm 0.06$ . The error provides the standard deviation of the non error weighted linear regression parameters derived from Fig. 7.

The product ( $\gamma_{\text{PA}} \times p_{\text{PA}}^0$ ) is calculated to be  $(3.0 \pm 1.5) \times 10^{-3} \text{ Pa}$ . According to Seinfeld and Pankow (2003)  $\gamma_i$  has typical values between 0.3 and 3, accordingly the effective vapour pressure of PA  $p_{\text{PA}}^0$  should be in the range of 0.01 to 0.001 Pa at 303 K, which is distinctively lower than the value of 8.4 Pa reported in the literature (Hallquist et al., 1997). The corresponding partitioning coefficient  $K_i$  of PA ( $K_{\text{PA}}$ ) at 303 K would be  $0.005 \pm 0.004 \text{ m}^3 \mu\text{g}^{-1}$ , with a total mass yield  $\alpha_{\text{PA,total}} = 0.37 \pm 0.08$  of PA ( $\alpha_{\text{PA,total}} = Y_{\text{PA,total}} \cdot M_{\text{PA}} / M_{\alpha\text{-Pinene}}$ ). Odum et al. (1996) used a two product model of a non-volatile oxidation product (1) and a semivolatile oxidation product (2) for the ozonolysis of  $\alpha$ -pinene to fit their data of SOA yields.

The parameters of their semivolatile proxy (2) ( $\alpha_2=0.326$  and  $K_2 = 0.004\text{m}^3\mu\text{g}^{-1}$ ) are in good agreement with our independently derived values of PA ( $\alpha_{\text{PAtotal}}=0.37$ ,  $K_{\text{PA}}=0.005\text{m}^3\mu\text{g}^{-1}$ ). As a consequence PA seems to be a good candidate to match the semivolatile proxy (2) in the  $\alpha$ -pinene ozonolysis. This requires an effective vapour pressure of PA ( $\gamma_{\text{PA}} \times p_{\text{PA}}^0$ ) substantially lower than assumed so far. In other chamber studies and field measurements PA was also often found in a significant fraction in the condensed phase demonstrating that PA can contribute to aerosol mass even at ambient temperatures (Plewka et al., 2006; Yu et al., 1999a). In our study  $\gamma_{\text{PA}}$  has to be in the order of  $10^{-3}$ , to achieve such a low effective vapour pressure considering the previously measured  $p_{\text{PA}}^0$  of 8.4 Pa. Such low activity coefficients would normally imply specific chemical interactions e.g. adduct formation. Stabilized criegee intermediates (SCI) have been suggested to form adducts with carbonyl compounds to yield secondary ozonides (SOZ) (Bonn et al., 2002). A reaction of e.g. a  $\text{C}_{10}$ -SCI with PA would yield a  $\text{C}_{20}$ -SOZ that will have a significant lower vapour pressure than pure PA. The observed effective vapour pressure of PA would thus be reduced. In fact, the sectional experimental procedure adopted in the present study will enhance the probability of  $\text{C}_{10}$ -SCI to react with PA since initially produced PA will be present as reactive SCI are produced in the subsequent steps of  $\alpha$ -pinene additions. SOZ are known to be thermally labile yielding the corresponding acids and carbonyl compounds e.g. PA (Story et al., 1968). Furthermore, experiments dedicated to low temperatures would enhance the lifetime of the SOZ so that they can partition to the particulate phase. The measurements with a filter in line held at experimental temperature retains the particulate SOZ. Without the filter in line the respective SOZ formed from PA with a Criegee Radical would thermally decompose in the heated sampling line of the PTRMS inlet and PA would be detected. Assuming formation of SOZ could explain the observations from low temperature with and without the filter in the sampling line as well as the low effective vapour pressure determined at 303 K. However, quenching of SCI with water may reduce the importance of the proposed SOZ formation under humid conditions. Therefore other reversible adducts of PA in gas or particle phase cannot be excluded.

