Anonymous Referee #1

The paper by Denjean et al. titled "Aging of secondary organic aerosol generated from the ozonolysis of a-pinene: effects of ozone, light and temperature" presents results of chamber simulations of alpha-pinene SOA formation and aging. To the present date, alpha-pinene is almost certainly the most studied biogenic volatile compound (VOC),and many laboratory studies have used chamber experiments to understand the mechanisms of its formation and chemical evolution under different conditions. Typically, chamber experiments are conducted either under photo-oxidation conditions (i.e., using the hydroxyl radical OH which is usually produced by UV lights) or under dark conditions, using ozone (O3) as reactive agent (ozonolysis). In this paper, the authors chose to focus on the properties of alpha-pinene SOA initially generated via ozonolysis and subsequently exposed to either elevated O3 concentrations and visible light and / or heat. The idea underlying these experiments is that few studies so far have investigated the effects of light and temperature separately on alpha-pinene SOA generated by ozonolysis. The results of the study seem to be indicating that, surprisingly, the observed changes in the alpha-pinene properties are driven by direct changes in temperature rather that photochemistry. Although this conclusion can not be compared to other similar studies (as it seems), the paper is somewhat original in addressing a well-known system from a slightly different perspective. Therefore, I consider this work appropriate for ACP. The manuscript is extremely well written and clear in all the various sections. The introduction puts the work into context of previous literature and the references are adequate and up to date. The experimental part is accurately described and the authors provide extensive detail on the instruments used to characterized the SOA properties, and provide information regarding the measurement accuracy, detection limit and precision whenever possible. The amount of material (text and figures) provided for the discussion is sufficient and clear. The authors also acknowledge that these results are somewhat different from previous studies and critically discuss the possible reasons for the observed disagreement. I have a few comments and questions (see specific comments), but I believe that the paper can be published after minor comments are addressed.

We would like to thank the Referee for his/her insightful and helpful comments on the manuscript. These comments have helped us to improve the manuscript. Hereafter we answer all the comments.

General comments

Paragraph 2.3.2 In this paper, the author report oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios for the SOA, using an Aerodyne HR-ToF-AMS. Perhaps the authors are aware that a new parameterization for the O/C and H/C derived from the Aerodyne AMS was recently published on ACPD by Canagaratna et al. (ACPD, 2014). The link is: http://www.atmos-chem-phys-discuss.net/14/19791/2014/acpd-14-19791-2014.html. The paper offers an easy way to "correct" O/C and H/C numbers by applying a simple parameterization. I recommend using this new formulation since it will become the new standard. This would allow to put these measurements in context of the new corrections. However, since the paper is still under discussion, the authors can chose to report both old and new numbers and discuss whether it matters to report the new ones (and why).

Response: We thank Referee #1 for suggesting this new parameterization of the AMS data. In our paper, O/C and H/C were calculated using a modified fragmentation table in which the fragment H_2O^+ has been considered as all produced by fragmentation of organic compounds ($H_2O^+ \sim CO_2^+$) while in the default fragmentation table H_2O^+ from organic compounds is calculated as organic_$H_2O^+ = 0.225*CO_2^+$. For this reason, we have applied the new parameterization proposed by Canagaratna et al. (2014) to our data but using the default fragmentation table (organic_$H_2O^+ = 0.225*CO_2^+$). O/C ratio calculated using the default fragmentation table is 0.44 while the new proposed parameterization increases this value to 0.55 (20% increase). This difference is consistent with the results of Canagaratna et al. (2014) for laboratory generated organic aerosols and can be attributed to an underestimation in the Aiken-method of the CO^+ and H_2O^+ ions produced from many oxidized species. However, an O/C of 0.55 was also obtained using the Aiken-method with our modified fragmentation table in which the measured fragment H_2O^+ is assigned to organic compounds. This means that in extremely dry conditions (as in our experiments) the two methodologies agree.

We provided more details on the data treatment in section 2.3.2., as follows: "Additional modification of the fragmentation table was made for organic H_2O^+ *as suggested by Chen et al. (2011). Default fragmentation table derives the contribution from fragmentation of organic compounds (dehydration) to the ion* H_2O^+ *as* $organic\_H_2O^+=0.225*CO_2^+$ *considering that the measured excess is due to the interference of water. Because our experiments were run under very dry conditions (RH < 1%), the ion* H_2O^+ *has been totally assigned to fragmentation of organic compounds which corresponds to a ratio* $organic\_H_2O^+$ *to* CO_2^+ *of 0.8-1:1. Similar* $organic\_H_2O^+$ *to* CO_2^+ *were obtained in previous studies of alpha-pinene ozonolysis (Chen et al., 2011; Chhabra et al., 2010). Measurement uncertainties of O:C were estimated to be ±30%, as determined by Aiken et al (2007)."*

We added the comparison of our results with the new parameterization proposed by Canagaratna et al. (2014) in section 3.3., as follows: "A new parameterization of the O:C ratio derived from AMS measurements was recently presented by Canagaratna et al. (2014). Application of this new parameterization to our measurements resulted in O:C ratios of 0.55, similar to those obtained with our modified fragmentation table in which the measured fragment H_2O^+ *was assigned to organic compounds. This indicates that the two methodologies agree under very dry conditions (RH<1%). The average O:C ratio obtained with both parameterization were higher by 20% than the one obtained with the Aiken-method and can be attributed to an underestimation in the Aiken-method of the* CO^+ *and* H_2O^+ *ions produced from many oxidized species."*

Paragraph 3.2, page 22450, line 3 The authors state that particle aging did not change the light absorption properties of the studied SOA systems and that likely chromophores were not formed. The authors cite previous literature work that has looked at similar aspects of SOA particles. Can the authors add a statement where they compare these results with previous work cited in page 22441 - lines 14-20 - and also add a statement on why these results might be different. Is it the specific type of SOA (alpha-pinene in this case) that is not prone to chromophore formation ? Is it sensitivity issues of the instruments used to detect changes in the imaginary part of the refractive index ?

Response: The formation of chromophores has been observed previously from the ozonolysis of biogenic terpenes (Bones et al., 2010; Laskin et al., 2010; Zhong et al., 2012). Some oligomers formed in the particle-phase may contain a long conjugated structure which could increase the light absorption properties of SOA in the visible region. Our results indicate that this phenomenon occurred only weakly for α-pinene-O_3 *SOA and/or that the specific absorption of any potential aging products (i.e. heavily conjugated molecules) was not significant.*

We completed paragraph 3.2. as follows: "The formation of chromophores has been observed previously from the ozonolysis of biogenic terpenes (Bones et al., 2010; Laskin et al., 2010; Zhong et al., 2012). Some oligomers formed in particle-phase can contain long conjugated structures which increase the light absorption properties of SOA in the visible region. Interestingly, while one might have expected the formation of chromophores during the aging processes, our results indicate that this phenomenon occurred only weakly for α-pinene-O_3 *SOA and/or that the specific absorption of any potential aging products was not significant. Unlike toluene (Nakayama et al., 2010) or limonene (Bones et al., 2010), α-pinene-*O_3 *SOA products did not contain long conjugated structures which absorbed visible radiation, at least under our experimental conditions when conducted in the absence of NOx or seed particles."*

Paragraph 4, page 22453, lines 25-27 Are there any other studies that measure SOA volatility after many hours of ageing ? After reading the paper, I am under the impression that the methodology used in these experiments (ozonolysis and long time scale that allow evolution of the SOA before processing) is not common. If true, the authors should state this clearly. If other laboratories have used a similar approach, those results should be compared, at least qualitatively.

Response: We agree with Referee #1 that the originality of the methodology is not enough highlighted in the discussion.
We modified Paragraph 4 as follows: "First, in the present study, the long-time scale of the experiments (20 hours) allows the stability of the chemical composition of the semi-volatile component of SOA before processing. By contrast, in the previous studies, SOA volatility was measured only several minutes after its formation. Since the chemical composition of SOA has been observed to vary significantly during its formation (Shilling et al., 2008; Chhabra et al., 2010; