Molecular Formula Composition of β -Caryophyllene Ozonolysis SOA Formed in Humid and Dry Conditions

Shuvashish Kundu^{a,d,*}, Rebeka Fisseha^c, Annie L. Putman^c, Thom A. Rahn^c, Lynn R. Mazzoleni^{a,b,*}

^aDepartment of Chemistry and ^bAtmospheric Science Program, Michigan Technological University,
Houghton, MI 49931, USA

^cEarth and Environmental Sciences, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

^dNow at Department of Chemistry, University of Massachusetts - Amherst, MA 01003, USA

*Corresponding authors:

Shuvashish Kundu, Phone (413)-404-3560, Fax (413)-545-4490 and Email address drkundu@mtu.edu.

Lynn Mazzoleni, Phone (906)-487-1853, Fax (906)-487-2061, and Email address lrmazzol@mtu.edu.

ABSTRACT

We studied the molecular formula composition of six β -caryophyllene SOA samples using ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry under various reaction conditions. The SOA samples were generated in dry or low relative humidity (RH) chamber conditions with or without cyclohexane. All of the studied SOA mass spectra have three distinct clusters of hundreds of negative ions referred to as Group I ($100 < m/z < 400$), Group II ($400 < m/z < 700$) and Group III ($700 < m/z < 1000$) compounds. $C_{14-16}H_{22-28}O_{2-11}$, $C_{28-29}H_{42-48}O_{6-16}$ and $C_{42-43}H_{68-70}O_{14-16}$ were observed as highly abundant organic compounds in the compound class of Group I, II and III, respectively. The relative intensities of most analytes were higher in humid conditions compared to those in dry conditions, indicating the importance of water-dependent reactions and the catalytic role of water both in the presence and absence of cyclohexane. In addition, molecular formulas with higher average carbon numbers were observed in humid SOA than in dry SOA in the absence of cyclohexane, suggesting a decrease of cleavage reactions in humid condition. This study characterizes β -caryophyllene ozonolysis SOA based on ultrahigh mass resolution and demonstrates the significance of humidity in terms of the molecular distributions and relative abundances of the analytes. We also discuss the possible mechanism for the formation of Group I-III compounds based on the current understanding of SOA formation in the atmosphere.

Keywords: β -caryophyllene, Ozonolysis, Smog-chamber, SOA, High resolution mass spectrometry, FT-ICR

1. Introduction

Atmospheric organic aerosol (OA) is strongly linked to adverse human health effects, visibility reduction and climate change (Baltensperger et al., 2008; Fiore et al., 2012; Moise et al., 2015). Secondary organic aerosol (SOA) represents a major mass fraction of ambient OA (Hallquist et al., 2009; Zhang et al., 2007). Thus, an improved molecular understanding of SOA is urgently needed to unravel their complex formation processes and address the adverse effects of aerosol (Jimenez et al., 2009; Kroll et al., 2011; Kundu et al., 2012). β -caryophyllene ($C_{15}H_{24}$) is a bicyclic hydrocarbon with reactive endocyclic and exocyclic double bonds. It is the most common and abundant of the sesquiterpenes emitted by plants and agricultural trees (Duhl et al., 2008). Although sesquiterpene emission rates were estimated to be only 9-16% of the total terpene emissions (Duhl et al., 2008), they are more reactive to oxidants (OH radicals and O_3) and larger in size than monoterpenes (Lee et al., 2006a; Lee et al., 2006b). Thus, the aerosol mass yields from the ozonolysis of sesquiterpenes range from 12 to 100% and are one of the determinants of the SOA budget in the atmosphere (Chan et al., 2011; Hoffmann et al., 1997; Jaoui et al., 2013; Jaoui et al., 2007; Lee et al., 2006a; Lee et al., 2006b; Tasoglou and Pandis, 2015).

Ozone reacts rapidly with β -caryophyllene at the endocyclic double bond to form first generation oxidation products in the gas and aerosol phases (Chan et al., 2011; Kanawati et al., 2008; Li et al., 2011; van Eijck et al., 2013; Winterhalter et al., 2009). Second generation oxidation products are formed by additional ozonolysis at the exocyclic bond (Li et al., 2011; Winterhalter et al., 2009). Due to the high reactivity of these first and second generation oxidation products, they are further processed by a wide variety of oxidative and non-oxidative processes resulting in a very complex mixture of SOA components with multiple generations of oxidation products (Kundu et al., 2012; Putman et al., 2012). Previous studies determined the low molecular weight ($m/z < 300$) composition of SOA from β -caryophyllene ozonolysis (Chan et al., 2011; Jaoui et al., 2013; Kanawati et al., 2008; Li et al., 2011; Winterhalter et al., 2009). The analytical techniques used in these studies were either gas chromatography coupled with

mass spectrometry (GC-MS) (Jaoui et al., 2013; Jaoui et al., 2007; Kanawati et al., 2008) or liquid chromatography with mass spectrometry (LC-MS) (Chan et al., 2011; Kanawati et al., 2008; Li et al., 2011; Winterhalter et al., 2009). To date, the number of reported β -caryophyllene ozonolysis oxidation products is far less than the oxidation products of the ozonolysis of isoprene (Kourtchev et al., 2015; Nguyen et al., 2010), α -pinene (Kourtchev et al., 2015; Putman et al., 2012; Reinhardt et al., 2007), and limonene (Bateman et al., 2009; Kundu et al., 2012). Additionally, there are only a few SOA markers of β -caryophyllene oxidation that have been determined in atmospheric aerosols (Jaoui et al., 2007; van Eijck et al., 2013). Therefore, it can be assumed that there are many unrecognized organic compounds in ambient SOA from β -caryophyllene similar to those reported elsewhere (Mazzoleni et al., 2012).