For experiments at 243–253 K, the gas-phase molar yields of PA were below detection limit, and it was suspected that PA partitions strongly towards the condensed phase. The temperature dependence of the partitioning coefficient  $K_i$  can be expressed using the Clausius Clapeyron relationship for the temperature dependence of vapour pressure  $p_i^0(T)$  of the pure component  $i$  and assuming that  $\overline{M}\overline{W}_{om}$  and  $\gamma_i$  do not change with temperatures. Equation (3) describes the corresponding temperature dependence for  $K_i$

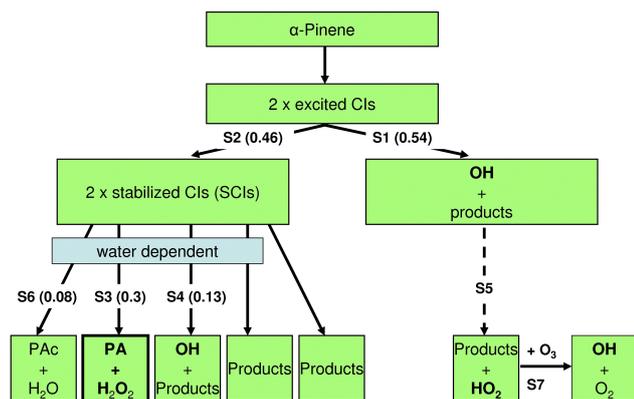
$$K_i(T) = K_i(T_{\text{Ref}}) \frac{T}{T_{\text{Ref}}} \exp\left(\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{Ref}}}\right)\right) \quad (3)$$

where  $T$  is the actual temperature,  $T_{\text{Ref}}$  the reference temperature,  $\Delta H_{\text{vap}}$  is the heat of vaporisation for PA and  $R$  the ideal gas constant. Combining Eq. (1) and (3) we derived a temperature and SOA mass concentration dependent gas phase molar yield of PA by:

$$Y_{i,\text{gas}}(T) = \frac{Y_{i,\text{total}}(T_{\text{Ref}})}{1 + \frac{RTM_{\text{org}}}{\overline{M}\overline{W}_{om}\gamma_i p_i^0(T_{\text{Ref}})} \exp\left(\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{Ref}}}\right)\right)} \quad (4)$$

Using the average molar PA yield measured at 273 K for humid conditions and the calculated total molar yield and saturation vapour pressure of PA, ( $\gamma_{\text{PA}} \times p_{\text{PA}}^0$ ), at  $T_{\text{Ref}}=303$  K, the heat of vaporization ( $\Delta H_{\text{vap}}$ ) was estimated from Eq. (4) to be  $(65 \pm 37)$  kJ mol $^{-1}$  as compared to  $(75.5 \pm 5.6)$  kJ mol $^{-1}$  measured by Hallquist et al. (1997) and  $(24 \pm 9)$  kJ mol $^{-1}$  determined by Saathoff et al. (2009). Gas phase molar yields at 253 K calculated by Eq. (4) are below 1% for SOA mass concentrations larger than  $50\mu\text{g m}^{-3}$  in agreement with the measurements. The measurements of PA at temperatures  $\leq 253$  K, when PA is suspected to fully remain in the condensed phase, were performed by removing the particle filter from the sampling line, allowing PA to evaporate. This was done during one humid experimental section at 243 K, and during two dry sections at 253 K. By assuming that PA was quantitatively transferred into the gas phase when the aerosol was heated up, this gives the total molar yield of PA. For humid and cold conditions the observed PA yield was 0.15, about half of the total molar yield of 0.3 at 303 K for humid conditions. In the dry and cold case a very low total PA yield of 0.02 was determined, which is distinctively smaller but still of the same order as in the warm, dry case (0.07). These results are also given in Table 1a.

The contribution of PA to the water effect on total SOA yield was estimated. For the experiments at low temperatures the water effect on SOA mass was most effective at 253 K (Fig. 3, green curves). We will use the total yields of PA determined under humid conditions at 243 K (0.15) and the gas-phase yields at 303 K (0.3) as lower and upper limits, respectively, assuming that the total yield of PA at 253 K is somewhere in between. In order to compare to the SOA mass growth curve, the molar yields of PA are converted into mass yields ( $\alpha$ ). This results in  $\alpha_{\text{PAtotal}}=0.19$  for the lower limit and  $\alpha_{\text{PAtotal}}=0.37$  for the upper limit, respectively. Since  $\alpha$ 's are total yields and not dependent on gas-to-particle partitioning, they are independent of the amount of SOA produced. In the growth curve picture (Fig. 3) they are straight lines through the origin where  $\alpha_{\text{PAtotal}}$  is determined by the slope. By adding the straight lines calculated as the lower and upper limit to the SOA growth curve of the dry case at 253 K and comparing the results to the humid SOA growth curve, we achieve an estimate of the upper and lower limit of the PA contribution to low temperature SOA mass production in humid case. In the lower limit, PA alone can already

