

1 Secondary Organic Aerosol (SOA) Formation from Hydroxyl 2 Radical Oxidation and Ozonolysis of Monoterpenes

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11 Abstract

12 Oxidation by hydroxyl radical (OH) and ozonolysis are the two major pathways of daytime
13 biogenic volatile organic compounds (VOCs) oxidation and secondary organic aerosol (SOA)
14 formation. In this study, we investigated the particle formation of several common monoterpenes
15 (α -pinene, β -pinene, and limonene) by OH dominated oxidation, which has seldom been
16 investigated. OH oxidation experiments were carried out in the SAPHIR chamber in Jülich,
17 Germany, at low NO_x (0.01~1ppbV) and low ozone (O₃) concentration (<20 ppbV). OH
18 concentration and total OH reactivity (k_{OH}) were measured directly, and through this the overall
19 reaction rate of total organics with OH in each reaction system was quantified. Multi-generation
20 reaction process, particle growth, new particle formation, particle yield, and chemical
21 composition were analyzed and compared with that of monoterpene ozonolysis. Multi-generation
22 products were found to be important in OH dominated SOA formation. The relative role of
23 functionalization and fragmentation in the reaction process of OH oxidation was analyzed by
24 examining the particle mass and the particle size as a function of OH dose. We developed a
25 novel method which quantitatively links particle growth to the reaction rate of OH with total
26 organics in a reaction system. This method was also used to analyze the evolution of
27 functionalization and fragmentation of organics in the particle formation by OH oxidation. It
28 shows that functionalization of organics was dominant in the beginning of the reaction (within

1 two lifetimes of the monoterpene) and fragmentation started to play an important role after that.
2 We compared particle formation from OH oxidation with that from pure ozonolysis. In
3 individual experiments, growth rates of the particle size did not necessarily correlate with the
4 reaction rate of monoterpene with OH and O₃. Comparing the size growth rates at the similar
5 reaction rates of monoterpene with OH or O₃ indicates that generally, OH oxidation and
6 ozonolysis had similar efficiency in particle growth. The SOA yield of α-pinene and limonene
7 by ozonolysis was higher than that of OH oxidation. Aerosol mass spectrometry (AMS) shows
8 SOA elemental composition from OH oxidation follows a slope shallower than -1 in the O/C
9 versus H/C diagram, indicating that oxidation proceeds without significant loss of hydrogen.
10 SOA from OH oxidation had higher H/C ratios than SOA from ozonolysis. In ozonolysis, a
11 process with significant hydrogen loss seemed to play an important role in SOA formation.

12

13 **1 Introduction**

14 As an important class of atmospheric aerosol, organic aerosol (OA) comprises a significant
15 fraction of aerosol mass. It accounts for around 50% of dry tropospheric submicron aerosol mass
16 in many urban and rural locations (Kanakidou et al., 2005; Jimenez et al., 2009; Zhang et al.,
17 2011). OA has an important impact on air pollution, human health and climate on the regional
18 and global scale. A large fraction of organic aerosol is contributed by secondary organic aerosol
19 (SOA). In spite of intensive studies in the recent years, the source of SOA still has considerable
20 uncertainties with the estimated global source ranging from 120 to 1820 Tg a⁻¹ (Hallquist et al.,
21 2009; Spracklen et al., 2011; Goldstein and Galbally, 2007). SOA is believed to mainly originate
22 from the biogenic volatile organic compounds (BVOCs) from plants (Hallquist et al., 2009).
23 Among them, monoterpenes are important due to their high emission rates and high reactivity
24 (Chung and Seinfeld, 2002; Guenther et al., 1995; Guenther et al., 2012).

25 The impact of SOA on the radiation budget of the Earth thus depends on its particle number
26 concentration, size distribution and composition, which affect optical properties and cloud
27 condensation nuclei (CCN) activity of an aerosol (Andreae and Rosenfeld, 2008). Understanding
28 particle formation and growth is therefore critical for assessing the impact of SOA.

1 Particle formation and growth from BVOC are mainly initiated by hydroxyl radical (OH) and
2 ozone (O₃) oxidation during daytime. SOA formation from ozonolysis of several monoterpenes
3 such as α -pinene, β -pinene and limonene has been studied extensively (Iinuma et al., 2005;
4 Presto et al., 2005; Shilling et al., 2009; Yu et al., 1999; Ortega et al., 2012; Saathoff et al., 2009;
5 Tillmann et al., 2010; Hoffmann et al., 1997; Griffin et al., 1999; Lee et al., 2006; Ma et al.,
6 2008). However, particle formation from OH oxidation of monoterpenes has been much less
7 investigated and pure OH oxidation of monoterpenes has seldom been investigated due to the
8 presence of O₃ formed in the photooxidation process (Eddingsaas et al., 2012; Ng et al., 2007;
9 Lee et al., 2006). SOA formation from pure OH oxidation of monoterpenes regarding the
10 reaction process such as the formation and role of multi-generation products, and the influence of
11 OH oxidation on particle growth is not clear. Particularly, despite the importance of the OH
12 oxidation in the particle formation, the quantitative effect of OH oxidation on particle growth is
13 not available. Here we focus on the SOA formation from OH oxidation of monoterpenes.

14 It is also interesting to compare the relative importance of OH oxidation with ozonolysis of
15 monoterpenes in particle nucleation and growth. A number of studies have investigated this
16 question (Bonn and Moortgat, 2002; Burkholder et al., 2007; Hao et al., 2009; Mentel et al.,
17 2009), but often at high VOC concentrations and the results are controversial. Some studies have
18 shown the importance of ozonolysis in new particle formation (NPF) (Bonn and Moortgat, 2002)
19 while others have emphasized the importance of OH oxidation (Burkholder et al., 2007; Hao et
20 al., 2009; Mentel et al., 2009). Studies at the simulation chamber JPAC (Jülich Plant Aerosol
21 Atmosphere Chamber) suggest OH and H₂SO₄ are needed to initiate NPF (Mentel et al., 2009;
22 Kiendler-Scharr et al., 2009a; Kiendler-Scharr et al., 2012; Ehn et al., 2014). Ehn et al. (2014)
23 suggest that α -pinene ozonolysis produces a class of extreme low volatile organic compounds
24 (ELVOC), a recently discovered highly oxidized multifunctional products, which are important
25 for the nucleation and possibly make up 50-100% of SOA in early stages of particle growth in
26 Hyytiälä (Ehn et al., 2012). Regarding particle growth, Burkholder et al. (2007) stated that
27 particle size growth rates for different oxidation sources are nearly indistinguishable. Yet, Hao et
28 al. (2009), using the real BVOC emissions from plants, showed a much more efficient role of
29 ozonolysis than OH oxidation in particle growth. One reason causing the different results on
30 nucleation could be that VOC oxidation products are not the nucleating agents. Another
31 important reason of the controversy on particle nucleation and growth is that the OH oxidation

1 and ozonolysis have seldom been separated when comparing the SOA formation from both
2 pathways.

3 In addition, the reaction rates of OH and O₃ with organics have to be quantified and comparable
4 when one investigates the relative role of OH oxidation and ozonolysis in particle formation. To
5 obtain the reaction rates of VOCs with OH, the OH concentration is a required parameter.
6 However, none of these previous studies directly measured the OH concentration, which was
7 either not stated or just modeled. Since the detailed chemistry, including HO_x generation
8 pathways, of BVOC photooxidation is still not well understood, modeled OH concentrations may
9 have significant uncertainties (Fuchs et al., 2013; Kaminiski, 2014; Kim et al., 2013; Whalley et
10 al., 2011). Consequently, the relative importance of OH oxidation and ozonolysis in particle
11 formation and growth may have large uncertainties when the comparison of both cases is based
12 on modeled OH concentrations and corresponding reaction rates with OH.

13 In this study, we investigated the SOA formation and growth of several common monoterpenes,
14 α-pinene, β-pinene and limonene, by OH oxidation at ambient relevant conditions (low NO_x
15 (0.01-1 ppbV), low VOC (~ 4 ppbV) and low particle concentrations (sub μg m⁻³ to several μg
16 m⁻³)). The OH oxidation experiments were conducted at low O₃ concentration (<20 ppbV) to
17 ensure that OH oxidation was the dominant reaction pathway. OH concentration was measured
18 directly, as was the total reactivity (k_{OH}) of the whole reaction system with respect to OH, so that
19 the overall reaction rates of organics with OH were directly quantified (Lou et al., 2010). Note
20 that k_{OH} denotes OH reactivity throughout this paper rather than the rate constant for the reaction
21 of individual species with OH. Direct derivation of the overall reaction rate of total organics with
22 OH (product of OH reactivity of total organics and the OH concentration) from measured
23 parameters is a unique feature of this study. The multi-generation reaction process, particle
24 growth, new particle formation, particle yield, and particle composition were analyzed. A novel
25 method which quantitatively established the relationship of particle mass growth rate with the
26 reaction rate with OH was developed for the first time here to the best of our knowledge. This
27 method was further used to analyze the multi-generation reaction process. Particle formation by
28 OH oxidation was compared with that by ozonolysis. Ozonolysis experiments were done in the
29 presence of CO as OH scavenger, so that ozonolysis was the dominant reaction pathway.
30 Compared with other OH scavengers, mainly organics such as butanol, cyclohexane etc., CO

1 helps keep the RO₂/HO₂ concentration low since in the atmosphere HO₂ usually exceeds or is
2 close to RO₂ concentration (Hanke et al., 2002; Mihelcic et al., 2003), in contrast with many
3 laboratory studies where RO₂ concentration is much higher than HO₂ concentration (Kroll and
4 Seinfeld, 2008). The relative roles of OH oxidation and ozonolysis in the SOA formation and
5 particle growth were evaluated from comparisons of OH and O₃ dominated experiments. In
6 particular, we used low VOC concentration (~4 ppb) with natural sunlight conditions resulting in
7 low particle loading (sub μg m⁻³ to several μg m⁻³). The low particle loading allowed us to
8 investigate the particle formation, particle growth and multi-generation reaction process under
9 ambient relevant conditions (Presto and Donahue, 2006; Shilling et al., 2008; Shilling et al.,
10 2009; Pathak et al., 2007). It also minimized the condensation of early generation products with
11 low oxidation state which is of little relevance for ambient conditions (Shilling et al., 2009;
12 Pfaffenberger et al., 2013).

13 **2 Experimental**

14 **2.1 Experiment setup and instrumentation**

15 The experiments were carried out in the outdoor atmosphere simulation chamber SAPHIR
16 (Simulation of Atmospheric PHotochemistry In a large Reaction chamber), Forschungszentrum
17 Jülich, Germany. SAPHIR is a 270 m³ double-wall Teflon chamber of cylindrical shape. The
18 details of the chamber have been previously described (Rohrer et al., 2005; Bohn et al., 2005).
19 The chamber uses natural sunlight as the light source and is equipped with a louvre system to
20 simulate dark processes when the louvre is closed. It is operated with high purity synthetic air
21 (Linde Lipur, purity 99.9999%). A continuous flow of 7-9 m³ h⁻¹ maintains the chamber at a
22 slight overpressure of ~50 Pa and compensates for the sampling losses by various instruments.
23 This flow causes dilution of the reaction mixture with clean air at an average loss rate coefficient
24 of $9.35 \times 10^{-6} \text{ s}^{-1}$ (residence time of ~30 h), agreeing well with the dilution rates determined from
25 measured H₂O and CO₂ time series. Pure nitrogen (Linde Lipur, purity 99.9999%) constantly
26 flushes the space between the inner and outer Teflon wall to prevent intrusion of contaminants
27 into the chamber. A fan ensures mixing of trace gases within minutes, but reduces aerosol
28 lifetime when it runs. The loss by dilution alone applies equally to suspended particles and gases.

1 For the experiments described here, the chamber was equipped with instrumentation
2 characterizing gas-phase and particle-phase species, as well as physical parameters including
3 temperature, relative humidity, flow rate and photolysis frequencies.

4 The actinic flux and the according photolysis frequencies were provided from measurements of a
5 spectral radiometer (Bohn et al., 2005). NO and NO₂ measurements were performed with a
6 chemiluminescence analyzer (ECO PHYSICS TR480) equipped with a photolytic converter
7 (ECO PHYSICS PLC760). For a time resolution of 90 s the detection limits of the NO_x analyzer
8 were 5 and 10 pptV and the accuracies 5% and 10% for NO and NO₂, respectively. O₃ was
9 measured by an UV absorption spectrometer (ANSYCO model O341M).

10 The concentrations of the VOCs were measured by a proton transfer reaction-mass spectrometer
11 (PTR-MS, Ionicon) (Jordan et al., 2009) and gas chromatography coupled to a mass spectrometer
12 (GC-MS, Agilent) (Apel et al., 2008; Kaminiski, 2014). From the measured monoterpene time
13 series (shown in Fig S3), the time dependent monoterpene consumed during an experiment is
14 obtained. The measured monoterpene consumed also agrees with that calculated from the initial
15 concentration and loss by the reaction with OH and dilution within the uncertainty of
16 measurement (PTR-MS: ±15%, OH concentration: ±10%) and the reaction rate constant of
17 monoterpene (Atkinson et al., 2006; Atkinson and Arey, 2003; Gill and Hites, 2002) as shown in
18 Fig. S6. In the ozonolysis experiments, reactions of VOCs with O₃ in the sample line were found
19 to cause additional monoterpene loss. Monoterpene concentrations were therefore also quantified
20 from initial monoterpene concentrations and the losses by reaction according to the reaction rate
21 of O₃ with monoterpenes determined from measured O₃ and by dilution.

22 OH, HO₂, and RO₂ radicals were measured using laser induced fluorescence (LIF). The
23 uncertainty of the OH measurement, determined by the accuracy of the calibration of the LIF
24 instrument, is 10% (1σ). The details of LIF instrument were described by Fuchs et al. (2012).
25 The OH radicals inside SAPHIR are mainly formed by the photolysis of HONO directly coming
26 off the chamber walls through a photolytic process, and to a minor fraction by O₃ photolysis
27 (Rohrer et al., 2005). No additional OH generator was used.

28 Total OH reactivity (k_{OH}), which is equivalent to the inverse atmospheric OH lifetime, was
29 measured also using flash photolysis/laser-induced fluorescence (FP/LIF) technique that was first
30 realized by Calpini et al. (1999) and later by Sadanaga et al. (2004). k_{OH} is a pseudo-first-order

1 rate constant, equal to the sum of products of the concentrations of all species reacting with OH
2 with their rate constants. Laser flash photolysis (LP) of ozone is used to produce OH in a sample
3 of air and laser-induced fluorescence (LIF) is applied to monitor the time dependent OH decay.
4 From the time dependent OH decay the k_{OH} was obtained. The instrument used in this work at
5 SAPHIR was deployed in previous field campaigns and is described in detail elsewhere
6 (Hofzumahaus et al., 2009; Lou et al., 2010).

7 The OH concentration was used to calculate the OH dose in order to better compare different
8 experiments. The OH dose is the integral of the OH concentration over time and gives the
9 cumulated OH concentrations to which gases and particles were exposed at a given time of an
10 experiment. One hour exposure to typical atmospheric OH concentrations of 2×10^6 molecules
11 cm^{-3} results in an OH dose of 7.2×10^9 molecules cm^{-3} s. The OH concentration and OH reactivity
12 were also used to calculate the reaction rate of OH with total organics.

13 Particle size distributions were measured by a scanning mobility particle sizer (SMPS, TSI
14 DMA3081/TSI CPC3785) with a size range 9.82-414.2 nm. Aerosol yield was calculated using
15 SMPS mass concentration assuming a density of 1 g cm^{-3} to compare with previous studies in the
16 literature. Aerosol density is assumed to be constant throughout one experiment since from our
17 previous studies the density was found to be relatively constant throughout the whole experiment
18 (Salo et al., 2011; Saathoff et al., 2009). Particles in the chamber are subject to wall losses as
19 reported previously (Salo et al., 2011; Fry et al., 2011). Size effects of the particle loss were
20 neglected here because of the narrow size distribution (geometric standard deviation < 1.3). In
21 this study, the particle wall loss rate was determined using an exponential fit of the decay of the
22 particle number concentration after the nucleation has stopped for several hours (Carter et al.,
23 2005; Fry et al., 2011; Pierce et al., 2008). In addition to particle wall loss, vapor wall losses to
24 the wall have been observed in the laboratory chamber studies (Matsunaga and Ziemann, 2010;
25 Zhang et al., 2014). The particle mass concentration corrected for dilution and wall loss is shown
26 here unless otherwise stated. Vapor wall losses were not corrected here due to the difficulty to
27 quantify, but the effect of vapor loss on the particle mass concentration is discussed. The
28 uncertainty of the particle mass concentration, due to uncertainty of the particle wall loss and
29 vapor wall loss is also discussed.

