



Are sesquiterpenes a good source of secondary organic cloud condensation nuclei (CCN)? Revisiting β -caryophyllene CCN

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Abstract. Secondary organic aerosol (SOA) was formed in an environmental reaction chamber from the ozonolysis of β -caryophyllene (β -C) at low concentrations (5 ppb or 20 ppb). Experimental parameters were varied to characterize the effects of hydroxyl radicals, light and the presence of lower molecular weight terpene precursor (isoprene) for β -C SOA formation and cloud condensation nuclei (CCN) characteristics. Changes in β -C SOA chemico-physical properties (e.g., density, volatility, oxidation state) were explored with online techniques to improve our predictive understanding of β -C CCN activity. In the absence of OH scavenger, light intensity had negligible impacts on SOA oxidation state and CCN activity. In contrast, when OH reaction was effectively suppressed (> 11 ppm scavenger), SOA showed a much lower CCN activity and slightly less oxygenated state consistent with previously reported values. Though there is significant oxidized material present ($O/C > 0.25$), no linear correlation existed between the mass ratio ion fragment 44 in the bulk organic mass (f_{44}) and O/C for the β -C- O_3 system. No direct correlations were observed with other aerosol bulk ion fragment fraction (f_x) and κ as well. A mixture of β -C and lower molecular weight terpenes (isoprene) consumed more ozone and formed SOA with distinct characteristics dependent on isoprene amounts. The addition of isoprene also improved the CCN predictive capabilities with bulk aerosol chemical information. The β -C SOA CCN activity reported here is much higher than previous studies ($\kappa < 0.1$) that use higher precursor concentration in smaller environmental chambers; similar results were only achieved with significant use of OH scavenger. Results show that aerosol formed from a mixture of low and high molecular weight terpene ozonolysis can be hygroscopic and can contribute to the global biogenic SOA CCN budget.

1 Introduction

Secondary organic aerosol (SOA) is an important contributor to atmospheric particulate mass (Seinfeld and Pankow, 2003). Atmospheric SOA can influence climate directly by absorbing and scattering light and indirectly via their ability to act as cloud condensation nuclei (CCN) and influence cloud formation. Goldstein and Galbally (2007) estimated SOA production of 510–910 Tg C yr⁻¹ from 1300 Tg C yr⁻¹, roughly a 50 % yield, from volatile organic compounds (VOCs). Biogenic volatile organic compounds (BVOC) may contribute to half of the global organic carbon (Hallquist et al., 2009) and isoprene, monoterpenes and sesquiterpenes dominate BVOC emissions (Guenther et al., 1999, 2000; Kanakidou et al., 2005). Terpenes are atmospherically abundant and reactive, as reflected by ephemeral chemical lifetimes (\sim several minutes, Goldan et al., 1993; Guenther et al., 1995; Neeb et al., 1997). Sesquiterpenes are the least abundant among the terpene classes but still play an important role in the tropospheric chemistry. Sesquiterpenes have highly reactive unsaturated double bonds and can form condensed phase products (Shu and Atkinson, 1994, 1995; Atkinson and Arey, 2003). Hence sesquiterpenes may have a similar large potential for SOA formation as monoterpenes; their contribution to global SOA formation may be as high as 9 % (Donahue et al., 2005; Griffin et al., 1999; Dekermenjian et al., 1999; Bonn and Moortgat, 2003).

β -caryophyllene (β -C, C₁₅H₂₄) is one of the most common and abundant sesquiterpenes and has been studied extensively. It is emitted by pine trees (Helmig et al., 2007), orange orchards (Ciccioli et al., 1999) and several agricultural plant species such as potato plants, leaves of tobacco, sunflower, maize and cotton (Hansen and Seufert, 2003; Duhl et al., 2008). Ozone (O₃) readily attacks the double carbon

bonds in β -C and the lifetime of β -C reacting with ozone is much shorter (~ 1 min) than with other oxidants in the troposphere (e.g., OH, NO₃) (Hoffmann et al., 1997). Ozonolysis is a significant pathway for ambient β -C removal; the relative contribution of O₃ reaction to tropospheric degradation is as much as 98 % (Hoffmann et al., 1997). Even though the reported reaction rate of β -C dark ozonolysis varies (Ghalaieny et al., 2012; Shu and Atkinson, 1995), aerosol is readily formed in this chamber and in other previous studies (e.g., but not limited to; Ng et al., 2006; Winterhalter et al., 2009; Chen et al., 2012).

Previous studies have focused on β -C SOA formation, product detection and identification (Jaoui et al., 2003; Winterhalter et al., 2009; Griffin et al., 1999). Aerosol yield parameters (stoichiometric factor, α , and equilibrium coefficient, K_{om}) for the photooxidation of β -C are 1.000 and 0.0416 (Griffin et al., 1999; Hoffmann et al., 1997), respectively. Jaoui et al. (2003) reported a number of products from O₃ oxidation (e.g., β -caryophyllone aldehyde, β -norcaryophyllone aldehyde, β -caryophyllonic acid, β -14-hydroxycaryophyllonic acid) with low vapor pressure that could contribute to formation of the secondary aerosols. Recently Li et al. (2011) reported formation of β -C SOA with low initial VOC concentration (1.7 to 46.4 ppbv) in the presence of seed aerosol ((NH₄)₂SO₄) and excess O₃. The elemental oxygen-to-carbon ratio (O/C) of first generation products (0.13–0.29, Li et al., 2011) were found to be lower than second generation products (0.2–0.5, Li et al., 2011) identified in the aerosol phase. The work was followed by additional seeded β -C ozonolysis experiments of Chen et al. (2012) that confirmed that excess ozone concentrations were necessary to form secondary generation products with higher oxidation states and aerosol densities.

Furthermore, previous β -C chamber experiments were not conducted in the presence of other terpene precursors. Isoprene (C₅H₈) contributes up to 44 % of total global VOC flux, ~ 1500 Tg C (Guenther et al., 1995) and high concentrations of isoprene have been measured with β -C emissions (Fu et al., 2010; Lewandowski et al., 2008). Unlike sesquiterpenes, the O₃-isoprene reaction produces significant amounts of higher volatility products and thus the O₃-isoprene yield is much smaller. However, global emissions of isoprene are sufficiently large that the formation of SOA, even in small yields, may result in substantial contributions to condensed phase materials (Carlton et al., 2009). Reported SOA yield of the O₃-isoprene reaction is between 0.001 and 0.01 (Czoschke et al., 2003; Jang et al., 2002; Kleindienst et al., 2007). Kleindienst et al. (2007) observed lower aerosol mass with the presence of OH scavenger for SOA formed from O₃-isoprene reaction, which is consistent with the higher yield of isoprene photooxidation by H₂O₂ (0.009–0.036) (Kroll et al., 2006). Products of OH-initiated isoprene photooxidation have been detected in a considerable amount in the filters collected in Amazonia, Brazil (Claeys et al., 2004). In the same AMAZE-08 campaign, the estimated sin-

gle hygroscopicity parameter, κ , of biogenic dominated SOA was $\sim 0.16 \pm 0.06$ (King et al., 2010). Chamber study of King et al. (2010) showed that the CCN activity of seeded isoprene SOA generated by irradiating H₂O₂ and isoprene was consistent with the Amazonian SOA ($\kappa = 0.10 \pm 0.03$). It indicates that biogenic isoprene is a major source of SOA and can act as CCN to influence the climate in the forest region. The less volatile fraction of the isoprene SOA was also less CCN active (Pöschl et al., 2010); similar to the less volatile and CCN active fraction of β -C SOA (Asa-Awuku et al., 2009). Thus the addition of reactive lower volatility materials to the β -C SOA may modify particle composition, density, volatility, and CCN characteristics and must also be explored.

To the best of our knowledge, only two studies have reported the CCN activity of β -C SOA (Asa-Awuku et al., 2009; Huff-Hartz et al., 2005). In both cases β -C SOA was formed in a 12 m³ chamber and was found to be less CCN active than monoterpene SOA, with activation diameter 152 ± 26 nm at 1 % supersaturation (ss) (Huff-Hartz et al., 2005; Asa-Awuku et al., 2009). Asa-Awuku et al. (2009) also found that the hygroscopic material in β -C SOA to be semi volatile, yet little or no information on β -C SOA characteristics such as O/C and density were measured with CCN properties.

SOA aging may lead to an increase of particle hygroscopicity and CCN activity (Jimenez et al., 2009). Asa-Awuku et al. (2009) reported significant aging of β -C ozonolysis SOA changed most CCN-relevant properties (e.g., activation diameter, water soluble fraction, droplet size) and resulted in increased CCN activity. However, Varutbangkul et al. (2006) observed the subsaturated hygroscopicity of SOA formed by photooxidation of β -C to decrease with aging, explained by the formation of higher molecular weight and less hydrophilic oligomers. For isoprene SOA, little or no aging has been observed; no aerosol growth was reported for methyl vinyl ketone (MVK), the most abundant first generation gas-phase product from isoprene oxidation reaction (Kroll et al., 2006). The aging of high and low molecular weight terpene precursor SOA is explored here.

O/C has been considered an important factor to characterize the oxidation state of SOA and particle hygroscopicity (Jimenez et al., 2009; Kroll et al., 2011; Chang et al., 2010; Massoli et al., 2010; Lambe et al., 2011). Recent studies also indicated the relative abundance of organic fragment ion signal m/z 44 (f_{44}) as a marker for oxygenated species (Canagaratna et al., 2007; Alfarra et al., 2007; Duplissy et al., 2011; Aiken et al., 2008). In Jimenez et al. (2009), ambient aerosols and chamber SOA from three different precursors showed the same trend of increasing hygroscopicity with increasing O/C. Duplissy et al. (2011) also found strong correlation between hygroscopicity with f_{44} for SOA formed in an environmental chamber and from two field experiments. In this study, we characterize β -C SOA formed under different conditions and evaluate the effects of hydroxyl radical, light and addition of isoprene on SOA formation and CCN

properties. We report density, volatility, O/C, and CCN activity to improve predictions for terpene SOA CCN systems.

2 Experimental methods

This study was conducted in the University of California-Riverside/CE-CERT indoor environmental chamber (Carter et al., 2005). Two 90 m³ Fluorinated Ethylene Propylene (FEP) copolymer Teflon[®] film reactors were suspended by a rigid steel framework within the temperature-controlled enclosure (temperature range 5–45 °C, normally set to 27 °C for experiments). Both the chamber and the enclosure were continuously flushed with purified air (Aadco 737 series air purification system (Clevs, Ohio)). 115 W Sylvania black lights simulate solar irradiation and ultraviolet (UV) light within the reactor. β -C and isoprene were introduced to the chamber by passing a stream of pure nitrogen (N₂) over a known volume of liquid in a glass injection manifold. O₃ was formed using two Dalton ozone generators (Model Type: OZG-UV-01) and injected similarly with flushing pure N₂. Relative humidity (RH) inside the chamber was maintained at or below 0.1 % RH. The reaction time for each experiment ranged from 6 to 8 h. For experiments with photochemistry, black lights were turned on after injection of parent VOCs and oxidants.

Real-time particle density was measured using an Aerosol Particle Mass Analyzer (APM) (Kanomax model 3600) and SMPS (Scanning Mobility Particle Sizer) in series. Compared to traditional DMA (Differential Mobility Analyzer)-APM configuration, the APM-SMPS setup reduces sampling time, avoids the need to vary angular rotational speed and voltage applied to the APM, and increases the system signal to noise ratio. Density data was acquired every 75 s. Details of the instruments and theory are described elsewhere (Malloy et al., 2009; Ehara et al., 1996).

Particle volatility was monitored with a custom-built Volatility Tandem Differential Mobility Analyzer (VTDMA) (Burtscher et al., 2001; Rader and McMurry, 1986). The diameter of particles transmitted through the first SMPS (D_i) is selected to match the mode diameter of size distribution measured by a parallel SMPS. Then monodisperse particles are transported through a Dekati[®] thermodenuder (TD, residence time: ~ 17 s, adjustable temperature). The diameter of particles leaving the TD (D_f) is then measured by fitting a log-normal size distribution curve from a second SMPS. Volume fraction remaining (VFR) is then calculated as the volume ratio before and after the TD, i.e., $VFR = (D_f/D_i)^3$. Note that the “volume” in VFR measurement is based on mobility diameter measurement which may include void space and void space is assumed negligible in SOA systems. The VTDMA was calibrated using the VFR of dry (NH₄)₂SO₄ seed aerosol at room temperature as correction factors.

The evolution of particle elemental composition is tracked using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006; Jimenez et al., 2003). The HR-ToF-AMS design is based on the on-line quantitative mass spectra measurements using a heated surface for particle vaporization followed by a standard 70 eV electron impact ionization and subsequent ion analysis with a time-of-flight mass spectrometer (Drewnick et al., 2005). The HR-ToF-AMS can provide quantitative data on both the non-refractory chemical species present in aerosol particles as well as the size of the particles (Jayne et al., 2000; Jimenez et al., 2003). Atomic O/C of SOA was calculated with elemental analysis of the HR AMS data (Aiken et al., 2007).

Aerosol from the chamber was classified by a scanning mobility particle sizer (SMPS 3080), followed in parallel by a condensation particle counter (TSI CPC 3772) and a Droplet Measurement Technologies (DMT) Continuous-Flow Streamwise Thermal Gradient CCN Counter (CF-STGC) (Lance et al., 2006; Roberts and Nenes, 2005). The total aerosol concentration (CN) of the monodisperse particles was counted by the CPC and the CCN concentration was measured by the CCN counter. The DMA with the CCN counter was operated at a sheath-to-aerosol flow ratio of 10:1. The design and operating principles of the CCN counter are based on the model of Roberts and Nenes (2005). ss settings used in this study ranged from 0.2 % to 1 % and were calibrated using (NH₄)₂SO₄ aerosol (Supplement). Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010) provides size resolved CCN activity using data from the CCN counter and SMPS. By keeping constant instrument ss during the scanning cycle of the SMPS, we obtain the time series of CN and CCN counts, then determine the CCN/CN ratio as a function of dry mobility diameter. This procedure is repeated over multiple ss, giving a characterization of the size-resolved CCN properties every 135 s (one cycle for SMPS). SMCA has been evaluated for calibration, laboratory and ambient aerosol, SOA filter samples, biomass burning aerosol (Asa-Awuku et al., 2008, 2010; Moore et al., 2010; Padró et al., 2007) and monoterpene SOA (Engelhart et al., 2008). The CCN counter is calibrated with atomized (NH₄)₂SO₄ solution (1 g l⁻¹). Measured and calculated activation diameters for (NH₄)₂SO₄ at multiple ss have been compared to theoretical values (Fig. S1). In this study, the activation diameters are converted to the single hygroscopicity parameter, κ , using κ -Köhler theory (Petters and Kreidenweis, 2007) as follows,

$$\kappa = \frac{4A^3}{27\ln^2 S_c d_s^3}; \text{ where } A = \frac{4M_w\sigma_w}{RT\rho_w} \quad (1)$$

and M_w and ρ_w are the molecular weight and density of water, respectively, R the universal gas constant, and T , the ambient temperature. κ assumes the surface tension of the droplet is that of pure water, $\sigma_w = 72 \text{ mN m}^{-1}$. S_c is the

critical saturation for a dry particle of diameter d_s . In our experiments we determine the critical particle mobility diameter for instrument ss with SMCA.

3 Results and discussion

3.1 SOA formation, density, and volatility

In the absence of OH scavenger, the yield of β -C- O_3 SOA was 25–49 % for initial β -C concentration of 5 ppb and increased up to 40–71 % for 20 ppb β -C. This result is consistent with previously reported yield of 45 ± 2 % in Lee et al. (2006). To explore the role of hydroxyl radicals in the β -C- O_3 reaction, low (~ 1 ppm) and high (~ 11 ppm) concentrations of OH scavenger (2-butanol) were injected into the chamber before the start of the reaction. The concentration of 2-butanol ($C_4H_{10}O$) was determined by comparing the reaction rate of OH-2-butanol with that of OH- β -C, with the reaction rate for the 2-butanol 100 times larger. The addition of 2-butanol at low concentrations (~ 1 ppm) did not affect the aerosol yield (25–40 %, 41–49 %) for both 5 and 20 ppb β -C. Adding high concentrations of 2-butanol (~ 11 ppm) to the system resulted in relatively lower yields (15–33 %, 11–43 %). Using Carbon Monoxide (CO) as the scavenger reduced the aerosol yield to the same extent. Our result is consistent with Chen et al. (2012), in which SOA yield of β -C dark ozonolysis in the excess of O_3 (200 ppb) was $21.9\% \pm 2.0\%$ for 3.3 ppb β -C and $46.1 \pm 4.2\%$ for 6.6 ppb with cyclohexane as OH scavenger. The decreased yields for the reactions free of OH radicals confirmed that OH radicals played a significant role in the β -C- O_3 reaction chain.

With the presence of ~ 1 ppm OH scavenger, 0.25 ppm and 0.7 ppm isoprene- O_3 SOA yields were both 4 %, higher than literature values (0.0015 in Czoschke et al., 2003 and 0.002 in Jang et al., 2002). Kleindienst et al. (2007) estimated the ozone-isoprene reaction yield to be 0.01, with complete suppression of OH-isoprene reaction, and even higher yield without the presence of OH scavenger. When 0.25 ppm isoprene and 5 ppb β -C were both precursors, the aerosol yield was close to isoprene SOA (~ 3 %). When the precursor was 0.7 ppm isoprene and 5 ppb β -C, higher yield (6 %) was observed. For low yielding SOA precursor, there is the possibility that not all systematic errors have been accounted for. Causes that may lead to the underestimation of isoprene- O_3 yield include: (1) no correction of aerosol chamber wall loss, (2) the use of unit density instead of real time measured density ($\sim 1.36 \text{ g cm}^{-3}$ as reported in this study), (3) over estimation of reacted isoprene amount due to the lack of gas phase online measurements, and (4) different experimental conditions, for example, presence of seed aerosol (Czoschke et al., 2003).

Figure 1 shows the evolution of aerosol density, ρ_a , as a function of time for O_3 reactions. The ρ_a of β -C SOA decreased moderately after initial particle formation

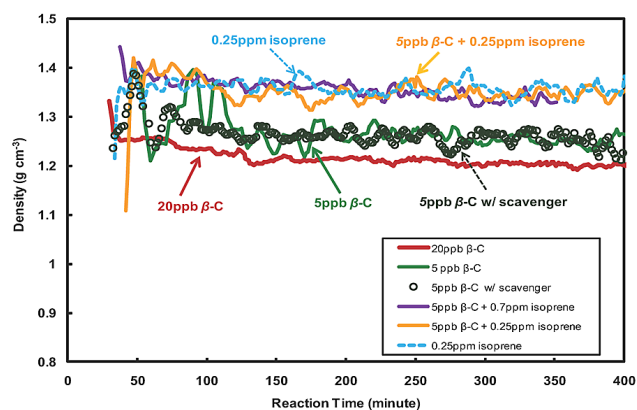


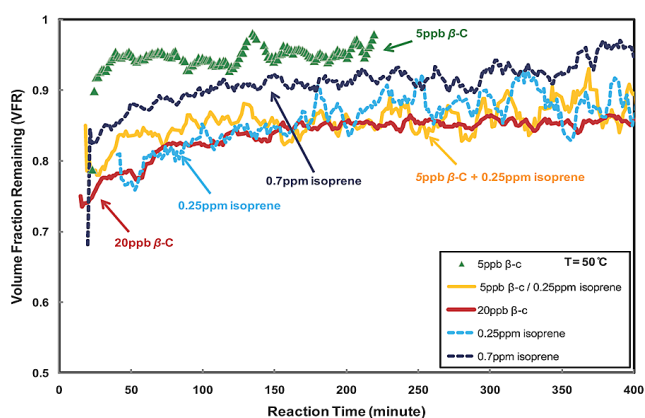
Fig. 1. Particle density, ρ_a (g cm^{-3}), as a function of reaction time. In each reaction, ozone was the oxidant and no OH scavenger was present unless specified (e.g., 5 ppb β -C w/ scavenger).

($\sim 0.10 \text{ g cm}^{-3}$). Measured densities were insensitive to oxidant concentrations (O_3 or OH); the addition of the OH scavenger had negligible effect on β -C SOA. Average ρ_a was $1.26 \pm 0.04 \text{ g cm}^{-3}$ and $1.20 \pm 0.01 \text{ g cm}^{-3}$ for β -C- O_3 reactions with precursor concentrations of 5 ppb and 20 ppb, respectively. This result agreed with the dependence of density on organic mass concentration in Chen et al. (2012) and the prediction of aerosol density from O/C and H/C AMS data sets (Nakao et al., 2012; Kuwata et al., 2012). Higher density ($\rho_a = 1.36 \pm 0.02 \text{ g cm}^{-3}$) was observed for isoprene SOA and β -C-isoprene SOA, suggesting that isoprene-generated aerosol likely dominated the SOA formed from the mixed hydrocarbon precursors when isoprene accounted for > 95 wt % in precursor mixtures.

Volatility measured by VTDMA also proved that isoprene-generated SOA determined volatility of the SOA mixture. It required ~ 100 min to reach steady state of gas-to-particle phase partitioning, but the aged β -C-isoprene oxidation products showed similar volatility to isoprene SOA, with no dependence of volatility on the initial isoprene concentration. Isoprene reacting with O_3 formed notably more volatile aerosol than 5 ppb β -C; VFR of isoprene SOA and β -C SOA at 50°C were ~ 0.85 and ~ 0.95 , respectively. The volatility of β -C SOA was lower with the presence of the hydroxyl radicals (data not shown), suggesting the suppressed β -C-OH reaction could produce more volatile material than β -C- O_3 reaction. Increase in the initial precursor concentration (5 to 20 ppb for β -C and 0.25 to 0.7 ppm for isoprene) had different effects on the SOA VFR. For β -C, SOA formed with higher precursor concentration exhibited higher volatility (Fig. 2), consistent with Duplissy et al. (2008) who suggested that at higher precursor concentration, more volatile, less oxygenated compounds could partition into the particle phase. The opposite trend was observed for isoprene. Higher isoprene concentrations formed low volatility products quickly and suggest an increased fraction

Table 1. Experimental conditions without OH scavenger.

β -caryophyllene (ppb)	Isoprene (ppm)	Oxidant		Lights	Average O/C	Average κ	Yield
		O ₃ (ppb)	H ₂ O ₂ (ppm)				
5		235		On	0.30 ± 0.09	0.217 ± 0.019	0.20
5		290		Off	0.27 ± 0.04	0.221 ± 0.024	0.38
20		100		On	0.25 ± 0.01	0.188 ± 0.020	0.52
20		250		Off	0.25 ± 0.01	0.163 ± 0.017	0.31
5			0.5	On	0.25 ± 0.04	0.100 ± 0.018	1.06
5	0.7	150		On	0.50 ± 0.05	0.204 ± 0.009	0.14
5	0.7	150		Off	0.49 ± 0.02	0.181 ± 0.007	0.14
5	0.25	435		On	0.34 ± 0.03	0.159 ± 0.015	0.04
5	0.25	436		Off	0.32 ± 0.07	0.141 ± 0.015	0.04
	0.25	215		Off	0.48 ± 0.04	0.083 ± 0.007	0.01

**Fig. 2.** Time series of volume remaining fraction (VFR) of β -C SOA and isoprene SOA at 50 °C. There was no OH scavenger in all the experiments shown in the graph.

of oligomer formation with higher isoprene precursor concentration.

3.2 AMS chemical composition

The chemical composition of the aerosol was characterized with online HR-AMS measurements. High resolution mass spectra of β -C SOA and isoprene SOA formed under different conditions can be found in the Supplement (Figs. S2–S5). Figure 3a showed the O/C ratio as a function of reaction time for the studied SOA systems. For the same precursor concentration, O/C of the SOA was comparable with and without the UV lights (Tables 1 and 2); in both cases, stable O/C suggested no apparent aging of the formed aerosol. Slightly larger O/C was observed for SOA formed from 5 ppb β -C (0.30 ± 0.07) than 20 ppb (0.26 ± 0.02). The inverse correlation between organic aerosol mass and oxidation state has also been observed in Chen et al. (2012). As pointed in Chen et al. (2011), the O/C and H/C ratios for SOA measured by

AMS is systematically too low. Without specific calibration for CO^+ and H_2O^+ , the reported O/C of 0.28–0.37 corresponds to our result of 0.24–0.35 (Fig. 4b). When OH reaction pathway was suppressed with high concentration of OH scavenger (~ 11 ppm), SOA with lower O/C formed in the first 50 min and correspond to first-generation products of β -C ozonolysis (0.13–0.29; Li et al., 2011). Then, first generation products convert to second generation products with higher O/C (0.2–0.5; Li et al., 2011). Comparison of high resolution mass spectra suggested that contribution of oxygen-containing ion fragments (e.g., $\text{C}_2\text{H}_3\text{O}^+$, CO_2^+) increased with the formation of second generation products. Complete scavenging of OH oxidation pathway had negligible effect on SOA oxygenation state for 5 ppb and 20 ppb β -C SOA, as well as 1 ppm scavenger (Fig. 4b, Table 2). Molecules containing more oxygen atoms are heavier, so that O/C values corresponded to aerosol density, in a manner of high O/C versus high density.

Isoprene oxidation products showed even higher O/C (~ 0.5) than β -C SOA (Figs. 3a and 4b, Table 1), independent of initial isoprene concentration. Aerosol yield data suggested higher isoprene concentrations produce more isoprene-generated SOA to the mixture precursor system. Hence O/C of SOA formed from 0.7 ppm isoprene and 5 ppb β -C was analogous to that of single isoprene system (~ 0.5), while from 0.25 ppm isoprene and 5ppb β -C, O/C was only 0.33. Unlike the β -C- O_3 reaction, small amounts of OH scavenger in the mix-precursor system with 0.25 ppm isoprene resulted in more oxidized SOA (O/C ~ 0.4 compared to ~ 0.33), while no impact on the system with 0.7 ppm isoprene (still ~ 0.5) was observed. It is inferred that changes in the mix-precursor aerosol are caused by changes in isoprene-generated SOA properties (with lesser O/C material) as β -C-generated SOA is not affected by OH scavenger. Kleindienst et al. (2007) suggested that up to 50 % of the formed aerosol in an isoprene- O_3 reaction derived from the OH channel without an OH scavenger present. Isoprene-OH reaction

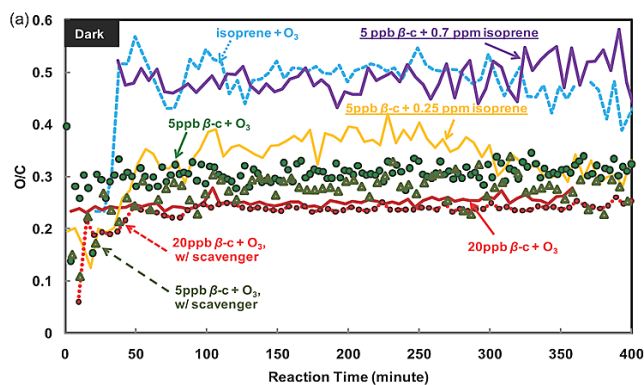


Fig. 3a. Time series of O/C for dark experiments between O₃ and β-C/ isoprene. No OH scavenger was present in the reaction unless specified.

produced less oxidized SOA than isoprene-O₃ reaction; so as the fraction of OH-initiated SOA decreased, O/C of the formed aerosol increased as a result of the OH scavenger present.

Aiken et al. (2008) suggested a linear correlation between the fraction of *m/z* 44 in total organics (f_{44}) and O/C in ambient data sets, $f_{44} = (0.0382 \pm 0.0005) \times (O/C) + (0.0794 \pm 0.0070)$ (Fig. 3b). This correlation can be used to estimate elemental composition from unit-mass resolution data of ambient SOA. Here we applied this method to the SOA formed from β-C and isoprene with O₃. The squared correlation coefficient (R^2) of f_{44} and O/C was lower than 0.55 for β-C-O₃ and isoprene-O₃ systems, except for the β-C-H₂O₂ system ($R^2 = 0.84$). f_{44} of β-C-OH SOA was much lower than that of β-C-O₃ SOA (Fig. 3b) and close to that of ambient aerosol (Duplissy et al., 2011) such that high f_{44} presence may be a reason for the weak correlation of f_{44} and O/C of chamber β-C SOA. Another difference between chamber SOA and ambient aerosol is that for chamber β-C SOA no time resolved change of f_{44} and O/C was observed, however, R^2 improved with the presence of isoprene. This suggested that in ambient conditions, where lower molecular weight terpenes coexists with sesquiterpene and OH radical chemistry is prevalent, the f_{44} with O/C correlation may hold for BVOC SOA.

3.3 CCN activity

β-C SOA was less CCN active than (NH₄)₂SO₄ ($\kappa \sim 0.6$) but was more active than the previous measurements (Huff-Hartz et al., 2005; Table 1). In Huff-Hartz et al. (2005), the activation diameter at $ss = 1.0\%$ was reported to be 152 ± 26 nm for the SOA formed from 50 ppb β-C and 100 ppb O₃ (mixing ratio 1 : 2) in the presence of 2-butanol (6–13 ppm). Assuming constant surface tension and complete solubility, κ was calculated to be 0.004. Asa-Awuku et al. (2009) reported smaller activation diameter at $ss = 1.02\%$,

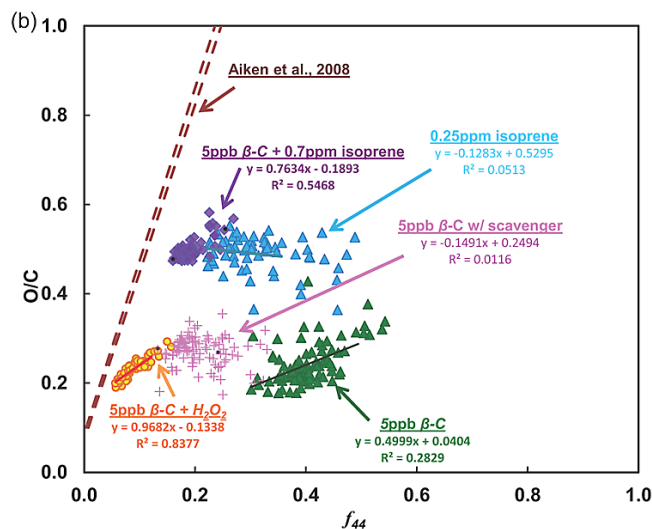
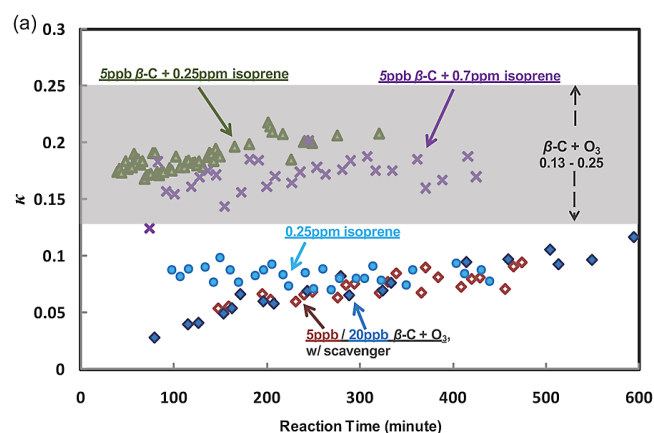


Fig. 3b. Scatter plot of aerosol f_{44} as a function of O/C with equation and R^2 of linear regression fit. The two dashed lines represent upper and lower bound of f_{44} -predicted O/C using the empirical correlation of f_{44} and O/C described in Aiken et al. (2008), $f_{44} = (0.0382 \pm 0.0005) \times (O/C) + (0.0794 \pm 0.0070)$.

with 22 ppb β-C as precursor; activation diameter decreased from 90 nm to 70 nm within about 4 h, with κ increasing from 0.018 to 0.038. In summary, β-C SOA formed in the Carnegie Mellon University 12 m³ chamber exhibited very low hygroscopicity ($\kappa < 0.04$) and was not affected by the presence of OH scavenger. In our study, the mixing ratio of β-C to O₃ was around 1 : 10 (20 ppb β-C) or 1 : 40 (5 ppb β-C) with excess O₃ (initial concentration ranged from 100 ppb to 290 ppb). With ~ 11 ppm 2-butanol present, the activation diameter of dark ozonolysis SOA was much smaller, with a higher average κ of 0.066 ± 0.019 (Table 2). In comparison with the previous studies, the decrease of precursor concentration from 50 to 20 ppb or 5 ppb led to enhancement of the β-C SOA hygroscopicity, with an increase in κ by a factor of 16.5. This observation is consistent with Duplissy et al. (2008) that showed the less oxygenated compounds formed at higher precursor concentration could result in less hygroscopic SOA. SOA was even more hygroscopic when no OH scavenger was present in the β-C-O₃ reaction. κ ranged from 0.13 to 0.25 (Fig. 4a) and higher when precursor concentration was low (5 ppb). Low concentration of OH scavenger also notably depressed CCN activity of β-C SOA (Table 2, Fig. 4b), while lights had negligible effect. Asa-Awuku et al. (2009) confirmed that the hygroscopic fraction of β-C SOA was volatile. Here we can confirm that OH-participated reaction contributed to the formation of more volatile and more hygroscopic fraction of the β-C SOA. Gradual aerosol hygroscopic aging was observed in the system with OH scavenger present. At the beginning of the experiment, $\kappa \sim 0.03$ was similar to Asa-Awuku et al. (2009). After 6 h, the SOA became moderately active ($\kappa \sim 0.09$). CCN activity of β-C

Table 2. Experimental conditions with OH scavenger.

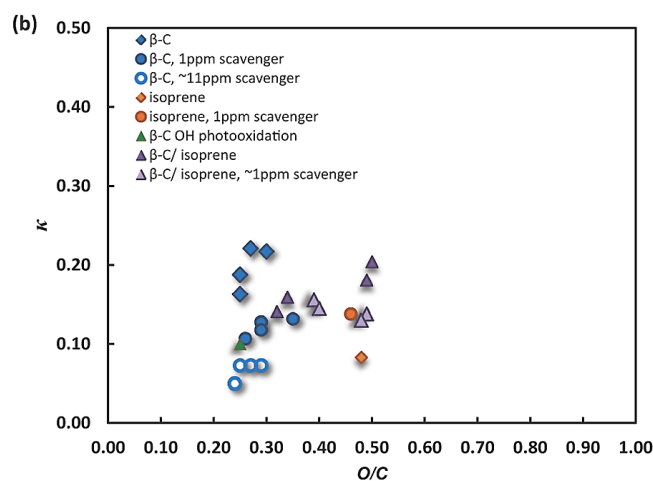
β -caryophyllene (ppb)	Isoprene (ppm)	O ₃ (ppb)	2-butanol (ppm)	Lights	Average O/C	Average κ	Yield
5		200	1	On	0.35 ± 0.07	0.132 ± 0.017	0.32
5		215	1	Off	0.29 ± 0.02	0.128 ± 0.020	0.25
20		110	1	On	0.29 ± 0.02	0.118 ± 0.010	0.33
20		160	1	Off	0.26 ± 0.01	0.107 ± 0.015	0.32
5	0.7	105	1	On	0.49 ± 0.03	0.138 ± 0.009	0.17
5	0.7	105	1	Off	0.48 ± 0.03	0.130 ± 0.006	0.17
5	0.25	235	1.58	On	0.39 ± 0.05	0.156 ± 0.014	0.03
5	0.25	236	1.58	Off	0.40 ± 0.04	0.145 ± 0.011	0.03
5		263	11	On	0.29 ± 0.03	0.073 ± 0.011	0.33
5		177	11	Off	0.27 ± 0.03	0.073 ± 0.007	0.15
20		170	11.85	On	0.25 ± 0.01	0.073 ± 0.024	0.23
20		180	13.43	Off	0.24 ± 0.01	0.050 ± 0.013	0.11
	0.7	160	1	Off	0.46 ± 0.05	0.138 ± 0.010	0.03

**Fig. 4a.** Time resolved κ values for different reaction systems. Without OH scavenger, κ of β -C SOA ranged from 0.13 to 0.25 (shade area) with no significant change during the period of each experiment.

SOA formed by OH photooxidation (H₂O₂ as hydroxyl radical source) was briefly examined. β -C-OH SOA showed lower hygroscopicity ($\kappa = 0.100 \pm 0.018$) than β -C-O₃ SOA, which suggests that OH indirectly promotes the formation of hygroscopic materials.

The hygroscopicity of isoprene SOA was lower than β -C SOA independent of initial isoprene concentrations ($\kappa = 0.083 \pm 0.007$ for 0.25 ppm and 0.138 ± 0.010 for 0.70 ppm; Tables 1 and 2, Fig. 4a). As expected, CCN activity of mixture SOA was between β -C SOA and isoprene SOA. A simple assumption can be made to estimate the contributions of hygroscopicity from isoprene and β -C like SOA. If additive,

$$\kappa_{\text{mixture SOA}} = \kappa_{\text{isoprene SOA}} \cdot x + \kappa_{\beta\text{-C SOA}} \cdot (1 - x) \quad (2)$$

**Fig. 4b.** Plot of average κ versus O/C using data in Tables 1 and 2.

where x is the contribution of isoprene SOA. 5 ppb β -C SOA has $\kappa \sim 0.22$, 0.25 ppm isoprene SOA $\kappa \sim 0.08$, and the mixture SOA have $\kappa \sim 0.15$. It is estimated that 50% of the aerosol exhibited β -C CCN behavior, when β -C accounted for < 5% of the initial terpene concentration. Unlike density, volatility, or O/C, small amounts of β -C in the precursor mixture have significant contributions to the overall particle hygroscopicity.

The relationship between bulk chemical composition and κ was explored. Unlike chamber SOA from photooxidation of trimethylbenzene, α -pinene and isoprene (Duplissy et al., 2008; Jimenez et al., 2009), the O/C and κ of the β -C SOA (without OH scavenger) remained nearly constant during the dark ozonolysis process (Fig. 3a). Stable O/C values were observed after initial particle formation, indicating the products were not further oxidized (Sect. 3.2). No correlation of O/C and κ has been observed for all conducted experiments

(Fig. 4b); R^2 value was consistently < 0.2 . This data set suggests that a simple AMS O/C and κ empirical relationship can be complex and may not be used to predict β -C SOA systems. As suggested by Cappa et al. (2011), the observed hygroscopicity might be best modeled by both O/C and molecular size, especially in the case of OH aged systems.

Recent studies have proposed use of the bulk composition, f_{44} as a predictor of organic CCN activity (Duplissy et al., 2011). f_{44} had little or no correlation to O/C or κ in the β -C system. Figure 4c shows R^2 of the hygroscopicity parameter κ versus different $f_{m/z}$ for four types of experiments (β -C-O₃ without scavenger, β -C-O₃ with ~ 11 ppm scavenger, isoprene-O₃, β -C-isoprene-O₃). The strongest correlation was observed for the system of β -C-O₃ with OH scavenger, in which R^2 between κ and the fraction of m/z 41, 42, 43, 44, 51, 67, 79 and 91 all exceeded 0.5. Except for m/z 43 (C₂H₃O⁺) and m/z 44 (CO₂⁺), all other abundant fragments consisted of one ion in the C_xH_y ion family. For β -C-O₃ experiment, f_{71} showed the strongest correlation with κ among all $f_{m/z}$ ($R^2 \sim 0.39$). In comparison with the other two systems (isoprene-O₃, β -C-isoprene-O₃), no $f_{m/z}$ correlated with κ with $R^2 > 0.39$. Linear correlations between κ and m/z of isoprene-O₃ SOA were the weakest but were improved by the presence of β -C. In conclusion, except for reaction systems with the additional presence of hydroxyl radicals, an empirical relationship with the mass fraction of fragment ions cannot be applied to predict β -C SOA CCN activity.

4 Summary and implications

In this study, β -C-O₃ reaction was examined in regards to influences of OH scavenger, lights and another prominent biogenic VOC, isoprene. Chamber experiments were conducted at β -C concentrations of 20 ppb and 5 ppb with excess ozone. Higher precursor concentration lead to more volatile products condensing into the particle phase. The measured differences in SOA properties agreed with this theory. Compared with 5 ppb β -C, 20 ppb β -C with O₃ formed more SOA with lower density, hygroscopicity, O/C and higher volatility. Low concentration of OH scavenger (~ 1 ppm) had notable impacts on SOA volatility and hygroscopicity; when β -C-OH reaction was completely scavenged, SOA showed lower O/C, lower volatility and similar density. Results indicated that β -C-OH reaction in the β -C-O₃ system promoted formation of highly oxidized and volatile aerosol. Loss of volatile components could explain the decrease of CCN activity in the OH-scavenged system. Given that β -C-H₂O₂ reaction does not produce more hygroscopic SOA than β -C-O₃ reaction, it supports the theory that OH reacts with key reactive intermediates to form second generation products with higher CCN activity.

This study suggests that β -C-O₃ SOA is a potentially important contributor to biogenic CCN. The hygroscopicity of

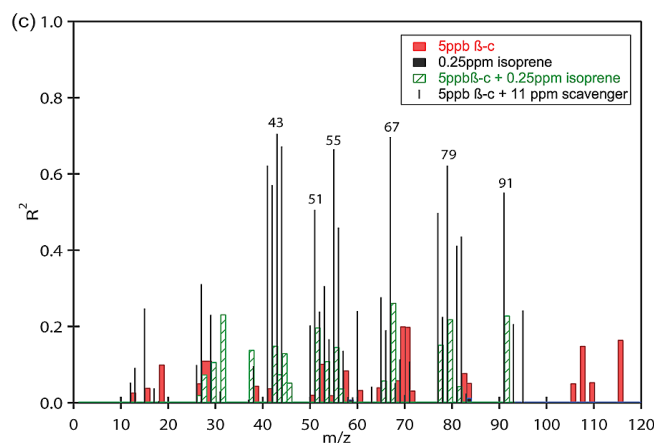


Fig. 4c. Linear regression correlations (represented by R^2) between κ and the abundant mass-to-charge ratios (m/z) of O₃-initiated SOA.

β -C SOA (average $\kappa \sim 0.2$) formed from 5 or 20 ppb β -C was higher than previous β -C studies with higher precursor concentration (50 ppb) and ambient SOA ($\kappa \sim 0.13$). Similar low κ values (< 0.1) as previously reported were only obtained in the presence of high OH scavenger concentrations; hence OH measurements may be required for a direct comparison of experiments conducted in different chambers. The highly hygroscopic β -C-O₃ SOA should be considered in global models as a contributor of biogenic CCN.

Isoprene with ozone showed a much smaller yield than β -C, but isoprene SOA was more oxidized yet less hygroscopic than β -C SOA. In the ambient, isoprene may coexist with β -C in many locations with densely populated plants. Thus it is necessary to study the SOA properties with multiple precursors. β -C precursor with the presence of isoprene formed SOA that physically (density, volatility) exhibited properties similar to isoprene SOA (independent of initial concentrations 0.25 ppm or 0.70 ppm). Chemically (e.g., oxidation state), the mix-precursor aerosol behaved more like 0.70 ppm isoprene SOA because of the larger contribution of isoprene-generated SOA to total SOA mass. However, β -C SOA still dominated the hygroscopicity of the mix-precursor SOA even when it was not the mass-predominant precursor. This result further emphasizes the significant role of β -C SOA as biogenic CCN in the ambient. O/C and f_{44} of the β -C-O₃ and isoprene-O₃ SOA showed weaker correlations than ambient SOA. The correlations of κ and the most abundant mass-to-charge ratios were also insignificant in this study, making β -C SOA a unique system that cannot be easily predicted with AMS data and an empirical correlation. Our study concludes that SOA formed from multiple precursors instead of a single VOC species are complex and their water-uptake exhibit significant non-linear behavior.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/12/8377/2012/acp-12-8377-2012-supplement.pdf>.

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