Response to Reviewer #2

We thank the reviewer for the helpful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer comments are in black, and author responses are in blue).

I have another, more general comment: Why is the role of secondary ozonides, as they are nicely discussed in depth e.g. by Yao et al., AE 2014, not discussed at all in this paper? Maybe this can be added?

Response: Yao et al. (2014) observed a gas-phase product with elemental composition of $C_{15}H_{24}O_3$ from ozonolysis of α-cedrene using CIMS and tentatively attributed it to secondary ozonides (SOZ) formed through intramolecular reactions of stabilized Criegee intermediates (SCI) of α-cedrene. Although SOZs were detected as the major products in the gas phase, they were not observed in the particle phase by HPLC-MS and GC-MS. In addition, it was found that the addition of a small amount of water vapor (6% RH) significantly suppressed the formation of the SOZ by scavenging SCI.

In the present study, ESI-MS was used to characterize the molecular composition of SOA from α-cedrene ozonolysis. A sodiated ion ($[M+Na]^+$) with m/z 275 and elemental composition of $C_{15}H_{24}O_3Na$, which is consistent with the SOZ, was observed in ESI (+) mass spectra. However, as shown in Fig. 12, the relative intensity of this ion in the mass spectra does not decrease at all at 75% RH and is still pronounced when a high concentration formic acid (15 ppm) was added as an SCI scavenger. This indicates that the contribution of the intramolecularly formed SOZ to the ion at m/z 275 is not important. Instead, we tentatively assigned this ion to 15-hydroxy-α-cedronaldehyde and 10-hydroxy-α-cedronaldehyde based on its elemental formula and fragmentation mass spectrum. However, it is not surprising that SOZ was not observed in the SOA in the present study or by Yao et al. (2014) given its relatively high vapor pressure (1.2×10^{-6} atm at 295 K) and therefore low potential to partition to the particle phase.

We have added the following paragraph to the end of Section 3.3.1 (P1 products) of the manuscript:

"Secondary ozonides formed through intramolecular reactions of SCI were observed as the major gas phase products from ozonolysis of α-cedrene (Yao et al., 2014) and β-caryophyllene (Winterhalter et al., 2009), with their formation being significantly suppressed by the addition of water vapor. In the present study, although a sodiated ion with m/z 275 and elemental composition of $C_{15}H_{24}O_3Na$, consistent with the mass and formula of the intramolecularly formed SOZ, was observed in ESI (+) mass spectra of α-cedrene SOA, as will be discussed in Sect. 3.4, the relative intensity of this ion in the mass spectra does not decrease at all at 75% RH and is still pronounced with high concentrations of formic acid (15 ppm) added as an SCI scavenger. This indicates that the ion at m/z 275 is unlikely to be the SOZ. Similarly, Yao et al.

(2014) did not observe the SOZ in the particle phase using HPLC-MS and GC-MS. A possible explanation is that the intramolecularly formed SOZ has a relatively high vapor pressure (1.2 × 10^{-6} atm at 295 K) and therefore a low potential to partition to the particle phase."

Details

Page 34984, line 1: '.... in some environments'. - Maybe rephrase - SQ SOA contributions are more of local to regional rather than global importance. Maybe that can also be stated in the introduction.

Response: We have rephrased this sentence as "Field and model studies have shown that sesquiterpene SOA comprises a significant fraction of ambient organic aerosol from local to regional scales (Sakulyanontvittaya et al., 2008b; Hu et al., 2008; Bouvier-Brown et al., 2009; Ding et al., 2014; Ying et al., 2015), with its contribution comparable to monoterpene SOA in a variety of environments including rural, suburban, and urban areas (Hu et al., 2008; Ding et al., 2014)."