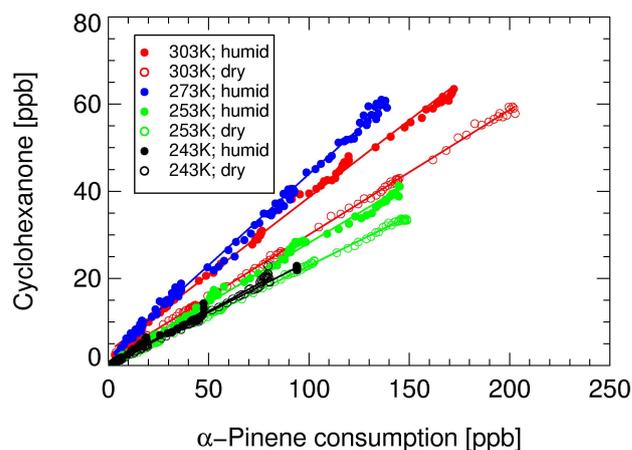


**Fig. 8.** Mutual constraints of the formation of OH and pinonaldehyde where CI denotes for Criegee Intermediate; SCI for Stabilized Criegee Intermediate; PAc for Pinonic Acid and PA for Pinonaldehyde. Details of the reaction sequences following S2 can be seen in Scheme 1 and Scheme 2. Determined branching ratios valid for 303 K at humid conditions are given in brackets.

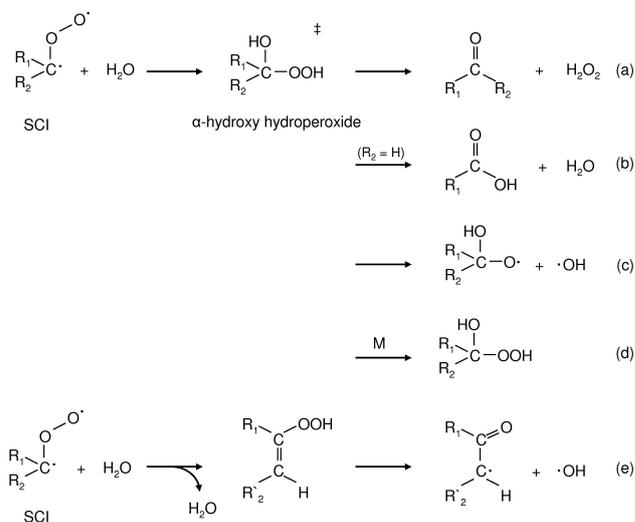
explain 56% of the humidity induced gain of the SOA mass production at 253 K. The remaining increase of 44% must result then from other water dependent product channels giving either other semi-volatiles condensing at 253 K or non-volatile products. Using the upper limit of  $\alpha_{\text{PA total}}$  attributes all of the yield increase to PA and leaves no extra freedom for additional compounds to contribute to the observed water effect on SOA yields.

The increase in SOA mass by the presence of water is less distinct at 243 K than at 253 K. While most experiments conducted under dry conditions were carried out at water mixing ratios  $\leq 10$  ppm, the dry case at 243 K contained 40 ppm of water in comparison to 370 ppm of water in the respective humid case. It can be speculated that the water dependent channels already become active for trace amounts of water, i.e. at 40 ppm. On the other hand the similarities between the humid SOA growth curve at 253 K and both SOA growth curves at 243 K suggest that the aerosol production has achieved its maximum at this point for  $\alpha$ -pinene ozonolysis. The observed maximum results in a mass conversion factor of 1.05. Assuming a maximum theoretical mass conversion factor of 1.26 (Saathoff et al., 2009) for the reaction of  $\alpha$ -pinene to its oxidized products, we end up with a deficit of  $1.26 - 1.05 = 0.21$  which is either due to wall losses of the particles or the less volatile vapours, or due to chemical production of small molecules like CO which also arise from the ozonolysis.