Humidity and aerosol liquid water content are important variables potentially affecting the molecular composition of SOA (Ervens et al., 2011; Jonsson et al., 2006, 2008; Ma et al., 2007; Tasoglou and Pandis, 2015; Tillmann et al., 2010; von Hessberg et al., 2009). Scavengers (e.g., cyclohexane, alcohols, carbon monoxide, etc.) are often used in chamber ozonolysis experiments with biogenic volatile organic compounds (BVOCs) to consume OH radicals resulting from the decomposition of Criegee biradicals and hydroperoxides (Atkinson and Aschmann, 1993). Thus, the use of scavengers may alter SOA composition by changing the HO_2/RO_2 ratios during the ozonolysis of monoterpenes (Docherty et al., 2005; Docherty and Ziemann, 2003) and may also modify the effect of humidity (Jonsson et al., 2008). High humidity has been reported to increase the gas-phase formation of the water dimer (Ryzhkov and Ariya, 2006), OH radicals (Wegener et al., 2007), the self-reactions of HO_2 radicals (Docherty and Ziemann, 2003), and reaction products from Criegee radicals-water interaction (Winterhalter et al., 2009), all of which are expected to increase the yield of aerosol phase compounds. Similarly, aerosol liquid water enhances the dissolution of hydrophilic organic precursors followed by their oxidation/accretion reactions, which results in the generation of SOA (Ervens et al., 2011). This interpretation is consistent with the observation of high SOA yields in humid condition during the

ozonolysis of β -caryophyllene (Winterhalter et al., 2009). However, little evaluation of the water effects has been done for the molecular composition of the condensed phase β -caryophyllene ozonolysis SOA using modern analytical approaches.

In this paper, we present the detailed molecular composition of β -caryophyllene SOA from six individual chamber experiments with varied relative humidity and the presence or absence of cyclohexane as a radical scavenger. Ultrahigh resolution Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to measure the analyte exact masses for a comprehensive molecular formula characterization of the β -caryophyllene ozonolysis SOA. The compositional similarities and differences of the SOA and their implications are discussed. We compare the molecular formulas in β -caryophyllene ozonolysis SOA with those previously found in the ozonolysis SOA of isoprene, α -pinene, β -pinene, and limonene to identify β -caryophyllene-specific formulas. The existence of β -caryophyllene-specific formulas are also explored in ambient aerosols (Mazzoleni et al., 2012) and cloud water (Zhao et al., 2013).

2. Materials and Methods

2.1 Chamber experiments

Six SOA samples were generated by the ozonolysis of β -caryophyllene with varied humidity and the presence or absence of cyclohexane for radical scavenging. The sample names (e.g., CP_{30%RH}, with CH) indicate the precursor (β -caryophyllene = CP), RH (Dry, 4% or 30%) and if included the presence of cyclohexane (with CH), as shown in Table 1 and Table S1. The experimental chamber was previously described (Kundu et al., 2012). Briefly, SOA samples were generated at dry ($0 \pm 2\%$), $4 \pm 2\%$ and $30 \pm 2\%$ relative humidity (RH) in a dark 1.5 m³ teflon bag chamber located at the Los Alamos National Laboratory. The temperature of the chamber was not controlled. However, a heat mat was placed under the chamber to facilitate the convective mixing and the temperatures therefore were slightly higher than room temperatures. Each of the experiments was carried out in the absence of seed aerosols with

the initial concentration of β -caryophyllene at 290 ppb and ozone at 250 ppb. Cyclohexane with a concentration of 3.7 ppm was added as an OH radical scavenger to some of the experiments. Cyclohexane was added in this study to investigate the modification of humidity effect by the scavenger, but not scavenging all of the OH radicals. The added cyclohexane is expected to scavenge ~32% of generated OH radicals (Atkinson and Aschmann, 1993). The oxidation of β -caryophyllene by the remaining ~68% of OH radicals is estimated to be relatively insignificant (< 5%) compared to the oxidation of β -caryophyllene by O_3 (> 95%) (Atkinson and Aschmann, 1993). The mixtures in the chamber are allowed to react over 1 hour. Under the chamber condition in this study, first generation oxidation products are not expected to be further oxidized (Winterhalter et al., 2009). Instead, they will participate in the accretion reactions to form high-molecular-weight compounds. Aerosols were collected at 6 LPM onto a prebaked quartz fiber filter without a denuder. Chamber blanks were collected following the same methods, except β -caryophyllene and ozone were not introduced into the chamber. We also generated and collected α -pinene, β -pinene and limonene ozonolysis SOA following the above procedure at $30 \pm 2\%$ RH using 500 ppb of α -pinene, β -pinene or limonene and 250 ppb of ozone. Here, we only use α -pinene/ β -pinene SOA formulas to identify unique β -caryophyllene formulas. Detailed discussion on α -pinene and β -pinene formulas has been reported elsewhere (Mazzoleni et al., 2012)

2.2 Sample Storage and Preparation

The filter samples were stored in petri dishes (Pall Corporation) wrapped with aluminum foil in a freezer at -5°C . The samples were shipped cold overnight with blue ice to Michigan Tech. Half of the filter was extracted with 5 mL of a 1:1 mixture of acetonitrile (Chromasolv, Sigma Aldrich) and water (ACS, Sigma Aldrich). The mixture of acetonitrile and water was used to ensure the extraction of both polar and non-polar molecules in SOA. The extraction was carried out in a sonicating bath for 30 min. Recently, an observation of the generation of free radicals during ultrasonication has been reported

(INSERT reference here); however, the reported low concentrations of reactive oxygen species are not expected to significantly alter the molecular composition. Afterward the solvent was decanted and kept at -20°C until further analysis. Acetonitrile was chosen for SOA extraction since it is not expected to react with the analyte molecules (Bateman et al., 2008). Water may hydrate analyte carbonyl functional groups potentially altering the molecular composition; however, similar modifications are expected to happen in cloud water and aqueous aerosol surfaces.