1 The chemical composition of SOA was characterized by a High-Resolution Time-of-Flight
2 Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., (DeCarlo et al., 2006)).
3 Particles enter the instrument through an aerodynamic lens and are focused to a particle beam.
4 The particles impact on a tungsten oven at 600 °C and are flash-vaporized into vapors under
5 vacuum. The vapors are then ionized by 70 eV electron impact (EI), and the resulting ions are
6 detected by a time-of-flight mass spectrometer operating at either a high-sensitivity mode (V-
7 mode) or a high mass resolution mode (W-mode). In this study we used the so-called MS mode
8 which gets the size integrated overall composition of SOA.

9 To characterize the degree of oxidation of particles, the O/C ratio was obtained. The O/C and
10 H/C ratio was derived by the elemental analysis of mass spectra obtained in the high mass
11 resolution W-mode as described by Aiken et al. (2007) and Aiken et al. (2008). An updated
12 procedure to calculate O/C and H/C was reported to be in development (Canagaratna et al.,
13 2014). However, the details have not been published yet, therefore, the traditional method is still
14 used here to derive the elemental ratio. Corrections for the minor influence of gaseous
15 components were done before the calculation of the H/C and O/C ratio. Chamber air contains
16 CO₂ and water vapor and both gas phase species contribute to the mass spectra. The contribution
17 of gas phase CO₂ and water vapor to m/z 44 and to m/z 18, respectively, was inferred from
18 measurements during periods when no particles were present. The values were subtracted to
19 obtain the particle signals before the elemental analysis (Allan et al., 2004). No collection
20 efficiency correction was further used.

21 **2.2 Experiment procedure**

22 Two kinds of experiments, photooxidation and ozonolysis of monoterpenes were carried out
23 under humid conditions with a starting RH ~75%. The summary of the experimental conditions
24 is shown in Table 1. All the experiments were conducted under NO_x <~1 ppb. No NO_x was added
25 to the chamber, and background NO_x originated mainly from the wall. In the photooxidation
26 experiments, the O₃ concentration was <3 ppb at the start of each experiment and did not exceed
27 20 ppb over the course of an experiment. The OH oxidation was the dominant oxidation pathway
28 (>~95% of monoterpene loss). In a typical procedure, air in the chamber was first humidified and
29 then the louvre system was opened for around 1.5 hours. Afterwards monoterpene was injected
30 and the reaction of monoterpene with OH occurred. After the photooxidation process, which was

1 finished by closing the louvre system, the reaction mixtures stayed in the dark for around 1 h
2 before they were flushed out. Before nucleation there were some background particles present
3 introduced after humidification which had relatively large diameter (median diameter 40-60 nm)
4 but with fairly low concentration (refer to Table 1). Particle size before nucleation was not
5 shown in order to avoid confusion. The ozonolysis experiments were conducted in the dark.
6 After humidification CO and monoterpene were added to the chamber. CO (~40 ppm) was used
7 as OH scavenger to ensure that oxidation by O₃ was the dominant reaction pathway (>95 % of
8 OH was scavenged) with little contribution of the OH oxidation to monoterpenes losses.
9 Afterwards, O₃ generated from an UV O₃ generator was added to the chamber to start ozonolysis
10 reaction of monoterpenes.

11 **3 Methods**

12 In the reaction of monoterpenes with OH and O₃, oxidation products are generated, which
13 condense on the particle phase resulting in particle growth. In the case of OH oxidation, multi-
14 generation products can be formed from the further reaction of first generation products with
15 OH, while for ozonolysis of monoterpenes with one carbon-carbon double bond the reaction
16 products do not react with O₃ any more since the double carbon bond has been broken down.
17 Particle growth depends on the condensation flux, thus the concentration of condensing products,
18 of all generations. Since the concentration of condensing products is a function of the reaction
19 rate, particle growth is closely related to the reaction rate of organics. We explored the
20 relationship between particle mass growth and reaction rate of the organics with OH. When
21 particles grow, the particle diameter enlarges and the particle mass increases due to the
22 condensation of the reaction products. Here we use the term “particle size growth rate” to denote
23 the particle diameter increase and “mass growth rate” to denote the particle mass increases. In
24 the following we will establish a quantitative relationship of the particle mass growth rate with
25 the reaction rate of OH with total organics for the first time, to the best of our knowledge. Since
26 all condensing species contribute to the particle mass growth rate, the particle mass growth rate
27 must be related to the reaction rate of total organic species with OH, which is directly accessible
28 from the OH concentration measurement and the k_{OH} measurement in this study. The particle
29 mass growth rate is derived from sum of the particle mass growth due to all condensing
30 compounds.

1 In a first step, we will relate the overall mass growth to the OH gas-phase reaction rates with
 2 total organic species. We describe that by a reaction of VOC i with OH, in which for simplicity
 3 one molecule of species i reacts with OH, forming one molecule of species $i+$ of the next
 4 generation:



6 According to the Raoult's law we have the following equation, assuming the gas phase and
 7 particle phase are in equilibrium:

$$8 \quad C_i^g = \frac{C_i^p}{C_t^p} \cdot C_i^0, \quad (1)$$

9 where C_i^g and C_i^p are the concentrations of i in the gas phase and in the particle phase (molecules
 10 cm^{-3}), C_i^0 is the saturation vapor pressure of i expressed as gas-phase concentration of i
 11 (molecules cm^{-3}) and C_t^p is the concentration of all molecules in the particle phase, thus C_i^p/C_t^p is
 12 the mole fraction of i . For high volatility species, C_i^0 is high for given C_i^g and thus C_i^p is low or
 13 even negligible. The opposite is true for low volatility species, C_i^0 is low and C_i^p is high.

14 When an infinitesimal concentration of i , dC_i^g , reacts via R1, corresponding to a change of i in
 15 the particle phase, dC_i^p , from Eq. (1), one can get Eq. (2). C_t^p is assumed to be constant in each
 16 time step because the change in each time step is minor compared to C_t^p , and additionally loss of
 17 i is compensated by gain in $i+$ when the vapor pressure of $i+$ is sufficiently low to be on the
 18 particle phase and thus C_t^p is approximately conserved.

$$19 \quad dC_i^g = \frac{dC_i^p}{C_t^p} \cdot C_i^0. \quad (2)$$

20 Re-arranging Eq. (2), one can get

$$21 \quad dC_i^p = \frac{C_t^p}{C_i^0} \cdot dC_i^g. \quad (3)$$

22 Similarly, one can get

$$23 \quad dC_{i+1}^p = \frac{C_t^p}{C_{i+1}^0} \cdot dC_{i+1}^g. \quad (4)$$

1 For the change of the particle mass concentration (m , $\mu\text{g m}^{-3}$) due to the reaction of species i by
 2 R1, we have

$$3 \left(\frac{dm}{dt}\right)_i = \frac{dm_{i+}^p}{dt} + \frac{dm_i^p}{dt} . \quad (5)$$

4 dm_i^p ($\mu\text{g m}^{-3}$) and dC_i^p can be related by

$$5 dm_i^p = \frac{dC_i^p \cdot M_i \cdot 10^6 \cdot 10^6}{N_A} , \quad (6)$$

6 where M_i is the molecular weight of species i (mol kg^{-1}) and N_A is Avogadro's Constant.

7 Similarly with Eq. (6), for species $i+$, one can get

$$8 dm_{i+}^p = \frac{dC_{i+}^p \cdot M_{i+} \cdot 10^6 \cdot 10^6}{N_A} . \quad (7)$$

9 By applying the relationship of i and $i+$ in the R1, we express,

$$10 dC_{i+}^g = -dC_i^g . \quad (8)$$

11 Substituting Eq. (3), (4), (6-8) into Eq. (5), one can get

$$12 \left(\frac{dm}{dt}\right)_i = \frac{dC_i^g}{dt} \cdot C_i^p \frac{10^6 \cdot 10^6}{N_A} \left(\frac{M_i}{C_i^0} - \frac{M_{i+}}{C_{i+}^0}\right) . \quad (9)$$

13 Assuming M_{i+} and M_i are similar, with an average molecular weight M , one can get

$$14 m_t = C_i^p \frac{10^6 \cdot 10^6}{N_A} M , \quad (10)$$

15 where m_t is total particle mass concentration.

16 Substituting Eq. (10) into Eq. (9), one can get

$$17 \left(\frac{dm}{dt}\right)_i = \frac{dC_i^g}{dt} \cdot m_t \left(\frac{1}{C_i^0} - \frac{1}{C_{i+}^0}\right) . \quad (11)$$

18 If we relax our assumption that one molecule of $i+$ is formed from the loss of one molecule of i
 19 in the R1, e.g. in case of fragmentation, Eq. (11) still holds (as shown in Appendix A).

1 According to the reaction of i with OH, we have

$$2 \quad \frac{dC_i^s}{dt} = -R_{OH,i}, \quad (12)$$

3 where $R_{OH,i}$ is the reaction rate of species i with OH.

