

Towards closing the gap between hygroscopic growth and CCN activation for secondary organic aerosols – Part 3: Influence of the chemical composition on the hygroscopic properties and volatile fractions of aerosols

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Abstract. The influence of varying levels of water mixing ratio, r , during the formation of secondary organic aerosol (SOA) from the ozonolysis of α -pinene on the SOA hygroscopicity and volatility was investigated. The reaction proceeded and aerosols were generated in a mixing chamber and the hygroscopic characteristics of the SOA were determined with the Leipzig Aerosol Cloud Interaction Simulator (LACIS) and a Cloud Condensation Nuclei counter (CCNc). In parallel, a High-Resolution Time-of-Flight Aerodyne Aerosol Mass Spectrometer (HR-ToF-AMS) located downstream of a thermodenuder (TD) sampling from the mixing chamber, to collect mass spectra of particles from the volatile and less-volatile fractions of the SOA. Results showed that both hygroscopic growth and the volatile fraction of the SOA increased with increases in r inside the mixing chamber during SOA generation. An effective density of 1.40 g cm^{-3} was observed for the generated SOA when the reaction proceeded with $r > 1 \text{ g kg}^{-1}$. Changes in the concentrations of the fragment CO_2^+ and the sum of $\text{C}_x\text{H}_y\text{O}_z^+$ (short name CHO) and C_xH_y^+ (short name CH) fragments as measured by the HR-ToF-AMS were used to estimate changes in the oxidation level of the SOA with reaction conditions, using the ratios CO_2^+ to CH and CHO to CH. Under humid conditions, both ratios increased, corresponding to the presence of more oxygenated functional groups (i.e., multifunctional carboxylic acids). This result is consistent with

the α -pinene ozonolysis mechanisms which suggest that water interacts with the stabilized Criegee intermediate. The volatility and the hygroscopicity results show that SOA generation via ozonolysis of α -pinene in the presence of water vapour ($r < 16.9 \text{ g kg}^{-1}$) leads to the formation of more highly oxygenated compounds that are more hygroscopic and more volatile than compounds formed under dry conditions.

1 Introduction

It is well established that atmospheric aerosols have an important impact on the atmosphere with respect to their direct and indirect effects on climate (IPCC, 2007). The ability of aerosol particles to serve as cloud condensation nuclei (CCN) can impact cloud formation, cloud albedo and cloud lifetime (Albrecht, 1989; Petters et al., 2006; Twomey, 1977), potentially also modifying precipitation formation and intensity. The thermodynamic properties that determine the ability of particles to serve as CCN are directly related to their chemical composition. Thus, it is essential to simultaneously characterize aerosol thermodynamic properties and chemical composition. Recent improvements in aerosol chemistry instrumentation enable measurements of chemical composition at similar time resolutions to those of instruments used to study aerosol physical properties (Sullivan and Prather, 2005). For example, the Aerodyne Aerosol Mass Spectrometer (AMS, Jayne et al., 2000) was recently used in parallel with a Hygroscopicity-Tandem Differential Mobility



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Analyser (H-TDMA, Aklilu et al., 2006; Gysel et al., 2007; Shinozuka et al., 2009) and a multiple-relative humidity Differential Aerosol Sizing and Hygroscopicity-Spectrometer Probe (DASH-SP, Hersey et al., 2009) to correlate the hygroscopic growth factor with the chemical composition of the observed aerosol.

Particles can be directly emitted to the atmosphere as primary aerosol or be formed from condensation of gas-phase oxidation products of inorganic compounds or volatile organic compounds (VOCs); these VOCs are either of anthropogenic or biogenic origin. Monoterpenes such as α -pinene represent one important biogenic set of secondary organic aerosol precursors (SOA, Kanakidou et al., 2005), and for this reason many studies focused on the oxidation mechanisms and aerosol products formed from this precursor (e.g. Berndt et al., 2003; Fick et al., 2003; Iinuma et al., 2004; Ma et al., 2008; Yu et al., 2008; Shilling et al., 2008) and characterized the water uptake of the generated SOA (e.g. Duplissy et al., 2008; Meyer et al., 2009; Prenni et al., 2007; Saathoff et al., 2009; Varutbangkul et al., 2006).

One interesting aspect of SOA water uptake behaviour that has been observed is that the CCN activity of SOA particles is much larger than the result of extrapolation of hygroscopic growth factors obtained at 90% RH to supersaturated conditions (Prenni et al., 2007). Prenni et al. (2007) suggested several hypotheses to explain this type of behaviour but could not adequately constrain the proposed mechanisms because of measurements at $\text{RH} > 90\%$ were not available during their study. We therefore designed a set of experiments that included hygroscopic growth measurements at $\text{RH} > 90\%$. The obtained data suggest that the unusually large CCN activity of SOA is only in part due to reduced surface tension of the aqueous solution at the point of activation (Wex et al., 2009), as a strong increase in hygroscopicity was found for $\text{RH} > 98\%$. Further, Petters et al. (2009) suggest that the seeming disparity between hygroscopic growth and CCN activity is due to thermodynamic arguments related to the types of functional groups present in the likely SOA product molecules. In our previous papers (Petters et al., 2009; Wex et al., 2009), we were focused on the determination of the hygroscopic properties of the generated SOA, particularly on solving the issue regarding the generally observed low hygroscopic growth but rather high cloud droplet activation potential for SOA. In this third paper, we will focus on two main points: how the presence of water vapor induced modification on the chemical composition of the SOA and how the changes on the chemical composition can be linked to the observed deviation of the SOA volatility and hygroscopic properties.

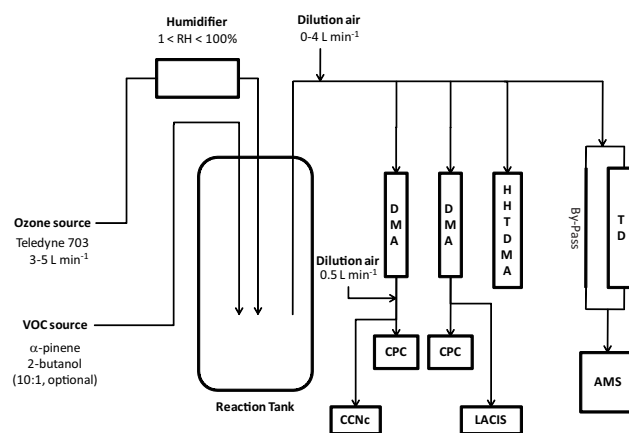


Fig. 1. Schematic of experimental setup for the measurements (Wex et al., 2009).