2.3 Ultrahigh resolution FT-ICR MS analysis

Consistent with previous studies (Kundu et al., 2012; Mazzoleni et al., 2010; Putman et al., 2012), aerosol extracts were analyzed using a 7 T FT-ICR MS (LTQ FT Ultra, Thermo Scientific) equipped with an electrospray ionization (ESI) source at the Woods Hole Oceanographic Institution. The instrument was externally calibrated in the negative ion mode with standard solutions of sodium dodecyl sulfate and taurocholic acid as prescribed by Thermo Scientific for mass calibration of the FT-ICR MS instrument. The resulting mass accuracy was better than 2 ppm. Consistent with Putman et al., 2012, the diluted solution (organic carbon concentration: $< 10^{-3}$ M) was directly injected into an electrospray ionization (ESI) interface at a flow rate of $4 \mu\text{L min}^{-1}$. Dilute solutions are important in direct infusion analyses because they have a reduced potential for adduct formation (Constantopoulos et al., 1999). The needle voltage was set between -3.7 and -4.0 kv and no sheath gas was used. The capillary temperature was maintained at 265°C. Full scan mass spectra were acquired in the negative ion mode (m/z 100 – 1000) using a mass resolving power set at 400,000 (defined at m/z 400). Automatic gain control was used to consistently fill the mass analyzer with the same number of ions ($n = 1 \times 10^6$) and to avoid space charge effects associated with over-filling the mass analyzer (Kido Soule et al., 2010). Over 200 individual mass spectra were collected and stored as individual transient files (time domain ICR signal) using Xcalibur 2. This number of transients was selected based on observations of mass spectral reproducibility and signal-to-noise (Kido Soule et al., 2010).

2.4 Molecular Formulas Assignment

Approximately 200 transients recorded in the time domain were co-added to enhance the analyte signal-to-noise ratios (Kujawinski et al., 2002; Stenson et al., 2003). Several high relative abundance SOA components were used as internal recalibrants (Kundu et al., 2012; Putman et al., 2012) to improve the analyte mass accuracy. The molecular formula calculator (Sierra Analytics Composer) was used to assign molecular formulas to the masses of singly charged recalibrated ions of $100 < m/z < 1000$ and relative abundances (RA) > 15 times the signal-to-noise observed between m/z 950-1000. The calculator was set to allow up to 100 carbon, 200 hydrogen, and 50 oxygen atoms per elemental composition and used a CH_2 formula extension approach. Unequivocal formula assignments are expected for masses up to 1000 Da when only C, H and O are included (Kundu et al., 2012; Putman et al., 2012). Minimal fragmentation of the molecular ions may occur despite the use of very low ionization energy in the ESI method, however since no evidence of fragmentation was observed the detected ions were treated as molecular ions. Assigned molecular formulas were validated using the rules and assumptions described elsewhere (Koch et al., 2005). Briefly, the maximum numbers of hydrogen and heavy atoms are restricted by the equations (< 2 times carbon number + 2) and ($< \text{nominal mass}/13$), respectively. The O:C and H:C ratios were restricted to values ≤ 2.0 and ≥ 0.3 , respectively, and the sum of the rings and double bonds in each formula (aka double bond equivalents, $\text{DBE} = \text{carbon number (c)} - \text{hydrogen number (h)}/2 + 1$) must result with a positive integer value for uncharged molecules. Approximately 94% of the monoisotopic molecular formula peaks reported in this study were accompanied by their ^{13}C peaks, providing an intrinsic validation of the molecular formula assignment (Koch et al., 2005). About 21% of the ions were common between blanks and aerosol samples. Blank subtraction was not applied because the abundance of the common ions in the blank sample was significantly less (< 5) than those in the experimental SOA samples indicating low-level resuspension of analytes in the electrospray source (Mazzoleni et al., 2012).

3. Results and discussion

3.1 General overview

The ultrahigh resolution ESI FT-ICR mass spectra of the β -caryophyllene ozonolysis SOA samples were observed to be quite complex with hundreds of ions across the mass range of 100-1000 Da (Fig. 1 and Table S2), which is consistent with previous studies of α -pinene and limonene SOA products (Kundu et al., 2012; Putman et al., 2012; Reinhardt et al., 2007). To date, studies of β -caryophyllene SOA have reported molecular formulas from ~30 negative ions with m/z values < 300 (Chan et al., 2011; Jaoui et al., 2013; Jaoui et al., 2007; Kanawati et al., 2008; Li et al., 2011; Winterhalter et al., 2009). The ions of the previously observed molecular formulas along with hundreds of additional negative ions observed in this study are shown in Fig. 1. Such a high number of compound identification in β -caryophyllene SOA in this study is due to the deployment of ultrahigh resolution mass spectrometry after soft-ionization. Many of the analytes we observed, such as $C_{16}H_{26}O_6$, $C_{14}H_{22}O_{5-7}$, and $C_{14}H_{24}O_7$ had relative abundances greater than $C_{10}H_{16}O_4$, $C_{11}H_{20}O_3$, $C_{14}H_{22}O_4$, and $C_{14}H_{22}O_3$. These molecular formulas could be related to previously reported β -caryophyllene SOA markers in atmospheric aerosols, including 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid ($C_{10}H_{16}O_4$), 3,3-dimethyl-2-(3-oxobutyl)-cyclobutanecarboxylic acid ($C_{11}H_{20}O_3$), β -caryophyllinic acid/ β -nocaryophyllonic acid ($C_{14}H_{22}O_4$), and β -caryophyllonic acid ($C_{14}H_{22}O_3$), respectively. The previously determined gas and aerosol phase products from the oxidation of β -caryophyllene cannot fully explain the reacted β -caryophyllene carbon (Jaoui et al., 2003). If newly determined organic compounds such as those reported in this study were quantified, they may explain more of the reacted β -caryophyllene carbon.

A majority of the observed ions were commonly found in all 6 experiments with three characteristic clusters despite the varied experimental conditions (Fig. 1). The analyte clusters are here forward referred to as Group I, Group II, and Group III and contain the assigned molecular formulas within the following mass ranges: $100 < m/z < 400$, $400 < m/z < 700$ and $700 < m/z < 1000$. The observation of

three groups of compounds in all the SOA mass spectra suggests that there are common reaction processes that are insensitive to humidity and the presence or absence of cyclohexane in terms of the formation of these clusters of compounds. The common and condition-specific reaction processes are discussed in further detail in the following sections.

3.2 β -Caryophyllene SOA molecular trends

The chemical characteristics and potential building units of the molecular formulas were evaluated using Kendrick mass analysis (Kendrick, 1963). In this approach, the measured m/z values are converted to Kendrick masses with respect to any specific Kendrick base (Eq. 1). Then, the Kendrick mass defect is determined (Eq. 2).

$$\text{Kendrick mass (base)} = \text{Observed mass} \times [(\text{Nominal mass of base})/(\text{Exact mass of base})] \quad (\text{Eq. 1})$$

$$\text{Kendrick mass defect (base)} = |\text{Nominal mass} - \text{Kendrick mass (base)}| \quad (\text{Eq. 2})$$

CH_2 , O, or any combination of atoms can be used as a Kendrick base. Using Eq. 1 and 2, we evaluated the β -caryophyllene SOA using the following Kendrick bases: CH_2 , O, formaldehyde (CH_2O), acetaldehyde ($\text{C}_2\text{H}_4\text{O}$), acetone ($\text{C}_3\text{H}_6\text{O}$), glyoxal ($\text{C}_2\text{H}_2\text{O}_2$), methylglyoxal ($\text{C}_3\text{H}_4\text{O}_2$), and β -caryophyllon aldehyde ($\text{C}_{15}\text{H}_{24}\text{O}_2$). Consistent with the chamber SOA from isoprene, α -pinene and limonene oxidation (Heaton et al., 2009; Kundu et al., 2012; Nguyen et al.; Putman et al., 2012), many CH_2 and O-homologous series were observed over the whole mass range (Fig. 2A and Figs. 3 and 4). Similarly, high occurrences of other homologous series were observed. For example, 81 - 87% of the compounds were found to be involved in CH_2O series, 87 - 91% in $\text{C}_2\text{H}_4\text{O}$ series, 73 - 81% in $\text{C}_3\text{H}_6\text{O}$ series, 64 - 74% in $\text{C}_2\text{H}_2\text{O}_2$ series, 68 - 77% in $\text{C}_3\text{H}_4\text{O}_2$ series, and 70 - 79% in $\text{C}_{15}\text{H}_{24}\text{O}_2$ series. High occurrences of these types of homologous series were also found in the organic matter from other environmental samples such dissolved organic matter in river water, fulvic acid and humic acid (Hughey et al., 2001; Kim et al., 2003; Mazzoleni et al., 2010; Stenson et al., 2003). The presence of homologous series is either merely

a coincidence of the complex mixture or a reflection of the chemical processes, which yield organic species by the addition of Kendrick bases.

We investigated the formation processes of the most abundant selected O-homologous series found in Group I based on the known reaction processes (Fig. 3). The immediate gas-phase oxidation products of β -caryophyllene ozonolysis are reported to be primary/secondary ozonide, Criegee radicals, hydroperoxides, and dioxiranes as shown in SI Fig. S-1 (Jenkin et al., 2012; Nguyen et al., 2009; Winterhalter et al., 2009). The dioxirane channel has been estimated to be a prominent pathway for the formation of aerosol-phase compounds in β -caryophyllene ozonolysis SOA (Nguyen et al., 2009). The $C_{14}H_{24}O_{2-9}$ and $C_{14}H_{22}O_{2-10}$ homologous series are dominant oxidation products as shown in Fig. 3A and their formation can be explained by the dioxirane pathway (Fig. 3B). Dioxirane yields a peroxy radical ($C_{14}H_{23-x}O_3(OH)_x$, $x = 0$), which is converted to multi-hydroxylated peroxy radicals ($C_{14}H_{23-x}O_4(OH)_x$, $x = 1-7$) by the repetition of the OH-enhancement reaction scheme resulting in $C_{14}H_{24}O_{2-9}$ and $C_{14}H_{22}O_{2-10}$ homologous series.

The formation of $C_{15}H_{24}O_{3-10}$ and $C_{15}H_{22}O_{4-10}$ homologous series can be explained by the hydroperoxide pathways (Fig. 3C). Hydroperoxide is transformed to peroxy radical ($C_{15}H_{24-x}O_4(OH)_x$, $x = 0$), which is further converted to multi-hydroxylated peroxy radicals ($C_{15}H_{24-x}O_4(OH)_x$, $x = 1-6$) following the repetition of the OH-enhancement reaction scheme ($RO_2 \rightarrow RO \rightarrow OH-RO_2$). The disproportionation reactions between hydroxyperoxy radicals (shown for $C_{15}H_{24-x}O_4(OH)_x$, $x = 0-1$) produces neutral alcohol and carbonyl compounds resulting in the formation of two homologous series $C_{15}H_{24}O_{3-10}$ and $C_{15}H_{22}O_{4-10}$. Interestingly, we observed $C_{15}H_{26}O_{4-9}$, $C_{16}H_{26}O_{4-11}$ and $C_{16}H_{28}O_{4-10}$ homologous series as dominant oxidation products in β -caryophyllene ozonolysis SOA (Fig. 3A). However, their formation processes cannot be explained by known pathways because of the enrichment of hydrogen and carbon atoms compared those in β -caryophyllene precursor.

Elemental ratios of hydrogen-to-carbon (H:C) and oxygen-to-carbon (O:C) are useful for the classification of complex organic compounds (Kim et al., 2003; Mazzoleni et al., 2010) and for evaluating the formation processes of SOA (Bateman et al., 2008; Kroll et al., 2011; Kundu et al., 2012). We observed the average O:C ratios of β -caryophyllene SOA to decrease with the increase in the MW of SOA components. In addition to this, the ranges of O:C values for each analyte Group also decreases, they are: 0.41 - 0.48, 0.37 - 0.41 and 0.33 - 0.37 (Fig. 2b, Table 1). A single factor ANOVA analysis shows that the mean O:C ratios between the groups are significantly different in the 95% confidence interval for each SOA sample. This is consistent with other monoterpene ozonolysis studies (Bateman et al., 2009; Kundu et al., 2012; Putman et al., 2012). The average H:C ratio remained constant at 1.6 for all 3 groups.

The number of double bond equivalents (DBE) and the number of oxygen atoms were plotted with respect to the number of carbon atoms for all of the β -caryophyllene SOA assigned molecular formulas (Fig. 4). The 3 groups are clearly distinguished from the background by the colored symbols representing the relative abundance. Thus, the plots provide a visual indication of the trends between the analyte groups. For example, Group II analytes have approximately 2 times the average DBE, number of oxygen atoms and number of carbon atoms compared to Group I analytes. Similarly, the average DBE, number of oxygen atoms and number of carbon atoms of Group III analytes increased by approximately 3 times compared to those of Group I analytes and approximately 1.5 times compared to those of Group II analytes. The changes in DBE patterns are indicative of the accretion reactions via the non-condensation (hemiacetal, hydroperoxide and Criegee) and condensation (aldol and esterification reactions) reactions (Bateman et al., 2009; Kundu et al., 2012).

The trends of change in the O:C and H:C ratios and DBE from Group I to III compounds are also consistent with the concept of oligomerization, which occurs via non-condensation (hemiacetal, hydroperoxide and Criegee reactions) and condensation (aldol and esterification reactions) reactions (Bateman et al., 2009; Kundu et al., 2012). The decrease in O:C ratios from Group I to Group III in

terpene ozonolysis SOA has been attributed to the elimination of H₂O as a result of condensation (aldol and esterification) reactions (Bateman et al., 2009; Reinhardt et al., 2007). However, the observation of no change of H:C ratios from Group I to Group III suggests a lesser importance of the condensation reactions than the non-condensation reactions (hydroperoxide, Criegee radical and hemiacetal reactions) where water molecules are not eliminated.

To better understand the importance of condensation reactions over non-condensation reactions, we investigated the formation of the most abundant homologous series of Group II-III compounds as shown in Fig. 5A, B, where the symbol size indicates the analyte relative abundance. The formation of C₂₉H₄₈O₆₋₁₅ homologous series can be explained by combining two most abundant Group I compounds following non-condensation (hydroperoxide, hemiacetal, and Criegee) and condensation (aldol but not esterification) pathways with more possible combinations following the hydroperoxide and hemi-acetal pathway (Fig. 5C, D). Similarly, other homologous series in Fig. 5A can be explained always by hydroperoxide and hemiacetal pathways and aldol condensation pathway (Fig. S3 to Fig. S7). Occasionally, the most abundant Group II compounds cannot be explained by esterification and Criegee pathways. Due to the constant average H:C ratios for Group I-III compounds and an increased number of possible combinations between abundant Group I for the formation of Group II-III compounds via hemiacetal and hydroperoxide pathways, the most abundant Group II-III compounds (m/z > 400-1000) are inferred to form more importantly via hemiacetal and hydroperoxide pathways than via condensation pathways. Our previous study demonstrated the greater importance of the non-condensation reactions over the condensation reactions using MS/MS fragmentation analysis of selected high-molecular-weight organic compounds in limonene ozonolysis SOA (Kundu et al., 2012).

3.3 Composition Differences with Humidity

The role of water in the formation of SOA was inferred to be consistent with previous observations (Tasoglou and Pandis, 2015; Winterhalter et al., 2009) from comparisons of the identified molecular

compositions of CP_{Dry} and CP_{30%RH}. These two experiments represent the two extremes with respect to RH and were conducted without cyclohexane for radical scavenging. A simple comparison of the composition using the ratios of peak intensities in humid SOA samples to those in dry SOA samples is shown in Fig. 1. Although intensity (or relative abundance) does not directly reflect the analyte concentration, it is often used as a proxy especially when similar electrospray efficiencies are expected. The intensity ratios of more than 98% of the common molecular formulas between CP_{30%RH} and CP_{Dry} samples were >2 to 163. For example, the intensity ratios of chemical formulas C₁₀H₁₆O₄ and C₁₄H₂₂O₄, related to β -caryophyllene SOA markers 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid and β -caryophyllinic acid/ β -nocaryophyllonic acid are 3 - 6 times higher in CP_{30%RH} than those in CP_{Dry}. The Group II to Group I intensity ratios under humid condition are higher than those under dry condition (Fig. 1). These results suggest an overall enhancement in the SOA production with water and the formation Group II-III compounds is more sensitive than that of Group I compounds, being consistent with the observation of higher aerosol yield in β -caryophyllene ozonolysis (Winterhalter et al., 2009).

High SOA yields in humid conditions can be attributed to the enhancement of water-dependent reactions in the gas- and aerosol-phase. Possible gas-phase reactions include: a) reactions of the water dimer with Criegee radicals and secondary ozonides, which is associated with a decrease in the cleavage of the Criegee radicals by the hydroperoxide and dioxirane channels (Winterhalter et al., 2009), b) the catalytic role of water via the migration of H atom from β -carbon to the terminal oxygen in Criegee radicals resulting in the formation of hydroperoxides (Ryzhkov and Ariya, 2004) and c) the destruction of HO₂ radicals by water (Jonsson et al., 2006). Aerosol-phase reactions include reactive uptake of carbonyls via the hydration reactions and various other accretion reactions (non-condensation and condensation reactions (Bateman et al., 2009; Kundu et al., 2012)).