4 Substitute Eq. (12) into Eq. (11),

$$5 \quad \left(\frac{dm}{dt}\right)_i = R_{OH,i} \cdot m_t \left(\frac{1}{C_{i+}^0} - \frac{1}{C_i^0}\right). \quad (13)$$

6 Considering all the species contributing to the particle phase, we have

$$7 \quad \frac{dm_t}{dt} = \sum_i R_{OH,i} m_t \left(\frac{1}{C_{i+}^0} - \frac{1}{C_i^0}\right). \quad (14)$$

8 Re-arrange Eq. (14),

$$9 \quad \frac{dm_t}{dt} = m_t \frac{\sum_i R_{OH,i} \left(\frac{1}{C_{i+}^0} - \frac{1}{C_i^0}\right)}{\sum_i R_{OH,i}}. \quad (15)$$

10 Summing up all the species, we have

$$11 \quad R_{OH} = \sum_i R_{OH,i}, \quad (16)$$

12 wherein R_{OH} is the reaction rate of total organics with OH.

13 In the next step, we will derive a system characterizing quantity in order to overcome the
14 underdetermined knowledge about the individual components due to the complexity of
15 monoterpene degradation. We define a new metric, $GE_{OH}(t, i)$ (particle growth efficiency in
16 respect to the reaction of OH with total organics in the whole reaction system (including the
17 VOCs and their oxidation products)) in Eq. (17) for species i :

$$18 \quad GE_{OH}(t, i) = \frac{1}{C_{i+}^0} - \frac{1}{C_i^0}. \quad (17)$$

19 One can also define

$$1 \quad \frac{\sum_i R_{OH,i} \cdot \frac{1}{C_{i+}^0}}{\sum_i R_{OH,i}} = \frac{1}{\bar{C}_{i+}^0}, \quad (18)$$

2 and

$$3 \quad \frac{\sum_i R_{OH,i} \cdot \frac{1}{C_i^0}}{\sum_i R_{OH,i}} = \frac{1}{\bar{C}_i^0}. \quad (19)$$

4 \bar{C}_{i+}^0 and \bar{C}_i^0 are obtained from the average of $1/C_i^0$ for all organics weighed by the reaction rate
5 with OH, which in a certain way reflect the overall saturation vapor pressures.

6 Substituting Eq. (16), (18) and (19) into Eq. (15), one can get

$$7 \quad \frac{dm_t}{dt} = R_{OH} \cdot m_t \cdot \left(\frac{1}{\bar{C}_{i+}^0} - \frac{1}{\bar{C}_i^0} \right). \quad (20)$$

8 Then, as Eq. (17), one can also define

$$9 \quad GE_{OH}(t) = \frac{1}{\bar{C}_{i+}^0} - \frac{1}{\bar{C}_i^0}. \quad (21)$$

10 $GE_{OH}(t)$, a system describing quantity, is derived here in order to characterize the chemical
11 system. It is an overall average of $GE_{OH}(t, i)$ weighted by reaction rate with OH of each species.

12 The molecular weight of $i+$ is assumed to be similar with that of i , i.e., neither functionalization
13 nor fragmentation change the molecular dramatically. In the case of fragmentation which could
14 change molecular weight significantly, the relationships above still hold with slight change of the
15 format (as shown in Appendix A).

16 Substituting Eq. (21) into Eq. (20),

$$17 \quad \frac{dm_t}{dt} = R_{OH} \cdot m_t \cdot GE_{OH}(t) \quad (22)$$

18 Arranging Eq. (22), one can get

$$1 \quad GE_{OH}(t) = \frac{\frac{dm_t}{dt}}{R_{OH} \cdot m_t} \quad (23)$$

2 Equation (22) shows a quantitative relationship of the particle mass growth rate with the reaction
 3 rate of OH with total organics, which are linked by $GE_{OH}(t)$. $GE_{OH}(t)$ is the mass growth rate
 4 normalized to the OH reaction rate and mass concentration, i.e. the mass growth rate per OH
 5 reacted per aerosol mass concentration (as shown in Eq. (23)). It is a metric of how effectively
 6 the reaction with OH changes the mass growth rate at a given mass concentration in a reaction
 7 system. $GE_{OH}(t)$ has a unit of $\text{cm}^3 \text{ molecules}^{-1}$ (reciprocal of the unit of the concentration). It
 8 relates to the change of overall saturated concentration of reaction products upon reaction with
 9 OH as shown in Eq. (21). In our case, where we measured OH and k_{OH} , R_{OH} is directly
 10 accessible. The reaction rate of OH with total organics was calculated using the measured k_{OH}
 11 and subtracting the OH reactivity of inorganic species (NO, NO_2 , CO). The contribution of
 12 HONO to the total OH reactivity is neglected (<1%) since the HONO concentrations are fairly
 13 low in these experiments (maximum peak concentration 300 pptv as measured by a LOng-Path-
 14 Absorption-Photometer(LOPAP) (Häseler et al., 2009)).

15 Note that in Eq. (1) we assumed that the particle is in equilibrium with the gas phase. When the
 16 concentrations of condensing species changes slowly relative to the timescale for the gas-particle
 17 equilibrium, gas-particle equilibrium is assumed to be established at any moment (Zhang et al.,
 18 2012). This quasi-equilibrium approach was used here and compounds partition between gas and
 19 particle phase through dynamic condensation and evaporation (Pankow, 1994; Odum et al.,
 20 1996). Theoretically many factors such as diffusion, surface accommodation etc. can affect the
 21 timescale for gas-particle equilibrium (Shiraiwa and Seinfeld, 2012) and hence affect the particle
 22 mass growth. For example, several recent studies suggests that particles may exist in a viscous
 23 state (e.g., (Vaden et al., 2011; Virtanen et al., 2010; Renbaum-Wolff et al., 2013) and particle
 24 phase diffusion could play a role in the particle growth kinetics. In addition, the particle-phase
 25 photolysis is not included in this derivation, which could also potentially affect the gas-particle
 26 equilibrium. As a result, the gas-particle equilibrium may not necessarily be reached all the time.
 27 These are the limitations of the method used in this study. If the equilibrium is not reached, the
 28 mass growth rate in this case is the lower limit for the contribution from gas phase condensation.
 29 The deviation from the equilibrium would result in a higher $GE_{OH}(t)$.

1 **4 Results and discussion**

2 **4.1 Multi-generation reaction process and particle growth**

3 Figure 1 shows the time dependent particle “growth curve” (particle mass concentration as a
4 function of measured monoterpene consumed) from the OH oxidation of α -pinene, β -pinene and
5 limonene. After one monoterpene life time (when the monoterpene concentration decreased to
6 $1/e$ of the initial concentration), only 13%, 33%, and 25% of the total mass was reached for the
7 OH oxidation of α -pinene, β -pinene and limonene, respectively. This indicates the importance of
8 higher generation products in the SOA formation from OH oxidation of each monoterpene (Ng et
9 al., 2006). Our results differ from several previous studies carried out at much higher VOC and
10 SOA concentrations (Ng et al., 2007; Ng et al., 2006). Ng et al. (2006) showed that the time
11 dependent growth curve is almost linear for terpenes with one double bond such as α -pinene and
12 β -pinene. The difference can be attributed to the difference of VOC and particle concentration.
13 At high particle mass loading, the species with relatively high volatility such as first generation
14 products significantly condense. At low particle loading, only the species with relatively low
15 volatility which require more oxidation steps (by OH) can significantly condense onto the
16 particle phase. Consequently, the later generation products play important roles in the particle
17 formation in this study. The importance of multi-generation products agrees with Eddingsaas et
18 al. (2012), who showed that particle growth continues well after two lifetimes of α -pinene with
19 respect to OH oxidation at low NO_x condition.

20 In contrast to OH oxidation, the total mass concentration increased roughly linearly with the
21 consumed monoterpene concentration for the ozonolysis of each monoterpene (Fig. S1). The
22 time-dependent growth curves of three monopterenes in the ozonolysis experiments agree with
23 previous studies (Ng et al., 2006; Zhang et al., 2006) and a recent study of Ehn et al. (2014)
24 showing the formation of first generation products as the rate-limiting step. There was an
25 apparent positive offset on the hydrocarbon consumed for α -pinene and β -pinene, and barely an
26 offset for limonene, since the reaction products needed to reach their saturation concentration to
27 condense on the particle phase. For limonene, within the time resolution of our measurement
28 they reached the saturation concentration immediately. The offsets are consistent with the
29 findings of the nucleation threshold of monoterpenes (Bernard et al., 2012; Mentel et al., 2009).

1 The differences of the threshold concentrations of different monoterpenes are related to their
2 properties.

3 To further investigate the role of multi-generation oxidation by OH, the particle mass
4 concentration and the median size as a function of OH dose are shown in Fig. 2. For all three
5 monoterpenes, the particle mass concentration increased and size grew as the reaction proceeded
6 and monoterpene reacted with OH (increasing OH dose). Then the increase of the mass
7 concentration and growth of size with respect to OH dose started to slow down gradually and
8 subsequently leveled off. Particle size even decreased after leveling off in the case of limonene.
9 For α -pinene, the photooxidation reaction stopped in the dark after the louvre system of the
10 chamber had been closed before the particle mass could level off. The changes in the particle
11 growth in Fig. 2A were probably attributed to the significant fluctuation of OH concentration
12 resulting from the cloud coverage which also caused the significant fluctuations in the reaction
13 rate of total organics with OH in Fig. 4A.

14 In the beginning of the reaction, monoterpene reacted with OH generating low volatility
15 compounds by the functionalization process (Hallquist et al., 2009), which condensed on the
16 particle and resulted in the particle mass increase and size growth. The formation of the low
17 volatility compounds such as 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) has been
18 found from monoterpene oxidation in one of our previous studies (Emanuelsson et al., 2013).
19 This has also been found from the oxidation of monoterpene and its first generation products by
20 a number of studies (Hallquist et al., 2009; Jaoui et al., 2005; Szmigielski et al., 2007; Claeys et
21 al., 2007; Muller et al., 2012; Kristensen et al., 2014). These condensing compounds still
22 continued reacting with OH which could lead to functionalization as well as fragmentation
23 (Hallquist et al., 2009; Kroll et al., 2009). Fragmentation can generate high volatility species thus
24 promoting evaporation. Since fragmentation increased with O/C and the role of functionalization
25 decreased (Kroll et al., 2009; Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010),
26 the role of fragmentation became more and more significant as the reaction proceeded. When the
27 fragmentation dominated over functionalization, the overall volatility of the products increased,
28 i.e., the saturated vapor pressures increased. When the overall concentration of condensing
29 species dropped below the overall saturation concentration due to the reaction and dilution, a net
30 negative flux of condensable compounds occurred and these compounds started to evaporate

1 from the particles. Therefore, the particle size first reached a plateau and even diminished as
2 observed in the limonene oxidation experiment. For α -pinene, particle growth did not reach the
3 plateau phase. This is because the reaction was stopped by closing the louvre when particles
4 were still growing.

5 Moreover, time series of $GE_{OH}(t)$, the metric of particle growth efficiency due to reaction with
6 OH, shed light on the role of functionalization and fragmentation in the reaction process. Figure
7 3 shows that the $GE_{OH}(t)$ time series and the particle mass concentration as well as total OH
8 reactivity of organics for comparison. The change of $GE_{OH}(t)$ reflects the evolution of the overall
9 volatility of organics undergoing reaction with OH and the relative role of functionalization and
10 fragmentation. $GE_{OH}(t)$ was positive and increased fast in the beginning of the reaction. This
11 indicates that the reaction products had a lower volatility than the reactants, i.e., lower saturation
12 concentration (refer to Eq. (21)). As the volatility decreased, $GE_{OH}(t)$ increased. The decreased
13 volatility was caused by functionalization, which played a dominant role in the beginning.
14 Afterwards, $GE_{OH}(t)$ gradually decreased, which indicates the decrease of overall volatility of the
15 organics slowed down. This indicates an increasing role of fragmentation since fragmentation
16 cleaved the carbon frame and formed some smaller molecules with higher volatility. As the
17 reaction proceeded, the products got more oxidized and O/C ratio of products increased, the
18 fragmentation of the compounds became more and more significant (Kroll et al., 2009; Chacon-
19 Madrid and Donahue, 2011; Chacon-Madrid et al., 2010). After the continuous decrease,
20 $GE_{OH}(t)$ decreased to almost zero or even negative for the limonene case (Fig. 3C). This
21 indicates that overall volatility of organics almost stopped decreasing and even increased after
22 further reactions of the functionalized intermediates with OH (see limonene case in Fig. 3C).
23 When the overall volatility of the reactants is equal to that of the products, $GE_{OH}(t)$ is equal to
24 zero. From Fig. 3 one can recognize that $GE_{OH}(t)$ had decreased dramatically in the relatively
25 early period of the reaction (within approximate two lifetimes) when the mass concentration was
26 still low, indicating the fragmentation started to play an important role. The vibrations in the
27 $GE_{OH}(t)$ of α -pinene are attributed to the fast change of OH concentration due to the cloud
28 coverage and then clearing up, as mentioned above.

29 For comparison, the H/C and O/C time series of SOA are also shown in Fig. 3. The change of
30 H/C and O/C ratio supports our analysis of the role of functionalization and fragmentation.

1 $GE_{OH}(t)$ had decreased dramatically to a much lower value when O/C ratio increased to around
2 0.4 and leveled off. Accordingly, H/C started to decrease from the beginning of the reaction and
3 then leveled off at the same time as O/C. The decrease of $GE_{OH}(t)$ reflects the increasing role of
4 fragmentation. As a reference, Kroll et al. (2009) showed that for the reaction of squalane with
5 OH fragmentation dominates when the organics are moderately oxidized ($O/C \approx 0.4$), although the
6 reaction compounds are different. The branching ratio of fragmentation and functionalization has
7 been parameterized as the power law of O/C (Donahue et al., 2012; Jimenez et al., 2009). The
8 higher O/C, the higher the role of fragmentation plays. Based on the $GE_{OH}(t)$ time series, the
9 particle formation efficiency in respect to the reaction with OH was high in the beginning of the
10 reaction although the mass growth rate was low. In contrast, at the later period of the reaction,
11 $GE_{OH}(t)$ was low and the mass growth was mainly attributed to the role of favorable partitioning
12 at higher organics mass loading.

13 The occurrence of fragmentation in the reaction is supported by the formation of acetone, one
14 small volatile compound of monoterpene oxidation products. An increased acetone concentration
15 was observed in the OH oxidation of all monoterpenes as reaction proceeded (as shown in Fig.
16 3A for α -pinene as an example), implying the role of fragmentation in producing small volatile
17 compounds. The acetone concentration was corrected for the dilution loss. However, we did not
18 observe a significantly faster acetone formation rate in the later period of the reaction compared
19 to the early period of the reaction because acetone formation depends on its precursor
20 concentrations and OH concentration, which were not monotonic in our study. Unfortunately,
21 many of the products in the α -pinene oxidation cannot be detected and/or quantified by PTR-MS
22 or GC-MS due to the loss to the sampling line or degradation in the instrument, which prevents
23 us to do further in-depth analysis.

24 In addition, $GE_{OH}(t)$ can shed some light on the vapor pressure of the reaction products. Since
25 the volatility of products decreases around one to two order of magnitude in functionalization
26 (Ziemann and Atkinson, 2012), in the beginning of the reaction when functionalization
27 dominated, $C_{n,i+}^0 \ll C_{n,i}^0$. Then, based on Eq. (21), the following equation is tenable:

$$28 \quad GE_{OH}(t) = \frac{1}{\bar{C}_{n,i+}^0} \quad (24)$$

1 Since \bar{C}_{i+}^0 is an average saturation pressure weighed in a certain way as shown in Eq. (18).
2 Equation (24) provides a rough estimate of the overall vapor pressure of the organics from
3 experimentally obtained $GE_{OH}(t)$. For α -pinene, β -pinene and limonene OH oxidation, the
4 overall vapor pressure varied from around 2×10^{-4} to 1×10^{-3} Pa, 6×10^{-5} to 1×10^{-3} Pa, 8×10^{-5} to
5 2×10^{-3} , respectively. As a reference, the lower values for each monoterpene system is of the
6 same order of magnitude as the estimated vapor pressure of the middle between pinonic acid and
7 pinic acid, norpinonic acid and keto-limonic acid, respectively, based on the structure-activity
8 relationship (Compernelle et al., 2011).