2 Setup description

2.1 SOA chamber

To generate the SOA, a stainless steel mixing chamber of 12 L at typical room temperature of 24 °C was used. The main advantage of this setup is to generate a constant and reproducible SOA flow with fixed concentrations of reactants. A detailed description of the system setup is presented in Fig. 1 and a more complete description can be found in Wex et al. (2009). Hydrocarbon-free dry air (also denoted as zero air) entered the chamber with a flow rate of 6 L min⁻¹ resulting in an average residence time of 2 min in the mixing chamber. An excess of the organic precursor and controlled levels of ozone generated using a Teledyne Instrument ozone generator (Model 703) were continuously injected into the chamber. The α -pinene vapour was generated by injecting a liquid flow of α -pinene, controlled by a microliter peristaltic pump into a stainless Swagelok tube, fitting reducer (SS-200-R-2) where it evaporated into 5–10 L min⁻¹ of zero air. In the absence of chemical reactions, α -pinene concentrations were in excess of that of ozone, i.e. <1 ppmv. So the amount of VOC that reacted was controlled with the ozone concentration. Then, the SOA yield was only dependent on the ozone concentration that was followed during all experiments. Moreover, during some experiments 2-butanol was added as an OH scavenger with a ratio of 2-butanol to α -pinene of 10:1. Finally, the concentration of water vapour inside the chamber was controlled by flowing the ozone containing air above a temperature controlled water bath. Absolute moisture content was determined by monitoring the dew point of the output flow of the mixing chamber with a chilled mirror dew point hygrometer. No seed particles were employed, thus the SOA was produced by homogeneous nucleation from the gas-phase and condensational growth on the newly formed particles. Hygroscopic properties, number size distributions, and chemical compositions of the SOA

were measured using the Leipzig Aerosol Cloud Interaction Simulator (LACIS, Wex et al., 2005), a CCN counter (Droplet Measurement Technologies, Boulder, Roberts and Nenes, 2005), a High Humidity-Tandem Differential Mobility Analyzer (HH-TDMA, Hennig et al., 2005), a Differential Mobility Particle Sizer (DMPS), and a Thermodenuder-Aerosol Mass Spectrometer (TD-AMS where the AMS was a High Resolution Time of Flight AMS, HR-ToF-AMS) system. The SOA mass concentrations achieved at steady-state in the reactor were varied by adjusting the concentrations of ozone entering the reactor. A summary of the experimental conditions is presented in Table 1. Conversion of the dew point temperature to water vapour pressure (p_w) followed Murphy and Koop (2005):

$$\ln(p_w) \approx 54.842763 - \frac{6763.22}{T} - 4.210 \ln(T) + 0.000367T + \tanh(0.0415 \times (T - 218.8)) \quad (1)$$

$$(53.878 - \frac{1331.22}{T} - 9.44523 \ln(T) + 0.014025T)$$

Then, results were expressed in water mixing ratio according to the following equation:

$$r = 0.622 \times \frac{p_w}{p - p_w} \quad (2)$$

where 0.622 is the ratio of the molecular weight of water to dry air, and p the atmospheric pressure.

2.2 SOA chemical composition and volatile/less-volatile characterization

Volatile and less-volatile fractions of the SOA were measured by a Thermodenuder-AMS (TD-AMS) coupled system that was directly connected to the outlet of the chamber. A description of this TD-AMS setup and its performance is given by Wu et al. (2009). Compared with other techniques, such as the Volatility-Tandem Differential Mobility Analyzer (V-TDMA), the main advantage of this setup is that it simultaneously provides information about the full aerosol mass size distribution and chemical composition of the fraction remaining after transit through the TD. The TD used in this setup consists of two successive sections: a heating section where the temperature can be set up to 300 °C followed by a cooling section set to room temperature. The residence time of particles in the heating section was approximately 9 s (Wehner et al., 2002). A detailed description of the TD is given by Wehner et al. (2002). In parallel, a stainless steel tube kept at room temperature was added as a bypass to the TD. Downstream of the TD and the bypass, the flow direction was controlled by two three-way valves. By changing the flow direction, the particles entering into the AMS could optionally be denuded as show in Fig. 1. Room temperature data (i.e. TD was by-passed) were measured at the beginning of the experiment and during the stabilization time between

two different temperature values set to the TD. Moreover, the mass fraction remaining behind the TD at room temperature was close to 100% (according to sampling error measurements) confirming the fact that we did not have significant changes of the particles within the TD. For each TD temperature, SOA was sampled for 15 to 20 min at a time resolution of 1 min. Data were then averaged for each experimental condition. In the following, error bars represent the experimental uncertainties estimated for each condition by the standard deviation and according to the classical propagation error calculations for ratios.

The AMS connected to the TD is an Aerodyne High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS, here referred to simply as AMS, DeCarlo et al., 2006; Jayne et al., 2000; Jimenez et al., 2003). Briefly, the AMS allows two alternative detection modes to measure the particle size distribution (PTOF-mode) and the chemical composition of the particle (MS-mode). Before detection by the time of flight mass spectrometer, the particles are flash vaporized by impaction on a heated surface (600 °C) and the vapours are ionized by an electron impact ionization source at 70eV.

2.3 Determination of the hygroscopic properties of the SOA

The hygroscopic growth factor was measured by using LACIS (Stratmann et al., 2004), which is a laminar flow tube equipped with an optical particle spectrometer at the outlet. Briefly, the water vapour saturation ratio inside the tube is determined by controlling the dew point of the entering air and the wall temperature of the LACIS tube. During our study, LACIS was operated in its sub-saturated mode allowing a relative humidity in the range 80 to 99.4% (Wex et al., 2005). The hygroscopic growth factor was obtained by comparing the measured particle diameter at the outlet of LACIS divided by the corresponding dry diameter (selected by a DMA prior to its introduction inside the LACIS system) (see Table 1 for detail of the selected particle diameter used for each experiment).

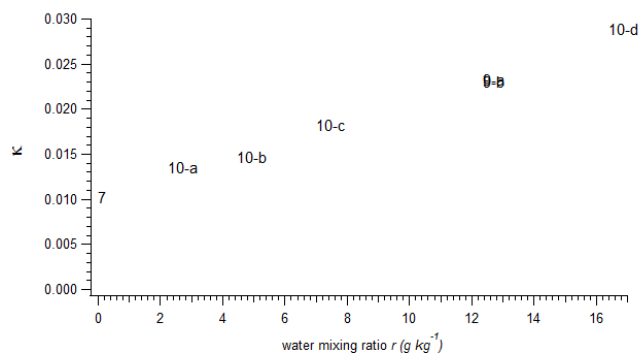
The hygroscopic properties of the particles can be characterized using the single parameter framework with parameter κ defined by Petters and Kreidenweis (2007):

$$\kappa = (gf^3 - 1)(1 - a_w)a_w^{-1} \quad (3)$$

where gf is the growth factor and a_w is the water activity in the particles. The water activity in the particles is computed from the RH to which the particles were exposed, assuming the particles are in equilibrium with their environment (Petters and Kreidenweis, 2007), and accounting for the particle curvature as described by the Kelvin term. As κ was found to vary significantly with aerosol water content, we only use values for κ derived from hygroscopic growth factor measurements at RH=99%. A discussion of the hygroscopic properties of SOA produced during these experiments and

Table 1. Details of the experimental conditions during this study.