Difference mass spectra can explain the varied reaction processes in humid (30 $\pm$ 2%) and dry conditions (0 $\pm$ 2%). A difference mass spectra (Fig. 6a) were determined based on a method described

elsewhere (Docherty and Ziemann, 2003). In the difference mass spectra, the normalized analyte intensities of CP_{30%RH} were subtracted from the normalized analyte intensities of CP_{Dry}. The analyte intensities were normalized by the summed total ion intensity of the assigned monoisotopic molecular formulas for each of the samples. Thus, the positive peaks represent those that are more dominant in the humidified experiment whereas the negative peaks are more dominant in the dry experiment. Group I-III analytes with higher carbon numbers, higher average H:C ratios, lower oxygen numbers, lower DBE and lower O:C ratios were observed with higher intensities in the SOA from the humid condition compared to the SOA from the dry conditions (SI Table S-3). For example, the most abundant Group I to Group III compounds in the CP_{30%RH} are C₁₆H₂₆O₆, C₂₉H₄₈O₁₁ and C₄₃H₇₀O₁₅, whereas the dominant Group I to Group III compounds in the CP_{Dry} are C₁₁H₁₈O₆, C₂₈H₄₂O₁₁ and C₃₈H₆₀O₁₄. The results suggest enhanced compound formation due to the cleavage of reaction products such as RO radicals in dry conditions and the cleavage is reduced in the presence of water probably due to the reactions of Criegee radicals and other reaction intermediates with water.

The molecular characteristics of the uniquely assigned chemical formulas between CP_{Dry} and CP_{30%RH} have been shown in the SI Table S-4 and Fig. 1. The majority of unique molecular formulas for the SOA generated at dry condition (CP_{Dry}) were observed in Group I (n = 190, comprising ~66% of total unique formulas in Group I to III) and most of the unique formulas for the SOA generated at 30 ± 2% RH (CP_{30%RH}) were observed in Groups II-III (n = 235, ~94% of total unique formulas in Group I to III). We also observed lower average numbers of carbon atoms in the unique molecular formulas for each of the groups in the dry SOA (n = 12, 26, and 40) compared to those of the humidified SOA (n = 16, 32 and 42). Additionally, the average numbers of oxygen in the unique molecular formulas are higher in the dry SOA (n = 6, 12 and 17) than in the humidified SOA (n = 4, 9 and 13). The average DBE values for the groups are also higher in the dry SOA (n = 4, 8 and 10) than in the humidified SOA (n = 3, 6 and 9). We also observed the O:C ratios of the uniquely assigned molecular formulas to decrease with an increase in the

molecular weight in the dry sample, but the O:C ratios increased with molecular weight in the humidified SOA sample. The above observations of lower carbon numbers, higher oxygen numbers and higher DBE values in the dry SOA (CP_{Dry}) compared to the humid SOA (CP_{30%RH}) further suggest an enhanced SOA formation likely due to the cleavage of reaction products such as RO radicals.

3.4 Composition differences due to the modification of water effect by radical scavenging with cyclohexane

The humidity effect may have been altered in the presence of cyclohexane due to: a) competition between H₂O and cyclohexane-derived RO₂ radicals with Criegee radicals (Jonsson et al., 2008), and b) enhanced production of cyclohexane-derived RO₂ due to more OH production in humid conditions than those in dry conditions (Winterhalter et al., 2009). Consistent with our observations of the increased analyte intensities in the β -caryophyllene SOA generated at 30 $\pm$ 2% RH without cyclohexane (CP_{30%RH}), the ion intensities of ~84% of chemical formulas in SOA generated at 30 $\pm$ 2% RH with cyclohexane (CP_{30%RH} with CH) are also significantly higher than those generated in dry conditions with cyclohexane (CP_{4%RH} with CH). For example, the intensity ratios of chemical formulas C₁₀H₁₆O₄ and C₁₄H₂₂O₄, related with ambient β -caryophyllene SOA markers 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid and β -caryophyllinic acid/ β -nocaryophyllonic acid are 1.6 - 2.0 times higher in CP_{30%RH} with CH than those in CP_{4%RH} with CH. The results show that high humidity can enhance aerosol generation even in the presence of cyclohexane following the reaction processes as described earlier. Humid to dry intensity ratios of 60% of analytes are close to unity in cyclohexane and non-cyclohexane experiments. But, those ratios are greater than 1 to 16 in 26% of the analytes and are less than 1 in 10% of the analytes, indicating that cyclohexane can modify the humidity effect in the formation of SOA.

The Fig. 6A shows that the molecular distributions and abundance ratios of SOA products in humid condition compared to dry condition in the absence of cyclohexane. The Fig. 6b shows the similar results, but the experiments were carried out in the presence of cyclohexane. It is apparent that the

molecular distributions and abundance ratios are different between cyclohexane and without cyclohexane experiments. For example, the most abundant Group I compounds in humid conditions with cyclohexane are $C_{11}H_{18}O_3$, $C_{14}H_{22}O_4$, $C_{13}H_{20}O_5$, $C_{15}H_{24}O_4$, and $C_{12}H_{20}O_5$, but they are $C_{16}H_{26}O_6$, $C_{16}H_{28}O_6$, $C_{16}H_{28}O_8$, $C_{15}H_{26}O_9$, and $C_{14}H_{22}O_7$ in humid conditions with no-cyclohexane. The O:C ratios for Group I to III unique compounds in humid conditions with cyclohexane are 0.42, 0.37 and 0.36, which are 0.24, 0.28 and 0.32 in humid conditions without cyclohexane (Table S-3). Similar differences in molecular distributions and abundances are also observed for Group II-III compounds. The above results indicate that the use of cyclohexane as an OH radical scavenger modifies the humidity effect on the molecular compositions of SOA. Reaction processes are likely altered by either a decrease in the reaction between H_2O and Criegee radicals or an increase in the reactions between cyclohexane- and β -caryophyllene-derived RO_2 .