P. 34986, l.1: Why were OH scavengers not applied?

Response: The addition of OH scavengers to the ozonolysis system isolates the pure O_3 reaction and helps to study the mechanisms of this reaction. However, the OH scavengers can perturb the radical chemistry, product distribution, and SOA formation. Such perturbations from scavengers may change the properties of the SOA such that it is not representative of that formed in the real atmosphere, where OH scavengers of such high concentrations are not present and the ozonolysis system intrinsically involves both O_3 and OH reactions. As the goal of this study is to probe formation and growth mechanisms, as well as the phase state, of SOA from α-cedrene ozonolysis, rather than the specific mechanisms of O_3 and OH oxidation, OH scavengers were not added to the system.

However, we reported in a previous study (Zhao et al., 2015) ESI mass spectra of SOA from ozonolysis of α-cedrene in the absence and presence of cyclohexane, which showed that the relative intensity of P2-P4 peaks in the presence of cyclohexane is smaller. This suggests that OH oxidation may contribute to the formation of higher molecular weight species.

We have added the following paragraph regarding the role of OH reaction in α-cedrene oxidation before Section 3.3.1 (P1 products) of the manuscript.

"Previous studies have reported an OH yield of 62-67% from ozonolysis of α-cedrene (Shu and Atkinson, 1994; Yao et al., 2014). Therefore, reaction with OH could play a role in α-cedrene oxidation in the absence of an OH scavenger. We reported in a previous study (Zhao et al., 2015) ESI mass spectra in the absence and presence of cyclohexane, which showed that the relative intensity of P2-P4 peaks in the presence of cyclohexane is smaller. This suggests that OH oxidation may contribute to the formation of higher molecular weight species."

P. 34988, l. 9: Was only one filter sampled over a period from t= 0 to t = 30 min, i.e. for a collected volume of 360 l? Please clarify. Would sequential filter sampling be possible?

Response: For chamber experiments CH1-CH3, filter sampling started after 30 min reaction time. The sampling lasted about 30 min at a flow rate of 12 L min^{-1} to collect a volume of 360 L. Because of the small volume of the chamber (450 L) used in this study and relatively low SOA mass loading for these experiments (e.g., ~ 70 µg m^{-3} for CH1 and CH2), in each experiment the SOA was sampled onto one filter to ensure enough mass for ESI-MS analysis.

To clarify this, we have changed the first sentence of that paragraph to the following:

"For experiments CH1-CH3 (Table 1), SOA composition was examined online by a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.), or by collection onto a PTFE filter at a flow rate of 12 L min^{-1}. Filter sampling started after 30 min reaction time and lasted about 30 min. Because of the small volume of the chamber (450 L) and relatively low SOA mass loading formed (see Table 1), in each experiment the SOA was sampled onto one filter to ensure enough mass for ESI-MS analysis."

P 34989: The array of analytical techniques applied for SOA characterisation is impressive.

Response: Thanks!

P.34994, l. 25: What does 'condense kinetically' mean? A similar expression is also used at p 35007, l 3.

Response: "Condense kinetically" means that organic species are irreversibly taken up by the particle surface, and thus their incorporation into particles depends on the collision frequency of the gas with the particle surface and the magnitude of the uptake coefficients. The kinetic condensation mechanism is characteristic of solid and semi-solid SOA, in which incorporated organic species undergo very slow evaporation because of the diffusion limitation.

We have included this explanation in the last paragraph of Section 3.5 (Mechanisms) of the manuscript, which now reads (changes underlined):

"The incorporation of 2-EHN into SOA and its very slow evaporation back out (Figs. 4 and 5) is consistent with a condensation type of growth mechanism (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006) in which organic species are irreversibly taken up by the particle surface and thus their incorporation into particles depends on the collision frequency of the gas with the particle surface and the magnitude of the uptake coefficient (Perraud et al., 2012). Such a growth mechanism is characteristic of highly viscous SOA, in which incorporated organic species undergo very slow evaporation because of the diffusion limitation, in contrast to an equilibrium mechanism that applies for low viscosity liquid particles."

References:

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