| Experiment number | Reaction conditions | Ozone (ppbv) | OH-scavenger | Dew point (K) | water mixing ratio (g kg^{-1}) | LACIS diameter (nm) | Effective density (ρ_{eff}) |
|-------------------|-----------------------------------|--------------|--------------|---------------|---|---------------------|---|
| 7 | O_3 | 927 | Yes | 233 | 0.118 | 350 | 1.55 |
| 9-a | $\text{O}_3 + \text{H}_2\text{O}$ | 2568 | Yes | 290.5 | 12.684 | 275 | 1.42 |
| 9-b | $\text{O}_3 + \text{H}_2\text{O}$ | 2000 | Yes | 290.5 | 12.684 | 275 | 1.40 |
| 10-a | $\text{O}_3 + \text{H}_2\text{O}$ | 2534 | Yes | 268.4 | 2.717 | 300 | 1.40 |
| 10-b | $\text{O}_3 + \text{H}_2\text{O}$ | 2534 | Yes | 276.5 | 4.922 | 300 | 1.40 |
| 10-c | $\text{O}_3 + \text{H}_2\text{O}$ | 2534 | Yes | 282.5 | 7.469 | 300 | 1.40 |
| 10-d | $\text{O}_3 + \text{H}_2\text{O}$ | 2534 | Yes | 295 | 16.884 | 300 | 1.40 |

**Fig. 2.** Relationship between kappa (κ) and water vapour mixing ratio (r) inside the reaction chamber, for all experimental conditions tested (Table 1).

of the variation of κ with the RH to which the particles were exposed in LACIS can be found in Wex et al. (2009) and Petters et al. (2009).

3 Results

3.1 Evolution of the physical properties of SOA generated in the presence of water vapour

3.1.1 Relation between κ and water vapour concentration during the reaction

We observed that the hygroscopic behaviour changed with the water vapour mixing ratio, r expressed as g water per kg dry air, in the reaction chamber during SOA generation (Table 1). The relationship between κ and r is shown in Fig. 2: κ increases linearly with increasing mixing ratio. Since the temperature in the reaction chamber was nearly constant, a similar relationship existed between κ and r , indicating that the SOA was more hygroscopic when the reaction proceeded under humid conditions. Vesna et al. (2008) investigated the modification of the hygroscopic properties of fatty acids in the condensed phase following ozonolysis

at different relative humidities in a flow reactor. Their results for the polyunsaturated arachidonic acid showed an increase of the growth factor when the heterogeneous reaction of condensed-phase products with ozone proceeded in the presence of water vapour, similar to our observations for SOA products formed in the gas-phase from ozonolysis of α -pinene.

3.1.2 Effective density of the SOA

In parallel to the AMS measurements, particles were also sized by a DMPS system. The effective density (ρ_{eff}) of the SOA is estimated by combining AMS and DMPS measurements, assuming spherical SOA particles according to the work of Zelenyuk et al. (2008). The relationship between the vacuum aerodynamic diameter D_{va} (obtained from AMS measurements) and the mobility diameter D_m (derived from DMPS measurements) can be computed from DeCarlo et al. (2004):

$$\rho_{\text{eff}} = \frac{D_{va}}{D_m} \rho_0 \quad (4)$$

where ρ_0 is corresponding to the unit density (1 g cm^{-3}). The effective densities found for the different experiments are given in Table 1. In the presence of water vapour ($r > 0.1 \text{ g kg}^{-1}$), effective densities were $\sim 1.40 \text{ g cm}^{-3}$. This implies that the effective density, for the range over which reaction parameters were varied, was independent of the ozone concentration and r . However, when SOA generation occurred under dry conditions ($r \sim 0.1 \text{ g kg}^{-1}$), an effective density of 1.55 g cm^{-3} was found. These values are within the range of α -pinene densities (1.19 to 1.65 g cm^{-3}) reported by Koustenidou et al. (2007); Saathoff et al. (2009) and Shilling et al. (2009). The differences in effective density observed in our experiments under dry and wet conditions were $\sim 10\%$, close to the uncertainty of the method (Bahreini et al., 2005). The presence of water during the α -pinene ozonolysis can induce modification of the physical properties of the generated SOA as we previously observed (Petters et al., 2009; Wex et al., 2009); however changes in effective

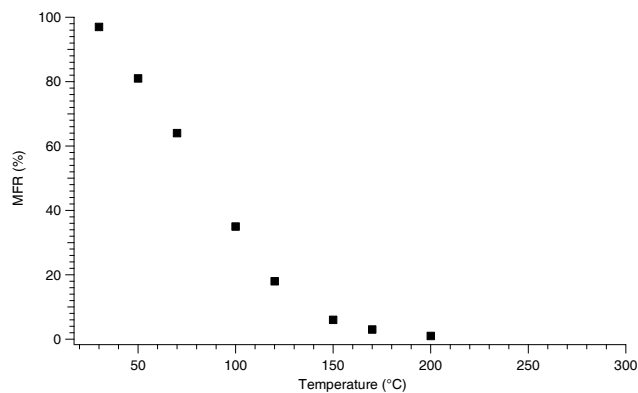


Fig. 3. Thermogram of the SOA formed under dry conditions (experiment number 7).

density are too small to be detected in our experimental conditions.

3.1.3 Dependence of SOA volatility on water vapour mixing ratios

Using the TD-AMS measurements, the volatile fraction of the SOA was characterized by the mass fraction remaining (MFR), which is defined as the ratio between the particle mass concentration measured at the given temperature to the particle mass concentration at room temperature. The resulting thermograms show similar profiles and a representative example from experiment 7 is presented in Fig. 3. The MFR rapidly decreases with increasing temperature in the TD and approaches zero at $\sim 200^\circ\text{C}$. At 100°C , MFR represents 35 % of the total aerosol mass. So far, only a few studies were focused on the volatility of α -pinene SOA produced in chamber experiments (e.g. Baltensperger et al., 2005; Jonsson et al., 2007; Meyer et al., 2009; Stanier et al., 2007). Baltensperger et al. (2005) obtained thermograms similar to ours after 10h of α -pinene photo-oxidation. Nevertheless, comparison of the MFR between different experiments is difficult due to the important and influencing parameter of residence time inside the heated part of the instrument (An et al., 2007).