4. Atmospheric Relevance

Several molecular formulas with higher relative abundances than the molecular formulas of several well-known β -caryophyllene SOA markers (e.g., β -nocaryophyllonic acid and β -caryophyllinic acid) were detected. This suggests the possibility of other SOA markers of β -caryophyllene oxidation in atmospheric aerosols. In this work, we identified ~400 molecular formulas in β -caryophyllene ozonolysis SOA, which were not previously observed in the ozonolysis SOA of isoprene (Nguyen et al.), α -pinene-, β -pinene and limonene (Kundu et al., 2012). Of these unique β -caryophyllene SOA formulas, over 50 (Table S5) were observed in ambient aerosols (Mazzoleni et al., 2012) and over 60 (Table S6) were detected in cloud water (Zhao et al., 2013) collected at the Storm Peak Laboratory near Steamboat Springs, CO. Since the analytical strategies between these samples were consistent, the results suggest the presence of additional β -caryophyllene SOA markers in the atmosphere. The carbon atom numbers of the β -caryophyllene-specific SOA formulas found in ambient samples ranged from 4-32 along with the

numbers of hydrogen and oxygen atoms as 6-56 and 2-11, respectively. Only 7 of the β -caryophyllene SOA markers were previously reported in ambient aerosols (van Eijck et al., 2013). Although humidity is highly variable in the atmosphere, most of the dominant β -caryophyllene SOA markers were commonly observed in our experimental SOA samples irrespective of humidity. Similarly, SOA markers, reported to be detected in high RH (80-85%) experiments of the oxidation of β -caryophyllene, were also found in our study (Jaoui et al., 2003). Therefore, observation of this study can be extrapolated to real atmospheric conditions. The modification of humidity effect due to the addition of cyclohexane demonstrates that the SOA composition of β -caryophyllene ozonolysis not only depend on the relative humidity but also other volatile hydrocarbons that are prevalent in the atmosphere. Aged β -caryophyllene SOA has been reported to significantly affect CCN-relevant properties (Asa-Awuku et al., 2009). The detailed molecular composition revealed in this study may help to better understand climate-relevant properties of atmospheric secondary organic aerosols.

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Appendix A. Supplementary data

A complete list of measured masses, errors, DBE values, molecular formulas and intensities of peaks for each of the samples are provided in Table S2. Also provided in Table S3-S4 are the calculated chemical characteristics of the molecular formulas including the number of carbon atoms, number of oxygen atoms, O:C ratios, H:C ratios and DBE values according to Group I-III analytes. Table S5-S6 shows the β -caryophyllene specific formulas found in atmospheric aerosols and cloud water. Furthermore, possible pathways for the formation of predominant homologous series are shown in Figs. S1 to S6.

Table 1. Chemical characteristics (range and average $\pm$ one standard deviation in the parenthesis) of β -caryophyllene ozonolysis SOA according to selected mass range Groups 1-III.

Sample Names ^a	Number of Carbon Atoms			Number of Oxygen Atoms		
	Group I	Group II	Group III	Group I	Group II	Group III
CP _{Dry}	3 - 23 (14 $\pm$ 4)	17 - 38 (27 $\pm$ 4)	33 - 45 (40 $\pm$ 3)	2 - 11 (6 $\pm$ 2)	5 - 17 (11 $\pm$ 3)	11 - 19 (15 $\pm$ 2)
CP _{4%RH}	8 - 23 (15 $\pm$ 3)	17 - 39 (28 $\pm$ 5)	34 - 46 (41 $\pm$ 3)	2 - 11 (6 $\pm$ 2)	5 - 16 (11 $\pm$ 2)	10 - 19 (15 $\pm$ 2)
CP _{30%RH}	8 - 23 (15 $\pm$ 3)	17 - 39 (28 $\pm$ 5)	34 - 46 (41 $\pm$ 3)	2 - 11 (6 $\pm$ 2)	4 - 16 (10 $\pm$ 3)	10 - 18 (14 $\pm$ 2)
CP _{Dry} , with CH	9 - 22 (15 $\pm$ 3)	18 - 39 (28 $\pm$ 4)	31 - 46 (40 $\pm$ 2)	3 - 10 (6 $\pm$ 2)	6 - 15 (11 $\pm$ 2)	10 - 19 (15 $\pm$ 2)
CP _{4%RH} , with CH	3 - 22 (14 $\pm$ 4)	19 - 38 (28 $\pm$ 4)	37 - 44 (41 $\pm$ 2)	2 - 10 (6 $\pm$ 2)	6 - 15 (10 $\pm$ 2)	11 - 16 (14 $\pm$ 1)
CP _{30%RH} , with CH	8 - 23 (15 $\pm$ 3)	17 - 40 (28 $\pm$ 5)	33 - 50 (41 $\pm$ 3)	2 - 11 (6 $\pm$ 2)	5 - 16 (10 $\pm$ 2)	10 - 19 (15 $\pm$ 2)
	H:C Ratios ^b			O:C Ratios ^b		
	Group I	Group II	Group III	Group I	Group II	Group III
CP _{Dry}	0.4 - 2 (1.5 $\pm$ 0.2)	1.3 - 1.8 (1.6 $\pm$ 0.1)	1.5 - 1.7 (1.6 $\pm$ 0.1)	0.1 - 1.3 (0.48 $\pm$ 0.19)	0.2 - 0.7 (0.41 $\pm$ 0.09)	0.3 - 0.5 (0.37 $\pm$ 0.06)
CP _{4%RH}	1.3 - 1.9 (1.6 $\pm$ 0.1)	1.4 - 1.9 (1.6 $\pm$ 0.1)	1.5 - 1.7 (1.6 $\pm$ 0.1)	0.1 - 0.7 (0.43 $\pm$ 0.13)	0.2 - 0.7 (0.39 $\pm$ 0.09)	0.2 - 0.5 (0.36 $\pm$ 0.06)
CP _{30%RH}	1.3 - 2.1 (1.6 $\pm$ 0.2)	1.4 - 2.0 (1.6 $\pm$ 0.1)	1.5 - 1.8 (1.6 $\pm$ 0.1)	0.1 - 0.7 (0.41 $\pm$ 0.14)	0.1 - 0.7 (0.37 $\pm$ 0.09)	0.2 - 0.5 (0.34 $\pm$ 0.05)
CP _{Dry} , with CH	1.3 - 1.8 (1.6 $\pm$ 0.1)	1.4 - 1.8 (1.6 $\pm$ 0.1)	1.5 - 2.0 (1.6 $\pm$ 0.1)	0.2 - 0.7 (0.42 $\pm$ 0.11)	0.2 - 0.6 (0.38 $\pm$ 0.08)	0.2 - 0.6 (0.37 $\pm$ 0.06)
CP _{4%RH} , with CH	1.0 - 2.0 (1.6 $\pm$ 0.2)	1.4 - 1.8 (1.6 $\pm$ 0.1)	1.5 - 1.7 (1.6 $\pm$ 0.03)	0.1 - 1.7 (0.47 $\pm$ 0.18)	0.2 - 0.6 (0.37 $\pm$ 0.08)	0.3 - 0.4 (0.33 $\pm$ 0.04)
CP _{30%RH} , with CH	1.2 - 1.9 (1.6 $\pm$ 0.2)	1.3 - 1.9 (1.6 $\pm$ 0.1)	1.4 - 1.7 (1.6 $\pm$ 0.1)	0.1 - 0.8 (0.42 $\pm$ 0.14)	0.2 - 0.6 (0.38 $\pm$ 0.10)	0.2 - 0.5 (0.36 $\pm$ 0.06)
	Double Bond Equivalents (DBE) ^c					
	Group I	Group II	Group III			
CP _{Dry}	1 - 9 (4 $\pm$ 2)	4 - 10 (7 $\pm$ 2)	7 - 11 (9 $\pm$ 1)			
CP _{4%RH}	2 - 6 (4 $\pm$ 1)	3 - 10 (7 $\pm$ 2)	7 - 12 (9 $\pm$ 1)			
CP _{30%RH}	1 - 8 (4 $\pm$ 1)	1 - 10 (6 $\pm$ 2)	6 - 12 (9 $\pm$ 1)			
CP _{Dry} , with CH	3 - 6 (4 $\pm$ 1)	4 - 10 (7 $\pm$ 1)	1 - 11 (9 $\pm$ 2)			
CP _{4%RH} , with CH	1 - 6 (4 $\pm$ 1)	4 - 10 (7 $\pm$ 1)	8 - 11 (9 $\pm$ 1)			
CP _{30%RH} , with CH	2 - 8 (4 $\pm$ 1)	3 - 10 (7 $\pm$ 2)	7 - 12 (10 $\pm$ 1)			