To summarize the water effect and the pinonaldehyde contribution to the effect on SOA the presence of water at each temperature clearly favours reaction channels in the  $\alpha$ -pinene ozonolysis in which PA is formed. The decreased gas-phase yield of PA in the humid cases at low temperatures is mainly due to partitioning into the particle phase. Therefore PA increasingly contributes to SOA mass going down



**Fig. 9.** Mixing ratio of cyclohexanone vs. the  $\alpha$ -pinene consumption. The slopes of the straight lines are proportional to the OH yield of the  $\alpha$ -pinene+ozone reaction.



**Scheme 2.** Pathways suggested for the reaction of water with the stabilised Criegee Intermediate (SCI).

to low temperatures and induces a humidity dependence on SOA yields. Nevertheless, the lower total PA yields at low temperatures suggest that the reaction pathways producing PA are decreasing in importance with decreasing temperature.

The molar yields of PA determined at ambient temperature were compared to the literature data (see Table 3). As can be seen in Table 3 there are plenty of experiments at a wide range of different experimental conditions with RH often not specified. Taking the literature data obtained from humid experiments ( $\text{RH} > 4\%$ ) in the presence of an OH scavenger provides a molar yield of PA in the range of 0.06–0.34. Our value under humid conditions of  $0.30 \pm 0.06$  is in support of the higher end of the given range. Experiments carried out in absence of an OH scavenger (Hatakeyama et al., 1989;

**Table 2.** Cyclohexanone and OH yields.

Temperature	Humidity Regime	Absolute Water [ppm]	Cyclohexanone yield <sup>c</sup>	OH yield <sup>a</sup>	OH yield <sup>b</sup>
303 K	wet (44% R.H.)	19500	0.354±0.002	0.67	0.71
303 K	dry (0% RH)	10	0.286±0.001	0.54	0.57
273 K	wet (70% RH)	4380	0.418±0.002	(0.79)	
253 K	wet (68% RH)	850	0.276±0.002	(0.52)	
253 K	dry (0% RH)	2	0.229±0.001	(0.43)	
243 K	wet (71% RH)	360	0.233±0.002	(0.44)	
243 K	dry (10% RH)	40	0.254±0.002	(0.48)	

<sup>a</sup> OH yields were calculated assuming a branching ratio of (0.53±0.06) for the channel of the OH+cyclohexane reaction leading to cyclohexanone according to Berndt et al. (2003). Values in brackets assume a constant branching ratio of 0.53 also for lower temperatures. The uncertainty of the OH yields is about 25%.

<sup>b</sup> Values are lower limits. The branching ratio for the channel of the OH + cyclohexane reaction leading to the sum of cyclohexanone + cyclohexanol according to Atkinson et al. (1992) was used to calculate the OH yields.

<sup>c</sup> Provided errors are the 1 $\sigma$ -precisions.

Warscheid and Hoffmann, 2001) have higher molar yields of PA (0.23–0.53) arising from the reaction of  $\alpha$ -pinene with OH radicals being produced during the ozonolysis (Atkinson and Arey, 2003). Literature data for dry conditions are inconclusive. Warscheid and Hoffmann (2001) found a lower value while Berndt et al. (2003) observed a higher value at dry compared to humid conditions. The trend with humidity observed by Warscheid and Hoffmann (2001) is in agreement with our observation however their values are larger because of the absence of a scavenger. Our value determined under dry conditions (0.07) is at the lower end of the molar yield range obtained of all studies, conducted under dry and humid conditions, in the presence of an OH scavenger. We suggest that a humidity independent reaction path exists for the ozonolysis of  $\alpha$ -pinene with a molar PA yield of 0.07 and a humidity dependent path beside, which adds up to a molar PA yield of  $\sim$ 0.3 at RH=40–50%.

### 3.4 OH radical formation

To get further insight into the mechanism of PA formation the production of OH radicals was also considered. A simplified, conceptual reaction scheme of the ozonolysis of  $\alpha$ -pinene is shown in Fig. 8, based on several previous studies (Anglada et al., 2002; Atkinson and Arey, 2003; Zhang and Zhang, 2005). As outlined in Fig. 8 the OH yield in the ozonolysis of  $\alpha$ -pinene puts a certain constraint to the PA yield. OH radicals can be produced from two main routes via CI (S1) or SCI (S4) of which S4 would be dependent on presence of water. In addition, HO<sub>2</sub> is possibly formed during the multistep degradation of the CI (S5), e.g. Atkinson and Arey (2003); Jenkin (2004). HO<sub>2</sub> can be converted to OH by the presence of the large O<sub>3</sub> concentrations (S7), which were typically applied in many laboratory studies. But the importance of the HO<sub>2</sub> channel is difficult to access. Basically, the molar yield of OH and PA should not sum up to more than unity, as long as S5 is unimportant.

The estimates on the OH yield were based on the cyclohexanone production from the OH initiated oxidation of cyclohexane, acting as OH scavenger. The consumption of cyclohexane could not be measured directly with necessary accuracy, due to too small changes in relation to the relatively large concentration of cyclohexane (500 ppm). Under the applied conditions of excess cyclohexane, the formation of cyclohexanone is a direct measure of the OH formation, since cyclohexane will scavenge most of the OH radicals, and cyclohexanone will not react further with OH. As shown in Fig. 9, the correlation of the mixing ratio of cyclohexanone with the consumption of  $\alpha$ -pinene is linear in all cases. The slopes of the linear fits to the data give the cyclohexanone yields per  $\alpha$ -pinene consumed and are listed in Table 2. The cyclohexanone yields as a function of humidity and temperature are all in a range of 0.23–0.42 (Table 2), but show considerable variation although the precision of the single determinations are high (compare Fig. 9).

In order to derive absolute values of the OH yield there is a need for an accurate number on the branching ratio of the reaction OH+cyclohexane into cyclohexanone (the second most stable product, cyclohexanol, could not be detected because of an interference with cyclohexane). Such branching ratios are currently only available for room temperature (Atkinson et al., 1992; Berndt et al., 2003). For example, Berndt et al. (2003) measured the cyclohexanone branching ratio at room temperature to be 0.53±0.06. By applying the data from Berndt et al. (2003) to the 303 K data one obtains an absolute OH yield of 0.67±0.17 under humid conditions (cf. Table 2). This value agrees exactly with the OH yield in the  $\alpha$ -pinene ozonolysis also observed by Berndt et al. (2003), however is lower than the OH yield of 0.80 as recommended by IUPAC (IUPAC, 2005). The OH yield under dry conditions at 303 K is 0.54±0.13, thus smaller by about 20% compared to humid conditions. The uncertainty of the cyclohexanone yields is about 11%. If we consider the uncertainty of the branching ratio of 12% as given by Berndt et

**Table 3.** Molar pinonaldehyde yields from the ozonolysis of  $\alpha$ -pinene compared to other studies.

$T$ [K]	RH [%]	Gas phase molar yield of PA [%]	Initial $\alpha$ -Pinene [ppb]	OH-Scavenger	Remarks	Reference
303 $\pm$ 1	n.s.	< 0.51 $\pm$ 0.06	1000	n.s.	Sum of all aldehydes produced except HCHO	Hatakeyama et al. (1989)
297 $\pm$ 2	n.s.	0.19 $\pm$ 0.04	1000	Cyclohexane		Hakola et al. (1994)
296 $\pm$ 2	$\sim$ 5	0.143 $\pm$ 0.024	1000	Cyclohexane		Alvarado et al. (1998)
306–308	n.s.	0.06–0.19	45.1–65.1	2-Butanol	SOA concentration: 38.8–65.1 $\mu\text{g m}^{-3}$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -seeds	Yu et al. (1999a)
296 $\pm$ 2	5–50	0.164 $\pm$ 0.029	1000	Cyclohexane, 2-Butanol	2-Butanol and Cyclohexane results in identical PA yields No humidity dependence	Baker et al. (2001)
296 $\pm$ 2	$\sim$ 60	0.53 $\pm$ 0.05	350	None		Warscheid and Hoffmann (2001)
296 $\pm$ 2	< 1	0.23 $\pm$ 0.05	350	None		Warscheid and Hoffmann (2001)
295	High	0.32 $\pm$ 0.04	46–670	Cyclohexane	Flow tube (high surface to volume ratio)	Berndt et al. (2003)
295	Low	0.42 $\pm$ 0.05	46–670	Cyclohexane	Flow tube (high surface to volume ratio)	Berndt et al. (2003)
292	4.1	0.19–0.34	186	Cyclohexane	SOA concentration: 417 $\mu\text{g m}^{-3}$	Lee et al. (2006)
303.2	48–41	0.30 $\pm$ 0.06	17.3	Cyclohexane	SOA concentration: 16.3 $\mu\text{g m}^{-3}$ (at the end of 1st section)	This study
303.3	0.02	0.07 $\pm$ 0.02	21.0	Cyclohexane	SOA concentration: 10.5 $\mu\text{g m}^{-3}$ (at the end of 1 <sup>st</sup> section)	This study

n.s. not specified

al. (2003), we end up with an uncertainty of the OH yields of about 25%. Atkinson et al. (1992) determined the branching ratio for the sum of cyclohexanone and cyclohexanol and obtained an overall yield of 0.5. By applying this branching ratio to the current cyclohexanone measurements one can estimate a lower limit of the OH yields. These lower limits

are 0.71 in the humid and 0.57 in the dry case at 303 K (Table 2). At 296 K Atkinson et al. (1992) determined values of 0.85 $\pm$ 0.06 and 0.82 $\pm$ 0.06 for 4% RH and 35% RH, respectively. As a consequence the total molar PA yield of 0.3 $\pm$ 0.06 at 303 K under humid conditions is commensurable with the molar OH yield of 0.67 $\pm$ 0.13 based on our

measurement and the branching ratio for cyclohexanone of Berndt et al. (2003). The branching ratio of path S2 in Fig. 8 into SCI can be estimated to 0.46, if we assume that path S1, the decomposition of the excited CI, is given by the OH yield in the dry case, which is 0.54 (see below). The SCI to react to PA ( $0.3\pm 0.06$ ) and OH ( $0.13\pm 0.03$ ) would still leave some room for the formation of pinonic acid (Fig. 8, S6), which is known to be formed in small but significant yields (Ma et al., 2007). The CE/ESI-ITMS analysis of the front and back filters sampled during an ozonolysis experiment at 303 K under humid conditions leads to a lower estimate of the pinonic acid molar yield of 0.08. This molar yield is compatible with the determined branching ratios for S2, S3 and S4 considering their uncertainties. Regarding OH yields at low temperatures the corresponding temperature dependence of the product branching ratio for the reaction of OH+cyclohexane is unknown. Still it is evident from the current measurements that there must be substantial OH formation in the ozonolysis of  $\alpha$ -pinene, even at the lowest temperature of 243 K. The OH yields given in Table 2 for temperatures  $\leq 273$  K are calculated assuming a constant branching ratio of 0.53 (Berndt et al., 2003) for cyclohexanone in the OH+cyclohexane reaction.

#### 4 Implication for degradation mechanism of $\alpha$ -pinene

The implication of the presented results on the degradation mechanism of  $\alpha$ -pinene is basically to confirm suggested reaction steps and evaluate their temperature dependence. The temperature and humidity dependence on the OH yield indicates that there is a significant OH production in the absence of water. Assuming that the branching into cyclohexanone in the reaction OH+cyclohexane does not significantly depend on temperature, our observations suggest a negligible temperature dependence on the OH yield from ozonolysis of  $\alpha$ -pinene under dry conditions. In addition the dry and humid cyclohexanone yields, used as proxies for the OH yield, seem to converge for the experiments conducted at low temperatures to about 0.25, which is only 15% smaller than the OH yield at 303 K in the dry case. This could be caused by the relatively low absolute water concentrations at these low temperatures for dry and humid conditions (compare Table 2). The OH produced at dry conditions and for all experiments done at low temperature should therefore originate from the decomposition of the excited CI via the hydroperoxide channel (S1). This is then the first result showing no temperature dependence on this channel. The results from the humid experiments give support to the suggested water reaction with the SCI as shown in reaction Scheme 2 which is a detail of S2 in Fig. 8. In reaction Scheme 2 five pathways suggested for the reaction of water with the SCI are shown (a–d) (Anglada et al., 2002; Hasson et al., 2001).

As shown in Table 1a the total PA yield, suggested to originate from channel (a) in reaction Scheme 2, is decreasing by a factor of two from 303 K to 243 K. The OH production from channel (c) (or (e)) can be estimated by subtracting the OH formation contribution from the decomposition of the excited CI, i.e. the hydroperoxide channel at dry conditions. At 303 K the OH yield from channel (c)+(e) is then estimated to  $0.13\pm 0.03$ . However, this channel of OH production disappears completely when going down to low temperatures. It demonstrates that channel (c) and (e) have larger negative temperature dependencies than channel (a), which is the channel responsible for the production of PA. However, the absolute temperature dependence on channel (a) is not clear. It is rather complex to evaluate this since the absolute water concentration difference between dry and humid is not as large at low temperatures (40 vs. 370 and 2 vs. 870 ppm). However, there is still a significant difference in PA production for dry and humid conditions. This is also valid for the overall SOA yields obtained at low temperatures where the experiments at 253 K shows larger differences between dry and humid than the corresponding experiments at 243 K. It should be noted that the experiments at low temperatures are slower in the overall kinetics and a delay in aerosol production was observed (Saathoff et al., 2009). Clearly, there is also a need for a more profound understanding of the water competing reactions with SCI to aid for interpretation of these ozonolysis experiment. It has been suggested that e.g. aldehydes, acids or alcohols can react with SCI, see e.g. Docherty et al. (2005). These are all expected products in the ozonolysis of alkenes and at low temperatures, where the absolute water concentrations are rather low, these products may compete with water in reacting with the produced SCI. In the atmosphere this is not an issue since water is by far the most abundant trace gas and will be the major reaction pathway for any produced SCI. In addition, a large fraction of the overall reaction products are still expected from decomposition of the excited CI in line with the presented result on dry yield of OH radicals in the present experiments and the result by e.g. Docherty et al. (2005).

#### 5 Summary and conclusions

The ozonolysis of  $\alpha$ -pinene has been investigated and the mechanism has been evaluated with respect to the effect of water at different temperatures. As expected and described by Saathoff et al. (2009), the yield of SOA increased with decreasing temperatures, but in addition the presence of water lead to an increase of SOA. The difference between the dry and the humid experiments was greatest at 253 K and the effect was minor at 303 K. The large water effect at 253 K can be attributed to the water dependence of the production of semivolatile products such as PA. It was demonstrated that significantly more PA was formed, if water was available as expected from the suggested chemical mechanism (Anglada

et al., 2002; Jenkin, 2004). Moreover PA was observed in substantial fractions in all humid experiments. At 303 K PA was found in the gas phase, but it increasingly partitioned into the particle phase with increasing mass load of organic particles. At 253 K and 243 K PA was only found in the condensed phase, and for 253 K PA was estimated to contribute to at least 56% of the water induced increase in SOA for humid conditions. Only a small portion of the water effect could be assigned to physical uptake of water and thus, as for example shown for PA, the dominant part must be due to water effecting the organic product distribution.

The PA is formed via the SCI and decay of the excited CI is the major route to OH radical formation. Thus OH formation should constrain the maximum PA formation. In this context, the yield of cyclohexanone was determined, which originated from the OH initiated oxidation of the OH scavenger cyclohexane. On basis of these measurements and knowledge about the yield of cyclohexanone from degradation of cyclohexane, OH yields could be derived. The OH yields were commensurable with the PA yields observed. The presence of water at high temperatures increased the amount of cyclohexanone. Consequently, it was indirectly shown that OH formation from the ozonolysis of  $\alpha$ -pinene is dependent on the water available. Thus, our observations support mechanisms suggested earlier which state that OH production has two pathways: the hydroperoxide and the hydroxy hydroperoxide channel. At 303 K the ratio of these channels was about 1 to 3 with favour of the hydroperoxide channel. At low temperatures only the hydroperoxide channel was active with an approximate OH yield of 50%. Clearly, these absolute numbers at low temperatures should be taken with caution since they are based on the room temperature yield of cyclohexanone from OH + cyclohexane reaction. However, it is clear that the ozonolysis of  $\alpha$ -pinene will contribute with a significant part to OH radicals also at low temperatures.

Edited by: J. B. Burkholder

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