In the following analysis, we will use the MFR at 100°C to examine the relation between the aerosol volatility and the chemical composition in relation to r . This temperature was chosen because it represents a reasonable compromise; it is hot enough so that a significant fraction of the SOA is evaporated but the less-volatile fraction remains large enough to obtain accurate AMS measurements. The relation between the MFR at 100°C and the κ values of the corresponding experiment is presented in Fig. 4. We clearly observed that the MFR at 100°C decreased when κ increased, and the MFR approached a constant value at the highest κ observed. Meyer et al. (2009) demonstrated that the more hygroscopic compounds of the SOA generated from α -pinene photo-oxidation were found in the more volatile fraction of the SOA, as ob-

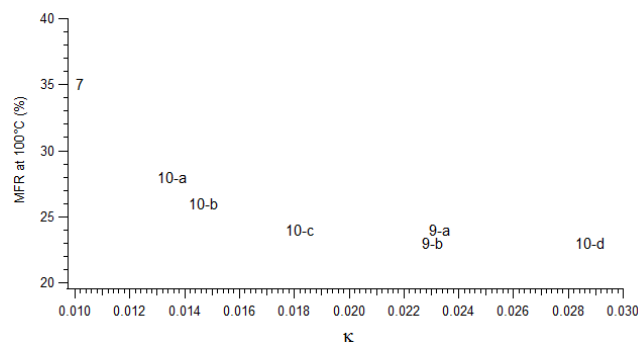


Fig. 4. The variation of MFR at 100°C with the hygroscopic properties of the SOA (numbers refer to the experiments listed in Table 1).

served from measurements of the hygroscopic properties of the SOA using a Volatility Hygroscopicity-Tandem Differential Mobility Analyzer (VH-TDMA). Jonsson et al. (2007), using V-TDMA measurements of α -pinene ozonolysis SOA, also observed that SOA generated in the presence of water vapour was more volatile than that generated in dry conditions. The authors noted that the most likely explanation of the modification of the SOA physico-chemical properties was a change in the chemical composition of the SOA, induced by slightly differing oxidation mechanisms between dry and humidified conditions. In this study, the simultaneous increase of κ and the volatile fraction of the SOA with r in the chamber also suggest that the volatile fraction is more hygroscopic than the less-volatile fraction.

3.2 Volatility and chemical composition

3.2.1 Impact of water vapour on SOA composition at room temperature and 100°C

Our results presented above suggest that the presence of water vapour during the ozonolysis of α -pinene induces modifications of the SOA physico-chemical properties, i.e. particle hygroscopicity and volatility, which are likely to be linked to changes in composition. To gain insight into the changes in the SOA chemical composition with varying water vapour concentrations during SOA generation, two different approaches were used. First, we compared the contribution of the fragment m/z 44 to the total organic signal for each experiment (ratio m/z 44 to organic signal). The mass m/z 44 is mostly corresponding to the fragment CO_2^+ coming from multifunctional organic acids, according to Takegawa et al. (2007), who determined the contribution of dicarboxylic and ω -oxocarboxylic acids to m/z 44 using field data and laboratory investigations. In our measurements, fragment m/z 44 has a linear relationship with the total mass loading in the presence and absence of water vapour in the chamber (not shown). For this reason the concentration of m/z 44 was

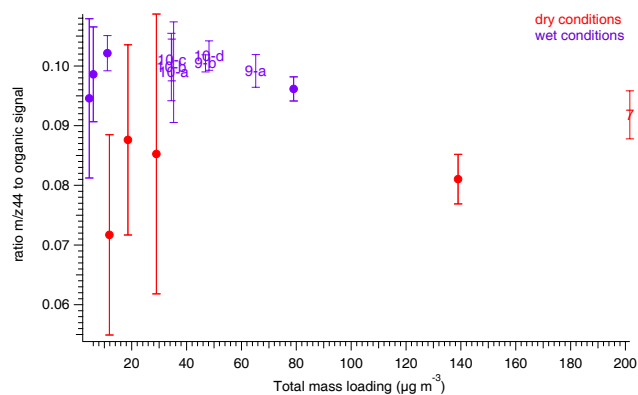


Fig. 5. Influence of the presence of water vapour during SOA generation to the oxidation level of the generated particles during preliminary test. Numbers in the plot refer to those experiments that are used in the following examinations presented in this study.

normalized to the total organic mass loading to consider only the impact of r .

However, the relative contributions of m/z 44 to total organic in wet and dry conditions differ (Fig. 5). Under wet conditions, the ratio m/z 44 to organic signal is always higher than ratio obtained in dry conditions and this ratio is approximately independent of the aerosol mass loading. This suggests that SOA are more acidic when the reaction proceeds under humid conditions. The ratio of normalized m/z 44 in wet conditions to normalized m/z 44 in dry condition is ~ 1.15 for all mass loading which represent impact of the water vapour on the α -pinene ozonolysis mechanisms. At low mass loadings ($< \sim 10$ – $20 \mu\text{g m}^{-3}$), the ratio m/z 44 to organic signal decreases for both humid and dry reaction conditions. This is consistent with the findings of King et al. (2009) who show that mass loading effects on κ only occur at low mass concentrations. The remaining question is then how κ and ratio m/z 44 to organic signal are related and this will be discussed further below.

Figure 6 shows that the ratio m/z 44 to organic signal was found to be around 9–10% in the presence of water vapour, which is in the same range as obtained by Alfarra et al. (2006) and Duplissy et al. (2008) during photo-oxidation of α -pinene, but was lower for the SOA generated under dry conditions. However, looking at Fig. 6 and considering the experimental uncertainties no strong trend concerning the dependence of ratio m/z 44 to organic signal on water mixing ratio can be observed. Figure 7 (left panel) shows that the ratio m/z 44 to organic signal increased also only slightly as κ increased between dry and wet-generation conditions.

We also considered the ratios of the observed mass concentrations of the $\text{C}_x\text{H}_y\text{O}_z^+$ family to the C_xH_y^+ family and CO_2^+ to the C_xH_y^+ family, to estimate the oxidation level of the SOA. The mass concentrations of the $\text{C}_x\text{H}_y\text{O}_z^+$ and C_xH_y^+ families were obtained by summing up the signal in-

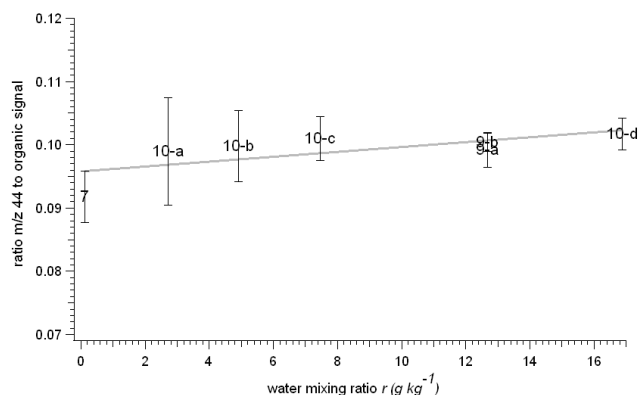


Fig. 6. Variation of the ratio m/z 44 to organic signal with water vapour mixing ratio (r) in the reaction chamber (numbers refer to the experiments listed in Table 1).

tensities of all the corresponding ions present in the mass spectra. If the CO_2^+ fragment is specific to acid functional groups, $\text{C}_x\text{H}_y\text{O}_z^+$ may be used to identify the contributions of other oxygenated groups, such as aldehydes and alcohols, and C_xH_y^+ may be assumed to represent contributions from aliphatic groups. In the following, for simplification, we use the notation CHO and CH for $\text{C}_x\text{H}_y\text{O}_z^+$ and C_xH_y^+ respectively. Using a similar approach as described above for m/z 44, the ratios CO_2^+/CH and CHO/CH are plotted as a function of the observed κ values in Fig. 7 (middle and right panels, respectively). In opposition to the previous observations of the m/z 44 to organic signal, considering the CO_2^+/CH and ratio CHO/CH a stronger trend, i.e. increasing ratios with increasing κ , becomes obvious. It should be noted that these conclusions are based on a limited number of measurements and should be evaluated using more experimental data.

In Fig. 8, we present data from experiment 10, in which SOA generation occurred at constant α -pinene and ozone concentrations but using different r in the chamber. The two ratios CHO/CH and CO_2^+/CH slightly increased with increasing water mixing ratio during generation, with slopes of $(3.32 \pm 0.14) \cdot 10^{-5}$ and $(4.12 \pm 0.31) \cdot 10^{-6}$, respectively. This finding suggests that the oxidation level of the SOA increased as the water vapour mixing ratio increased, and may be interpreted as increase in oxygenated functional groups relative to the total number of carbon molecules in the SOA. Vesna et al. (2008) used the ratio of carboxylic acid protons to aliphatic protons obtained by $^1\text{H-NMR}$ analysis to characterise the oxidation level of the products of ozonolysis of arachidonic acid in the condensed phase. This ratio increased with the relative humidity, up to double the initial value. Although the chemical systems and analysis methods differed between our study and theirs, the role of water in modifying the oxidation products seems to be similar in both.

Figure 8 also shows the ratios obtained after passing the SOA through the TD operated at 100°C . The ratio CO_2^+/CH

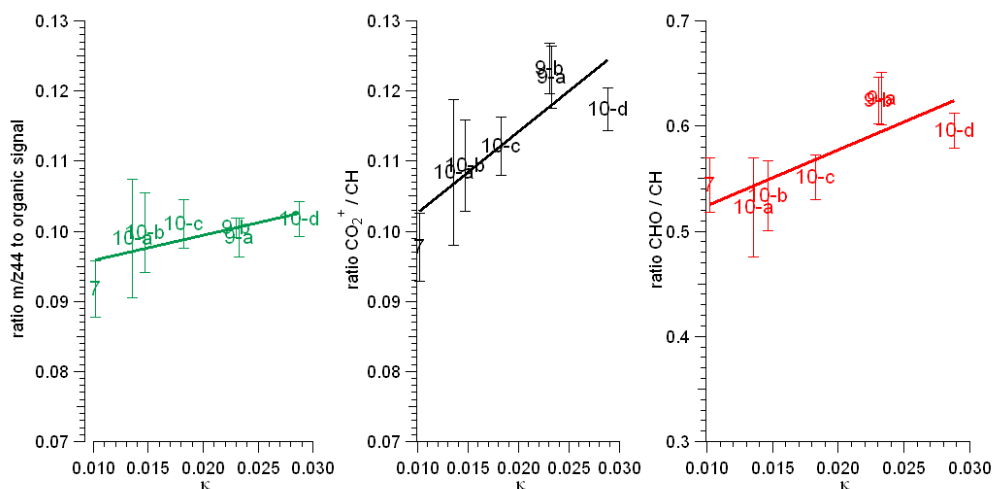


Fig. 7. Dependence of chemical composition tracers (ratio m/z 44 to organic signal in left panel, ratio CO_2^+/CH in middle panel and ratio CHO/CH in right panel) on hygroscopic parameter κ (numbers refer to the experiments listed in Table 1).

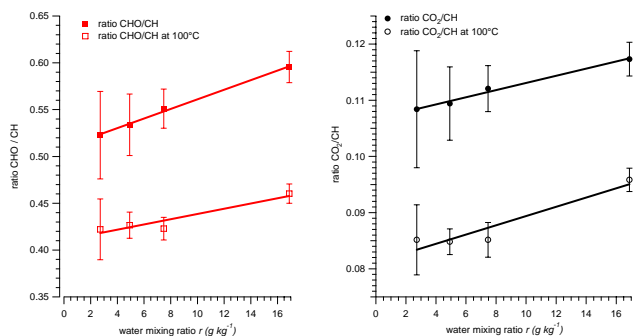


Fig. 8. Variation of the ratios CHO/CH and CO_2^+/CH with the water vapour mixing ratio (r) in experiment 10, before and after passing the SOA through the TD operated at 100°C .

in the MFR still increased with increasing r with a slope of $(5.31 \pm 0.12) \times 10^{-6}$, similar to the slope observed at room temperature. However, while the overall slope of the r – CO_2^+/CH relationship is similar at room temperature and 100°C , the shape is not. For $r < 8 \text{ g kg}^{-1}$, CO_2^+/CH is approximately constant. Only for $r > 16 \text{ g kg}^{-1}$ the CO_2^+/CH increases. The main difference between the $\text{MFR}_{100^\circ\text{C}}$ and room temperature SOA is the fraction of CO_2^+ fragments, which decreases by $\sim 20\%$ for the $\text{MFR}_{100^\circ\text{C}}$ samples. Because this ratio is approximately independent of r , we conclude that any additional polycarboxylic acid compounds produced in the experiments conducted in the presence of higher water vapour mixing ratios were not evaporated at 100°C , and contributed to the MFR at this temperature.

The ratio CHO/CH in the MFR from the heated samples varied with r with a slope of $(1.80 \pm 0.43) \times 10^{-5}$, which is about half of the value obtained for the ambient temperature samples. In this case, additional SOA products found

in this fraction that formed in the presence of water vapour were evaporated when the SOA was heated up to 100°C . Thus, in contrast to observations for the ratio CO_2^+/CH , the CHO fragments seemed to become more volatile with increasing water vapour mixing ratio. The results presented in Fig. 8 suggest that the observed overall increasing volatility of the SOA with increases in r (Fig. 4) was mainly due to CHO groups, while polycarboxylic acids contributed instead to the less-volatile fraction. Considering that CO_2^+ represents the most oxygenated functions while CHO represents the less oxygenated ones, we can conclude that the observed increase of SOA volatility with increasing of water vapour mixing ratio is mainly induced by the less oxygenated compounds (i.e. CHO) and the most oxygenated ones appear to be less volatile. In other words, the most oxygenated compounds were less volatile at 100°C than the less oxygenated ones. Our results are consistent with the observation that, for constant carbon chain length, the addition of a carboxylic group lowers the vapour pressure by several orders of magnitudes while the addition of a hydroxyl or carbonyl group has less effect on volatility (Chattopadhyay and Ziemann, 2005).

3.2.2 Correspondence with proposed α -pinene ozonolysis mechanisms

Although the AMS is not able to provide a complete molecular chemical composition of the SOA, our results can be integrated with the most recently postulated α -pinene ozonolysis mechanisms. So far, only a few studies addressed the impact of relative humidity on ozonolysis mechanisms (e.g., Berndt et al., 2003; Cocker et al., 2001; Docherty et al., 2005; Fick et al., 2003; Jonsson et al., 2008; Ma et al., 2008; Pommer et al., 2004; Jonsson et al., 2006; Warscheid and Hoffmann, 2001). The modification of the ozonolysis mechanisms in the presence of water vapour remains unclear, and results

available in the literature are somewhat contradictory. For example, Ma et al. (2008) observed that pinonic acid and pinonaldehyde formation strongly depended on the relative humidity. Their results are in agreement with those reported by Fick et al. (2003), and with the increase of the pinonaldehyde molecular yield observed by Warscheid and Hoffmann (2001). However, they are in contradiction with the results of Berndt et al. (2003), who observed a slightly lower gaseous pinonaldehyde yield in the presence of more water vapour. Different experimental conditions were used in these studies (initial concentration of reactants, relative humidity, presence and nature of the OH-scavenger), complicating the comparison. Nevertheless, it is commonly accepted that water vapour may interact with the stabilized Criegee intermediate, leading to a modification of the yield of the different oxidation pathways.

The recent α -pinene ozonolysis mechanism suggested by Ma et al. (2008) predicts the formation of two stabilized Criegee Intermediates (CI) in equal proportions. In the presence of water molecules, the first CI leads to the formation of pinonaldehyde and pinonic acid, and the second CI leads to the formation of only pinonaldehyde, as illustrated in Fig. 9. We suggest that these two compounds both contribute to the family CHO, but only pinonic acid contributes to the family CO_2^+ . Moreover, a comparison of the vapour pressures of these two reaction products demonstrates that pinonaldehyde is more volatile than pinonic acid (Capouet and Müller, 2006), which may be an explanation for the difference in volatility observed for the ratios CHO/CH and CO_2^+ /CH. Nevertheless, more detailed investigations are needed on this subject to confirm the products formed in the varying conditions and how they contribute to both hygroscopicity and volatility.

4 Conclusion

The properties of SOA produced in a continuous flow reaction chamber from α -pinene dark ozonolysis were studied for varying levels of water vapour mixing ratio during the reaction and aerosol formation. Modifications of the hygroscopic properties, volatility, and chemical compositions of total SOA as well as of the less-volatile fractions were observed. The parameter κ , expressing the hygroscopic properties of the SOA, depended on water vapour concentrations inside the chamber during SOA generation. In contrast, the effective density of the SOA was found to be independent of ozone concentration and of the different values of r within experimental uncertainty. Thermodenuder measurements showed that SOA evaporated completely at temperatures slightly below 200 °C. Approximately 65% of the SOA mass concentration was evaporated at 100 °C. The volatile fraction at 100 °C of the SOA increased with increasing water vapour mixing ratio in the mixing chamber.

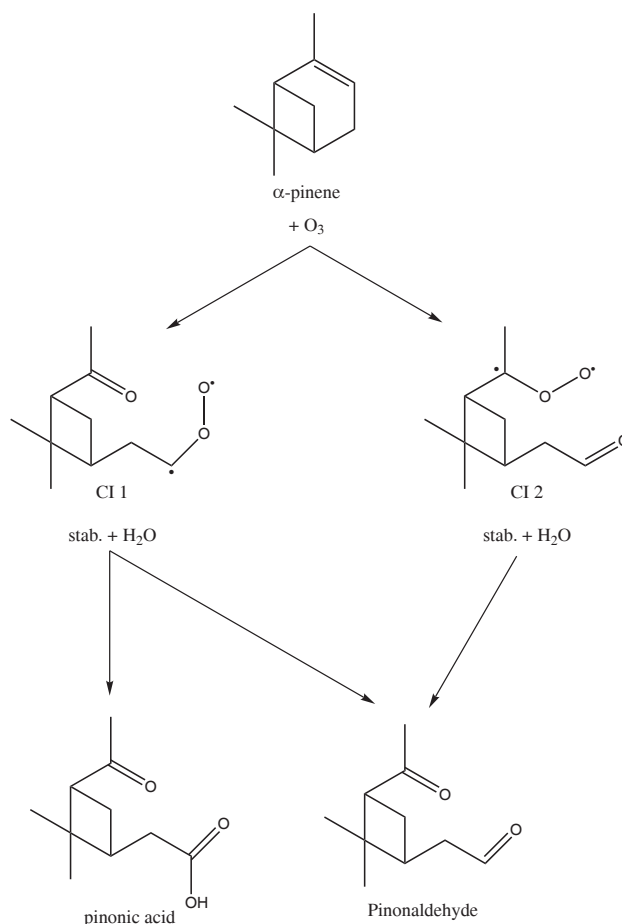


Fig. 9. Partial mechanism for α -pinene ozonolysis in the presence of water vapour, from Ma et al. (2008).

The oxidation level of the SOA was described using three parameters; the ratios m/z 44 to organics, CHO/CH and CO_2^+ /CH. All three parameters showed some trend with the hygroscopicity of the particles, which in turn was driven by changes in water vapour concentration during the reaction and corresponding increases in oxygenated compounds. The values of these ratios after heating the sample to 100 °C showed that the most oxygenated compounds (CO_2^+) were less volatile at 100 °C than the less oxygenated ones (CHO). The formation of more oxygenated compounds in the presence of water vapour is in agreement with current understanding of the interaction of water with the stabilized Criegee intermediate, leading to the formation of more pinonaldehyde (CHO) and pinonic acid (CHO and CO_2^+). Furthermore, comparison of their vapour pressures showed that pinonic acid is less volatile than pinonaldehyde in support of the observed volatility differences between the fragments (CHO and CO_2^+).

The ozonolysis of α -pinene in the presence of water vapour leads to the formation of highly oxygenated compounds that are more hygroscopic and more volatile than

compounds formed under dry conditions. Our results also demonstrated that the more volatile part of the SOA corresponded to the more hygroscopic fraction, which is in agreement with the findings of Meyer et al. (2009) but also with conclusions of Asa-Awuku et al. (2009) on β -caryophyllene SOA. Modification of the volatility and hygroscopicity may also contribute to modifications in the yield of SOA and to the ability of the SOA particles to serve as CCN in the atmosphere. However, further studies will be needed to improve the mechanistic understanding of the modification of the physical properties and chemical composition of SOA generated under varying humidity conditions.

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References

- Aklilu, Y., Mozurkewich, M., Prenni, A. J., Kreidenweis, S. M., Alfarra, M. R., Allan, J. D., Anlauf, K., Brook, J., Leaitch, W. R., Sharma, S., Boudries, H., and Worsnop, D. R.: Hygroscopicity of particles at two rural, urban influenced sites during Pacific 2001: Comparison with estimates of water uptake from particle composition, *Atmos. Environ.*, **40**, 2650–2661, doi:10.1016/j.atmosenv.2005.11.063, 2006.
- Albrecht, B. A.: Aerosols, Cloud Microphysics, and Fractional Cloudiness, *Science*, **245**, 1227–1230, 1989.
- Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prévôt, A. S. H., Worsnop, D. R., Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the photooxidation of anthropogenic and biogenic precursors in a reaction chamber, *Atmos. Chem. Phys.*, **6**, 5279–5293, 2006, <http://www.atmos-chem-phys.net/6/5279/2006/>.
- An, W. J., Pathak, R. K., Lee, B. H., and Pandis, S. N.: Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol, *J. Aerosol Sci.*, **38**, 305–314, doi:10.1016/j.jaerosci.2006.12.002, 2007.
- Asa-Awuku, A., Engelhart, G. J., Lee, B. H., Pandis, S. N., and Nenes, A.: Relating CCN activity, volatility, and droplet growth kinetics of β -caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, **9**, 795–812, 2009, <http://www.atmos-chem-phys.net/9/795/2009/>.
- Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and *m*-xylene using an Aerodyne aerosol mass spectrometer, *Environ. Sci. Technol.*, **39**, 5674–5688, doi:10.1021/Es048061a, 2005.
- Baltensperger, U., Kalberer, M., Dommen, J., Paulsen, D., Alfarra, M. R., Coe, H., Fisseha, R., Gascho, A., Gysel, M., Nyeki, S., Sax, M., Steinbacher, M., Prévôt, A. S. H., Sjogren, S., Wein-gartner, E., and Zenobi, R.: Secondary organic aerosols from anthropogenic and biogenic precursors, *Faraday Discuss.*, **130**, 265–278, doi:10.1039/b417367h, 2005.
- Berndt, T., Böge, O., and Stratmann, F.: Gas-phase ozonolysis of alpha-pinene: gaseous products and particle formation, *Atmos. Environ.*, **37**, 3933–3945, doi:10.1016/S1352-2310(03)00501-6, 2003.
- Capouet, M. and Müller, J. F.: A group contribution method for estimating the vapour pressures of alpha-pinene oxidation products, *Atmos. Chem. Phys.*, **6**, 1455–1467, 2006, <http://www.atmos-chem-phys.net/6/1455/2006/>.
- Chattopadhyay, S., and Ziemann, P. J.: Vapor pressures of substituted and unsubstituted monocarboxylic and dicarboxylic acids measured using an improved thermal desorption particle beam mass spectrometry method, *Aerosol Sci. Technol.*, **39**, 1085–1100, doi:10.1080/02786820500421547, 2005.
- Cocker, D. R., Clegg, S. L., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas-particle partitioning of secondary organic aerosol. Part I: α -pinene/ozone system, *Atmos. Environ.*, **35**, 6049–6072, 2001.
- DeCarlo, P., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part I: Theory, *Aerosol Sci. Technol.*, **38**, 1185–1205, doi:10.1080/027868290903907, 2004.
- DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, **78**, 8281–8289, doi:10.1021/ac061249n, 2006.
- Docherty, K. S., Wu, W., Lim, Y. B., and Ziemann, P. J.: Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O₃, *Environ. Sci. Technol.*, **39**, 4049–4059, doi:10.1021/es050228s, 2005.
- Duplissy, J., Gysel, M., Alfarra, M. R., Dommen, J., Metzger, A., Prévôt, A. S. H., Weingartner, E., Laaksonen, A., Raatikainen, T., Good, N., Turner, S. F., McFiggans, G., and Baltensperger, U.: Cloud forming potential of secondary organic aerosol under near atmospheric conditions, *Geophys. Res. Lett.*, **35**, L03818, doi:10.1029/2007GL031075, 2008.
- Fick, J., Pommer, L., Nilsson, C., and Andersson, B.: Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of α -pinene, *Atmos. Environ.*, **37**, 4087–4096, doi:10.1016/S1352-2310(03)00522-3, 2003.
- Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, *Atmos. Chem. Phys.*, **7**, 6131–6144, 2007, <http://www.atmos-chem-phys.net/7/6131/2007/>.
- Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A Tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity, *J. Aerosol Sci.*, **36**, 1210–1223, doi:10.1016/j.jaerosci.2005.01.005, 2005.
- Hersey, S. P., Sorooshian, A., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Aerosol hygroscopicity in the marine atmosphere: a closure study using high-time-resolution, multiple-RH DASH-SP and size-resolved C-ToF-AMS data, *Atmos. Chem. Phys.*, **9**,

- 2543–2554, 2009,
<http://www.atmos-chem-phys.net/9/2543/2009/>.
- Iinuma, Y., Böge, O., Gnauk, T., and Herrmann, H.: Aerosol-chamber study of the alpha-pinene/O₃ reaction: influence of particle acidity on aerosol yields and products, *Atmos. Environ.*, 38, 761–773, doi:10.1016/j.atmosenv.2003.10.015, 2004.
- Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for size and composition analysis of sub-micron particles, *Aerosol Sci. Technol.*, 33, 49–70, 2000.
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using an Aerodyne Mass Spectrometer, *J. Geophys. Res.-Atmosp.*, 108, 8425, doi:10.1029/2001JD001213, 2003.
- Jonsson, A. M., Hallquist, M., and Ljungstrom, E.: Impact of humidity on the ozone initiated oxidation of limonene, Δ^3 -carene, and α -pinene, *Environ. Sci. Technol.*, 40, 188–194, doi:10.1021/es051163w, 2006.
- Jonsson, A. M., Hallquist, M., and Saathoff, H.: Volatility of secondary organic aerosols from the ozone initiated oxidation of α -pinene and limonene, *J. Aerosol Sci.*, 38, 843–852, doi:10.1016/j.jaerosci.2007.06.008, 2007.
- Jonsson, A. M., Hallquist, M., and Ljungstrom, E.: Influence of OH scavenger on the water effect on secondary organic aerosol formation from ozonolysis of limonene, Δ^3 -carene, and α -pinene, *Environ. Sci. Technol.*, 42, 5938–5944, doi:10.1021/es702508y, 2008.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005,
<http://www.atmos-chem-phys.net/5/1053/2005/>.
- King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q., and Martin, S. T.: Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings, *Atmos. Chem. Phys.*, 9, 2959–2972, 2009,
<http://www.atmos-chem-phys.net/9/2959/2009/>.
- Koustenidou, E., Pathak, R. V., and Pandis, S. N.: An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, *Aerosol Sci. Technol.*, 41, 1002–1010, doi:10.1080/02786820701666270, 2007.
- Ma, Y., Russell, A. T., and Marston, G.: Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of α -pinene, *Phys. Chem. Chem. Phys.*, 10, 4294–4312, doi:10.1039/b803283a, 2008.
- Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Fletcher, C., Good, N., McFiggans, G., Jonsson, A. M., Hallquist, M., Baltensperger, U., and Ristvoski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and un-seeded SOA particles, *Atmos. Chem. Phys.*, 9, 721–732, 2009,
<http://www.atmos-chem-phys.net/9/721/2009/>.
- Murphy, D. M. and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, *Q. J. Roy. Meteor. Soc.*, 131, 1539–1565, doi:10.1256/Qj.04.94, 2005.
- Petters, M. D., Snider, J. R., Stevens, B., Vali, G., Faloona, I., and Russell, L. M.: Accumulation mode aerosol, pockets of open cells, and particle nucleation in the remote subtropical Pacific marine boundary layer, *J. Geophys. Res.-Atmosp.*, 111, D02206, doi:10.1029/2004jd005694, 2006.
- Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961–1971, 2007,
<http://www.atmos-chem-phys.net/7/1961/2007/>.
- Petters, M. D., Wex, H., Hallberger, E., Poulain, L., Carrico, C. M., McMeeking, G. R., Kreidenweis, S. M., Stratmann, F., and Massling, A.: Towards closing the gap between hygroscopicity and activation for secondary organic aerosol: Part II – theoretical approaches, *Atmos. Chem. Phys.*, 9, 3999–4009, 2009,
<http://www.atmos-chem-phys.net/9/3999/2009/>.
- Pommer, L., Fick, J., Andersson, B., and Nilsson, C.: The influence of O₃, relative humidity, NO and NO₂ on the oxidation of α -pinene and Δ^3 -carene, *J. Atmos. Chem.*, 48, 173–189, 2004.
- Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J., and Ziemann, P. J.: Cloud droplet activation of secondary organic aerosol, *J. Geophys. Res.-Atmosp.*, 112, D10223, doi:10.1029/2006jd007963, 2007.
- Roberts, G. C. and Nenes, A.: A continuous-flow stream-wise thermal-gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Technol.*, 39, 206–221, doi:10.1080/027868290913988, 2005.
- Saathoff, H., Naumann, K. H., Möhler, O., Jonsson, Å. M., Hallquist, M., Kiendler-Scharr, A., Mentel, T. F., Tillmann, R., and Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α -pinene and limonene, *Atmos. Chem. Phys.*, 9, 1551–1577, 2009,
<http://www.atmos-chem-phys.net/9/1551/2009/>.
- Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., McKinney, K. A., and Martin, S. T.: Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of α -pinene, *Atmos. Chem. Phys.*, 8, 2073–2088, 2008, <http://www.atmos-chem-phys.net/8/2073/2008/>.
- Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of α -pinene SOA particles, *Atmos. Chem. Phys.*, 771–782, 2009.
- Shinozuka, Y., Clarke, A. D., DeCarlo, P. F., Jimenez, J. L., Dunlea, E. J., Roberts, G. C., Tomlinson, J. M., Collins, D. R., Howell, S. G., Kapustin, V. N., McNaughton, C. S., and Zhou, J.: Aerosol optical properties relevant to regional remote sensing of CCN activity and links to their organic mass fraction: airborne observations over Central Mexico and the US West Coast during MILAGRO/INTEX-B, *Atmos. Chem. Phys.*, 9, 6727–6742, 2009, <http://www.atmos-chem-phys.net/9/6727/2009/>.
- Stanier, C. O., Pathak, R. K., and Pandis, S. N.: Measurements of the volatility of aerosols from α -pinene ozonolysis, *Environ. Sci. Technol.*, 41, 2756–2763, doi:10.1021/es0519280, 2007.
- Stratmann, F., Kiselev, A., Wurzler, S., Wendisch, M., Heintzenberg, J., Charlson, R. J., Diehl, K., Wex, H., and Schmidt, S.: Laboratory studies and numerical simulations of cloud droplet formation under realistic super-saturation conditions, *J. Atmos. Ocean. Tech.*, 21, 876–887, doi:10.1175/1520-0426(2004)021, 2004.

- Sullivan, R. C. and Prather, K. A.: Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation, *Anal. Chem.*, **77**, 3861–3885, doi:10.1021/ac050716i, 2005.
- Takegawa, N., Miyakawa, T., Kawamura, K., and Kondo, Y.: Contribution of selected dicarboxylic and ω -Oxocarboxylic acids in ambient aerosol to the m/z 44 signal of an Aerodyne aerosol mass spectrometer, *Aerosol Sci. Technol.*, **41**, 418–437, doi:10.1080/02786820701203215, 2007.
- Twomey, S.: Influence of Pollution on the Shortwave Albedo of Clouds, *J. Aerosol Sci.*, **34**, 1149–1152, 1977.
- Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, *Atmos. Chem. Phys.*, **6**, 2367–2388, 2006, <http://www.atmos-chem-phys.net/6/2367/2006/>.
- Vesna, O., Sjogren, S., Weingartner, E., Samburova, V., Kalberer, M., Gaggeler, H. W., and Ammann, M.: Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions, *Atmos. Chem. Phys.*, **8**, 4683–4690, 2008, <http://www.atmos-chem-phys.net/8/4683/2008/>.
- Warscheid, B., and Hoffmann, T.: On-line measurements of α -pinene ozonolysis products using an atmospheric pressure chemical ionisation ion-trap mass spectrometer, *Atmos. Environ.*, **35**, 2927–2940, 2001.
- Wehner, B., Philippin, S., and Wiedensohler, A.: Design and calibration of a thermodenuder with an improved heating unit to measure the size-dependent volatile fraction of aerosol particles, *J. Aerosol Sci.*, **33**, 1087–1093, 2002.
- Wex, H., Kiselev, A., Stratmann, F., and Zoboki, J.: Measured and modeled equilibrium sizes of NaCl and $(\text{NH}_4)_2\text{SO}_4$ particles at relative humidities up to 99.1%, *J. Geophys. Res.-Atmosp.*, **110**, D21212, doi:10.1029/2004JD005507, 2005.
- Wex, H., Petters, M. D., Hallberger, E., Poulain, L., Carrico, C. M., McMeeking, G. R., Kreidenweis, S. M., Stratmann, F., and Massling, A.: Towards closing the gap between hygroscopicity growth factor and activation of secondary organic aerosol: Part I - Evidence of measurements, *Atmos. Chem. Phys.*, **9**, 3987–3997, 2009, <http://www.atmos-chem-phys.net/9/3987/2009/>.
- Wu, Z., Poulain, L., Wehner, B., Wiedensohler, A., and Herrmann, H.: Characterization of the volatile fraction of laboratory-generated aerosol particles by thermodenuder-Aerosol Mass Spectrometer coupling experiments, *J. Aerosol Sci.*, **40**, 603–612, doi:10.1016/j.jaerosci.2009.03.007, 2009.
- Yu, Y., Ezell, M. J., Zelenyuk, A., Imre, D., Alexander, L., Ortega, J., D'Anna, B., Harmon, C. W., Johnson, S. N., and Finlayson-Pitts, B. J.: Photooxidation of α -pinene at high relative humidity in the presence of increasing concentrations of NO_x , *Atmos. Environ.*, **42**, 5044–5060, doi:10.1016/j.atmosenv.2008.02.026, 2008.
- Zelenyuk, A., Yang, J., Song, C., Zaveri, R. A., and Imre, D.: A New Real-Time Method for Determining Particles' Sphericity and Density: Application to Secondary Organic Aerosol Formed by Ozonolysis of α -Pinene, *Environ. Sci. Technol.*, **42**, 8033–8038, doi:10.1021/es8013562, 2008.