^aSample names were constructed to indicate β -caryophyllene (CP), relative humidity (Dry, 4% or 30%) and the presence/absence of cyclohexane (with CH).

^bRatios were calculated based on the number of carbon, hydrogen and oxygen atoms in the determined molecular formulas.

^cThe DBE values were calculated by the equation $c - h/2 + 1$, where c and h represent the number of carbon and hydrogen atoms.

431

432

Figure Captions

Fig. 1. Reconstructed negative ion ultrahigh resolution FT-ICR mass spectra of β -caryophyllene ozonolysis SOA without cyclohexane. The mass spectra of the SOA samples generated at dry ($0\pm 2\%$) (A) and $30\pm 2\%$ RH (B) are shown. The mass spectra were drawn from the assigned monoisotopic molecular formulas. Blue and red bars represent common and unique ions, respectively, between the two SOA samples generated at dry and $30\pm 2\%$ RH without cyclohexane.

Fig. 2. CH_2 -Kendrick plot of the assigned chemical formulas in β -caryophyllene ozonolysis SOA generated at $30\pm 2\%$ relative humidity in the absence of cyclohexane (A). Box plots of the O:C (B) and H:C (C) ratios according to the Groups I-III. The Group I-III compounds are defined as $100 < m/z < 400$, $400 < m/z < 700$ and $700 < m/z < 1000$, respectively. The lower, middle and upper lines of the box in the boxplot are the first (25th percentile), second (50th percentile) and third (75th) quartiles, respectively. The lower and upper whiskers are 10th and 90th percentiles, respectively, and the circles denote outliers.

Fig. 3. O-Kendrick plot of the most abundant selected homologous series of Group I compounds in β -caryophyllene ozonolysis SOA generated at $30\pm 2\%$ relative humidity in the absence of cyclohexane (A). Also shown are their potential formation mechanisms via the pathways of dioxirane (B), and hydroperoxide (C). Isomerization has been abbreviated as Isom and x represents the number of H atoms or OH functional groups. The term "Unknown" in the legend means unknown reaction pathway, which may be related with reactive uptake of carbonyls. However, the current knowledge of the oxidation of β -caryophyllene does not support the reactive uptake of carbonyls.

Fig. 4. Isoabundance plots for β -caryophyllene SOA molecular formulas generated at $30\pm 2\%$ relative humidity in the absence of cyclohexane: DBE vs. the number of carbon atoms (A) and the number of oxygen atoms vs. the number of carbon atoms (B).

458 **Fig. 5.** O-Kendrick plot of the most abundant selected homologous series of Group II (A) and Group III (B)
459 compounds in β -caryophyllene ozonolysis SOA generated at $30\pm 2\%$ relative humidity in the absence of
460 cyclohexane. The size of the solid circles represents the relative abundance of analytes. Also shown are the
461 potential formation mechanisms of $C_{29}H_{48}O_{6-15}$ homologous series via the pathways: B) non-condensation
462 (hydroperoxide, hemiacetal, and Criegee), and C) condensation (aldol and esterification) reactions. The letter
463 x represents the number of OH functional group. The formation mechanism of other Group II homologous
464 series has been shown in Fig. S2 to Fig. S6.

465

466 **Fig. 6.** Difference mass spectra of β -caryophyllene ozonolysis SOA generated at dry ($0\pm 2\%$) and $30\pm 2\%$ RH
467 both without cyclohexane (A) and dry and $30\pm 2\%$ RH both in the presence of cyclohexane (B). Difference
468 mass spectra are defined as the difference of relative intensities of the SOA sample generated under humid
469 conditions ($30\pm 2\%$ RH) from the relative intensities of the SOA sample generated under dry conditions. Peak
470 intensities are normalized by the total monoisotopic intensity. The most dominant peaks are labeled with
471 their chemical formulas.

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Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.