9 We established the relationship of particle mass growth rate with the reaction rate of OH with
10 organics. The relationship of the particle size growth rate with the reaction rate is not
11 straightforward. The size growth rate is proportional to the deviation of the concentrations of
12 condensing species from their equilibrium concentrations, while the reaction rate of monoterpene
13 with OH and O_3 is proportional to the rate of the increase of condensing species concentrations,
14 i.e., the derivative of the concentrations. Additionally, the equilibrium concentrations of the each
15 species changes continuously with their varying molar fractions in the particle phase during the
16 reaction. Therefore, the reaction rate is only indirectly related to the size growth rate and should
17 not necessarily correlate with size growth rate as observed in Fig. 4A and 4C. Still some
18 variations in the size growth rate and mass growth rate follow the variations of the reaction rate
19 of OH with organics and/or reaction rate of OH with monoterpenes (such as Fig. 4A, 4B and
20 4C). These variations in the reaction rates as well as the growth rates were mostly caused by
21 sudden changes of the OH concentration due to variations of solar radiation affected by cloud
22 coverage. In addition, the fluctuations in the growth rate were partly attributed to the fluctuations
23 in the particle mass or size and deriving the growth rate from fitting the particle mass or particle
24 size as a function of time.

25 Comparing the particle growth of OH oxidation and ozonolysis, the ratios of the peak OH
26 reaction rate to the O_3 reaction rate for α -pinene, β -pinene and limonene were around 1.0, 1.2
27 and 0.5, respectively. The corresponding ratios of peak size growth rates for OH oxidation to that
28 for ozonolysis were around 1.0, 1.5 and 1.1. At the similar monoterpene concentration and
29 similar reaction rate of OH or O_3 with monoterpene, the size growth rates were comparable. This
30 comparison indicates that generally OH oxidation and ozonolysis have similar efficiency in the

1 particle growth of α -pinene, β -pinene and limonene. This result is in contrast with the study of
2 Hao et al. (2009), who found a much more efficient role of ozonolysis in particle growth from
3 plant emissions than that of OH oxidation. Yet, our study agrees with Burkholder et al. (2007),
4 reporting the nearly indistinguishable particle size growth rate for different oxidation sources.
5 Nevertheless, our experiments differ from both of these studies in terms of OH scavenger used
6 (CO used in this study, cyclohexane and butanol in Burkholder et al. (2007) and Hao et al.
7 (2009), respectively). Since CO can cause a higher HO₂/RO₂ ratio than cyclohexane and butanol,
8 different OH scavengers could result in different radical chemistry which could further alter the
9 reaction pathways and products and finally could affect particle growth.

10 **4.2 New particle formation and SOA yield**

11 Figure 5 shows the particle number concentration, mass concentration, surface concentration and
12 median diameter of aerosol from each monoterpene by OH oxidation and ozonolysis. The
13 particle number concentrations of OH oxidation experiments were around 2×10^3 - 6×10^3 #/cm³.
14 The particle number concentrations from the ozonolysis of monoterpene were around 0.4×10^5 -
15 1.6×10^5 #/cm³, which were much higher than that generated by OH oxidation of the respective
16 monoterpene. However, we have no indications what compounds eventually initiated the new
17 particle formation (NPF) from ozonolysis in the SAPHIR chamber made of Teflon-FEP. The role
18 of OH oxidation and ozonolysis in the SOA nucleation and growth from monoterpenes have
19 been reported by a number of studies before with inclusive results (Bonn and Moortgat, 2002;
20 Burkholder et al., 2007; Hao et al., 2009; Mentel et al., 2009), however experiments were
21 performed often at higher VOC and aerosol concentrations. In addition, the role of monoterpene
22 ozonolysis in nucleation in the presence of SO₂ (without OH scavenger) was shown by Ortega et
23 al. (2012).

24 In our JPAC glass chamber (Mentel et al., 2009), OH and H₂SO₄ are needed to initiate NPF
25 (Mentel et al., 2009; Kiendler-Scharr et al., 2009a; Kiendler-Scharr et al., 2012; Ehn et al., 2014);
26 it is possible that in Teflon chambers in absence of OH and significant H₂SO₄ formation, other
27 unknown compounds (perfluorinated acids) may play a role.

28 SOA yields observed in this study are similar to those observed before. SOA yield of α -pinene,
29 β -pinene, and limonene by OH oxidation was 2.5%, 6.8% and 16.9% at the aerosol loading of

1 0.5, 0.8 and 2.1 $\mu\text{g m}^{-3}$, respectively (Fig. A2). Since the multi-generation oxidation was the rate-
2 limiting step, the “dynamic” yield from OH oxidation was not used (Presto and Donahue, 2006;
3 Ng et al., 2006) and only final yield was derived. The aerosol yield of α -pinene OH oxidation is
4 roughly consistent with a study (Henry et al., 2012), although there were only few data points in
5 that study overlapping the range of our study ($<1 \mu\text{g m}^{-3}$, exact data not available from Henry et
6 al. (2012) thus not shown in the figure). For β -pinene and limonene, there are few data of the
7 aerosol yield of OH oxidation available especially at the aerosol loading similarly low to this
8 study in the literature (Griffin et al., 1999; Hoffmann et al., 1997; Kim et al., 2012).

9 The particle yields for the ozonolysis experiments for α -pinene, β -pinene and limonene (shown
10 in Fig. S2, together with selected literature data at similar mass loadings) are approximately in
11 the range of or slightly higher than literature values (Pathak et al., 2008; Pathak et al., 2007;
12 Shilling et al., 2009; Saathoff et al., 2009; Zhang et al., 2006). The difference can be attributed to
13 the difference in experimental conditions such as OH scavenger type, the temperature and RH
14 etc. The aerosol yields of ozonolysis for α -pinene and limonene were higher than that of OH
15 oxidation, while similar between both oxidation cases for β -pinene. The difference in the aerosol
16 yield could be due to the difference in reaction pathways and products composition between the
17 OH oxidation and ozonolysis. Also the temperature of the ozonolysis was lower than the OH
18 oxidation, which may affect the SOA yield. However, Pathak et al. (2007) only observed weak
19 dependence of SOA yield from α -pinene ozonolysis on temperature from 288 to 303K, and
20 especially for at low α -pinene reacted there is little temperature dependence. Therefore,
21 temperature is likely to have only minor effect on the SOA yield of ozonolysis here.

22 **4.3 Chemical composition**

23 The H/C ratio versus the O/C ratio plot known as Van Krevelen diagram for the aerosol from OH
24 oxidation and ozonolysis is shown in Fig. 6. The O/C ranges for both oxidation cases were
25 similar, around 0.3-0.6. The O/C ranges are consistent with the O/C range from α -pinene
26 photooxidation and ozonolysis (Chhabra et al., 2011; Ng et al., 2011; Pfaffenberger et al., 2013).
27 They also agree with the O/C value (0.33 – 0.68) in a plant chamber observations for
28 monoterpene-dominated emission mixtures (Kiendler-Scharr et al., 2009b) when one calculates
29 O/C from f44 (the ratio of signal at m/z 44 (CO_2^+) to total organics) (Ng et al., 2010).

1 The H/C ratio of SOA from OH oxidation was around 1.4-1.6, slightly lower than that of the
2 precursor monoterpene (H/C=1.6). This indicates that during the reaction oxygen was added to
3 the monoterpene without significant loss of hydrogen especially in the initial period of the
4 reaction. SOA from OH oxidation of all three monoterpenes tended to follow a slope of
5 shallower than -1 starting from monoterpene in the Van Krevelen diagram (Fig. 6 A-C). This is
6 in contrast to the findings by Heald et al. (2010), but consistent with those of Chhabra et al.
7 (2011) and Ng et al. (2011). Heald et al. (2010) found atmospheric OA follows a slope of -1 in
8 the Van Krevelen diagram based on a variety of ambient and laboratory studies, which indicates
9 the addition of carboxylic group or equal addition of carbonyl and hydroxyl group to average
10 saturated hydrocarbon. However, in this study, monoterpenes are unsaturated hydrocarbons.
11 Therefore, oxidation such as adding two carbonyl or carboxylic acid groups per double bond can
12 happen without significant loss of hydrogen, resulting in a slope shallower than -1. This finding
13 agrees with that of Chhabra et al. (2011) who investigated a series of unsaturated hydrocarbons.
14 Oxidation without significant loss of hydrogen can be also achieved by a “non-classical” path,
15 inserting O (O-O) into C-H (C-C) bonds (Ehn et al., 2012; Ehn et al., 2014). In the classical path,
16 increasing carbonylization/carboxylation in saturated parts of the condensable molecules leads
17 to increase of O/C at simultaneous decrease of H/C. After the initial period of particle formation
18 (around one lifetime of monoterpene), elemental composition of SOA from OH oxidation
19 seemed to follow a slope of more close to -1. This indicates that the condensable species forming
20 SOA underwent more efficient hydrogen loss upon oxidation. Since the double bond is more
21 reactive and reacted first, the carbon chain in the initial products became more saturated. Further
22 “classical” oxidation of these products required hydrogen loss as ambient organic aerosols
23 (Heald et al., 2010). For the SOA from OH oxidation, H/C decreased and O/C increased
24 generally during the reaction. In the later period of the reaction the change of O:C and H:C was
25 quite minor (Fig. 3). The relative stability of the O/C and H/C is likely to be attributed to that in
26 the early period of the reaction (before O/C reaches the maximum value) low concentrations of
27 multi-generation products were generated via functionalization and had already condensed on the
28 particle phase. As the reaction proceeded, more of these similar multi-generation products were
29 formed and continued to condense on the particle. Further oxidation of the multi-generation
30 products may cause the fragmentation resulting in the formation high volatility oxidation
31 products, which did not condense significantly on the particle. As a result, the O/C ratio did not

1 manifest significant increase in the particle phase. This is consistent with the analysis of
2 functionalization and fragmentation via the evolution of $GE_{OH}(t)$. For β -pinene and limonene,
3 O/C even decreased slightly at the later period of the reaction (Fig. 6B). This could be due to
4 oligomerisation after condensation forming larger units while releasing of water (formation of
5 esters) or O_2 (dimerization of hydroperoxides) or be due to fragmentation of the products leading
6 to more volatile products.

7 For SOA from ozonolysis, the H/C was around 1.2-1.4, which was distinctively lower than that
8 of the OH oxidation. The lower H/C in the ozonolysis compared to photooxidation was reported
9 by Chhabra et al. (2011). It seemed that a process with significant hydrogen loss such as addition
10 of carbonyl plays a more important role in the SOA formation from ozonolysis compared to OH
11 oxidation. In the reaction of monoterpene with O_3 , taking α -pinene as an example, the $-CH_2-$
12 group can be converted to $-C=O$ group which reduces the H/C and increase O/C. One path way
13 is shown in Fig. S7. Monoterpene reacts with O_3 producing $RO_2\cdot$ radical, which can undergo
14 internal hydrogen shift forming another $R_1O_2\cdot$ radical (Ehn et al., 2014). The $R_1O_2\cdot$ radical can
15 react with other $RO_2\cdot$ radical forming $-C=O$ group at the same time losing two hydrogen atoms.

16 In the individual ozonolysis experiments, the O/C and H/C reached a stable value shortly (<1 h)
17 after the reaction started and then did not show significant change. The different trend with time
18 between the OH oxidation and ozonolysis was caused by the different reaction process. In the
19 OH oxidation, after the particle formed, the reaction products were subject to further reaction
20 with OH. Hence the reaction products, H/C and O/C kept evolving. In contrast, in the ozonolysis
21 the reaction ceased once O_3 reacted with monoterpene. Therefore, there was no further
22 significant change in the O/C and H/C in the ozonolysis.

23 **4.4 Uncertainty of particle mass concentration**

24 The particle mass concentration is used to derive the particle growth efficiency in this study.
25 Uncertainty of the particle mass concentration relates with uncertainties in particle wall loss,
26 dilution and vapor wall loss. The particle mass concentration has been corrected for the dilution
27 and particle wall loss. The corrected particle mass concentration may be affected by the
28 uncertainty of different particle correction methods. In this study, we determined the particle
29 wall loss rate using an exponential fit of the decay of the particle number concentration after the

1 nucleation has stopped for several hours (Carter et al., 2005; Fry et al., 2011; Pierce et al., 2008).
2 Another method that has been used to determine the particle wall loss rate is by fitting the decay
3 particle mass concentration after the condensation has finished (Presto and Donahue, 2006;
4 Pathak et al., 2007). In this study, we found in most of our experiments, the particle wall loss rate
5 determined through the decay particle mass concentration kept evolving until the end during the
6 photooxidation experiment. And this decay rate was lower than that of the period right after the
7 roof was closed and photooxidation stopped. This indicates that particle formation
8 (condensation) was still active and not finished in the light period. In contrast, the particle wall
9 loss rate through decay of particle number concentration was constant during the later period of
10 the photooxidation reaction and higher than that determined through the decay of particle mass
11 concentration, which supports the condensation did not finish. Therefore, the second method,
12 which used the mass concentration, did not apply to our study and we used the first method,
13 determining the wall loss rate by particle number concentration. Once the wall loss coefficient
14 was determined, the particle mass concentration was corrected in every step of the SMPS scans
15 by the dilution and wall loss rate. Pierce et al. (2008) compared the results from different wall
16 loss correction methods including these two methods mentioned here and a model approach,
17 showing that different methods agree within 10% for the faster limonene ozonolysis experiment
18 and a factor of two for the slow toluene oxidation experiment. Unfortunately we cannot compare
19 the difference of these two methods since the method using the particle mass concentration is not
20 suitable for this study. We estimated the uncertainty by investigating the variability of the
21 particle wall loss rate among different experiments. The relative standard deviation of the
22 particle wall loss rate is 11%. We did a sensitivity analysis to check the effect of uncertainty of
23 particle wall loss rate on the corrected mass as shown in Fig. S5. We found the corrected aerosol
24 mass concentration is not sensitive to the uncertainty of the particle wall loss rate. For α -pinene
25 experiment, a change of 10% and 50% only results in a change approximately 2% and 9% of the
26 final corrected particle mass concentration. Considering the uncertainty of our SMPS system
27 ($\pm 10\%$), we estimate uncertainty of the corrected particle mass concentration is 12%.

28 The wall loss of vapor and dilution can also affect the particle concentration which can result in
29 an underestimate of the particle concentration. But in presence of pre-existing particles,
30 condensation on them will be able to compete with wall loss, depending on the S/V of the
31 chamber which is very favorable in our large chamber and surface density of the particles. The

1 wall loss of vapor was investigated in our SAPHIR chamber using experiments in which
2 pinonaldehyde, one important first generation product from α -pinene oxidation, was injected into
3 the chamber. The concentration was monitored over several hours. Constant first-order decay
4 with a rate constant of $2.8 \times 10^{-6} \text{ s}^{-1}$ was observed over a period of 14 h and no equilibrium was
5 observed. It was not possible to detect rapid initial losses of pinonadehdyde in SAPHR chamber
6 due to the chamber setup and injection procedures. The vapor wall loss rate is on the same order
7 of magnitude as described by Loza et al. (2014) but lower than that given by Matsunaga and
8 Ziemann (2010) and Zhang et al. (2014). Different vapor wall loss rates in different chambers are
9 expectable since vapor wall loss rates depend on the mixing in the respective chamber, the
10 thickness of the diffusive boundary layer and penetration into the chamber wall (Zhang et al.,
11 2014). Matsunaga and Ziemann (2010) found that vapor wall loss depends on structure and
12 compound vapor pressure in contrast to Zhang et al. (2014) who used one vapor wall loss rate for
13 all compounds in the whole reaction system. It will result in uncertainties to extrapolate wall-loss
14 rates of pinonaldehyde to all products from monoterpene oxidation. However as a first approach,
15 we estimate the effect on the particle mass concentration, assuming the wall loss rate of
16 pinonaldehyde and same particle yields for all lost vapors (the same as in the reaction system).
17 The particle mass concentration would then be underestimated by approximately 17%.
18 Combining the particle wall loss and vapor loss by wall loss and dilution, the uncertainty of the
19 particle mass concentration is estimated to be approximately 30%. Without correcting the vapor
20 wall loss, the particle mass concentration is underestimated, and so is the particle growth
21 efficiency. In addition, the dilution may also affect particle mass concentration through altering
22 the gas-particle equilibrium. Due to the unknown identities, vapor pressure of the compounds
23 and unknown amounts on the particle, it is not possible in this study to correct this effect.
24 However, the compounds contributing to the particle growth here has very low vapor pressure,
25 which may make the effect of dilution on the gas-particle equilibrium less significant.

26 **5 Conclusion**

27 In this study, the SOA formation from OH oxidation of several monoterpenes, α -pinene, β -
28 pinene and limonene was investigated at ambient relevant conditions (low OA concentration,
29 low VOC and NO_x concentrations) and was compared with the SOA formation from ozonolysis
30 (CO as the OH scavenger). The OH dominant oxidation was achieved at low O_3 concentration.

1 Multi-generation reaction process, particle growth, new particle formation, particle yield, and
2 chemical composition were analyzed.

3 The aerosol ‘growth curve’ reflected the importance of multi-generation products in the OH
4 oxidation of three monoterpenes. In the OH oxidation, we found the transition of
5 functionalization and fragmentation correlated with the evolution of particle size and particle
6 mass as a function of OH dose. A novel method was developed which quantitatively linked the
7 particle mass growth rate to the reaction rate of OH with organics via a metric of particle growth
8 efficiency of OH reaction. This method was also used to examine the role of functionalization
9 and fragmentation during the particle formation of monoterpenes by OH oxidation.
10 Functionalization was found dominant in the beginning of the reaction (within approximately
11 two lifetimes of the monoterpene) and fragmentation started to play an important role after that.
12 The particle growth efficiency of the OH reaction was high in the beginning of the experiment,
13 although the mass growth rate was low due to the low particle mass. This new method also
14 provided an estimation of overall vapor pressure of the products when functionalization was
15 dominant. We show that the overall vapor pressures vary from 10^{-5} to 10^{-3} Pa in the OH
16 oxidation. The method of quantitatively linking particle mass growth rate to the OH reaction rate
17 with organics will be used in other VOC systems and ambient measurements to further
18 investigate the influence of OH oxidation on the particle growth. The relationship of overall
19 reaction rates of the total organics with OH with the particle growth rates applies well in well-
20 characterized chamber systems. Such relationship is being planned to be tested using more VOC
21 systems in the chamber. . For the atmosphere, it is much more complex to apply such method.
22 Different VOC types (such as sesquiterpene or isoprene or linear alkenes) contribute to overall
23 reaction rate of total organics with OH but may have different particle growth efficiencies
24 resulting in different particle growth rates. This has still to be characterized in experiments.

25 The particle size growth rate did not necessarily correlate directly with the reaction rate of
26 monoterpenes with OH and O₃ in individual experiments. Particle size growth rates induced by
27 the reaction with OH and ozonolysis were comparable in this study at similar reaction rates of
28 the monoterpenes with OH and O₃. This indicates that OH oxidation and ozonolysis have
29 comparable efficiency in particle growth. The SOA yields of OH oxidation and ozonolysis in this

1 study are generally consistent with the values in the literature. Ozonolysis of α -pinene and
2 limonene produced a higher aerosol yield than the respective OH oxidation.

3 SOA from monoterpene OH oxidation generally followed a slope of shallower than -1 in the Van
4 Krevelen diagrams, indicative of a process without significant loss of hydrogen during the
5 oxidation. In the later period of the reaction (after around one lifetime of monoterpene), SOA
6 followed a slope of close to -1. SOA from OH oxidation had a higher H/C than that from
7 ozonolysis. In ozonolysis, a process with significant hydrogen loss such as addition of carbonyl
8 seemed to play an important role in SOA formation.

9 In this study, we designed the experiment to study mechanistically the particle formation and
10 growth, therefore we used two extreme cases: pure OH oxidation and pure ozonolysis case. We
11 did not do experiments with both OH and O₃. In the atmosphere, where both OH and O₃ are
12 present, products from the reaction monoterpene with O₃ can further react with OH, hence the
13 chemical composition of aerosol (in terms of elemental composition) may keep evolving
14 continuously. In the atmosphere, both OH oxidation and ozonolysis of monoterpene are
15 important pathways for the particle formation and growth, with their relative importance
16 depending on the specific ambient conditions.

17 **Appendix A: Additional equations for the relationship of particle mass growth and** 18 **the reaction rate with OH**

19 In the case of fragmentation, there could be more than one product, i+₁, i+₂, i+_p. Eq. (11) in
20 the main text is in a slightly different form.

$$21 \left(\frac{dm}{dt}\right)_i = \frac{dC_i^g}{dt} \cdot m_i \left(\sum_{k=1}^p \frac{1}{C_{i+_k}^0} - \frac{1}{C_i^0}\right) \quad (\text{A1})$$

22 One can define

$$23 \frac{1}{C_{avg,i+}^0} = \sum_{k=1}^p \frac{1}{C_{i+_k}^0} \quad (\text{A2})$$

24 Fragmentation usually generates one small volatile molecule and one less volatile molecule
25 (assuming species P_{i+₁}).

$$1 \quad \frac{1}{C_{avg,i+}^0} \approx \frac{1}{C_{i+_1}^0} \quad (A3)$$

2 Thus $i+_1$ can directly correspond to $i+$ in Eq. (11) in the main text and will not change the
3 format of Eq. (11).

4 We assume that the molecular weight of $i+$ is similar with that of i , i.e neither functionalization
5 nor fragmentation change the molecular dramatically. In the case of fragmentation, when the
6 molecular weight could change significantly if the fragmentation happens in the middle of the
7 carbon bone. In this case we keep the molecular weight of each species.

8 Eq. 14 becomes:

$$9 \quad \frac{dm_t}{dt} = \sum_i R_{OH,i} m_i \left(\frac{M_{i+}}{C_{i+}^0} - \frac{M_i}{C_i^0} \right) \quad (A4)$$

10 Eq. 17 becomes:

$$11 \quad GE_{OH}(t,i) = \frac{M_{i+}}{C_{i+}^0} - \frac{M_i}{C_i^0} \quad (A5)$$

12 M_i and M_{i+} can be incorporated in the definition of the overall vapor pressure with a slight
13 change.

$$14 \quad \frac{\sum_i R_{OH,i} \cdot \frac{M_{i+}}{C_{i+}^0}}{\sum_i R_{OH,i}} = \frac{1}{C_{i+}^0} \quad (A6)$$

$$15 \quad \frac{\sum_i R_{OH,i} \cdot \frac{M_i}{C_i^0}}{\sum_i R_{OH,i}} = \frac{1}{C_i^0} \quad (A7)$$

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Table 1 Summary of experimental conditions. All experiments were performed at initial RH 75% and $\text{NO}_x < 1$ ppb

Experiment type	VOC type	VOC initial (ppb)	[OH] (10^6 molecules cm^{-3})	Initial O_3 (ppb)	Average T (K)	Initial mass ($\mu\text{g m}^{-3}$)	Rate coefficient ($\text{molecule}^{-1} \text{cm}^3 \text{s}^{-1}$) ^b
OH oxidation	α -pinene	4	6.4	1.0	299	6.1×10^{-3}	5.25×10^{-11}
	β -pinene	4	6.2	2.5	301	9.5×10^{-3}	7.89×10^{-11}
	limonene	4	6.4	2.2	298	12.2×10^{-3}	1.64×10^{-11}
Ozonolysis	α -pinene	4	NDs ^a	136	289	9.2×10^{-3}	8.72×10^{-16}
	β -pinene	4	NDs	760	294	5.7×10^{-3}	1.50×10^{-16}
	limonene	4	NDs	136	290	11.7×10^{-3}	2.08×10^{-16}

^a Below the detection limit of instruments (0.3×10^6 molecules cm^{-3})

^b Atkinson and Arey (2003)

Figure 1. Time dependent growth curve of aerosol from the OH oxidation of α -pinene (a), β -pinene (b) and limonene (c) as function of hydrocarbon(HC) consumed (monoterpene here) from measurement.

Figure 2. Particle mass concentration and median diameter as a function of OH dose for the OH oxidation of α -pinene (a), β -pinene (b) and limonene (c). The dashed vertical lines correspond to the one and two lifetimes of each monoterpene with respect to OH oxidation. The lifetime is the time when the monoterpene concentration decreases to $1/e$ of the initial concentration.

Figure 3. Time series of $GE_{OH}(t)$ (particle mass growth efficiency in respect to the reaction of OH with organics, refer to the text for details. For clarity 7 points moving average is shown.), $k_{OH}(\text{Org})$ (OH reactivity of total organics), O/C and H/C from AMS data, and aerosol mass concentration in the OH oxidation of α -pinene (a), β -pinene (b) and limonene (c). The shaded area shows the dark period. The dashed vertical lines in each panel show the one and two lifetimes of monoterpene.

Figure 4. Particle size growth rate, mass growth rate and reaction rate of OH or O_3 with α -pinene (a, d), β -pinene (b, e) and limonene (c, f). The top panels are from OH oxidation (the shaded area shows the dark period) and bottom panels from ozonolysis in the presence of CO as OH scavenger. For the OH oxidation, the overall reaction rate of OH with total organics (reaction rate(OH+Org)) is also shown.

Figure 5. Particle number concentration, mass concentration (not corrected for losses), surface concentration and median diameter of the aerosol from α -pinene (a, d), β -pinene (b, e) and limonene (c, f). The top panels are from OH oxidation (the gray shaded area shows the dark period) and bottom panels from ozonolysis. The grey hatched area corresponds to the flushing out period.

Figure 6. H/C and O/C ratio of SOA from the OH oxidation and ozonolysis of α -pinene (a, d), β -pinene (b, e) and limonene (c, f). The top panels are from OH oxidation and bottom panels from ozonolysis. Dark color denotes the beginning of the experiments and yellow denotes the later period. The red dashed line correspond to H/C=1.6. The black dashed lines correspond to the slope of -2, -1 and -0.5.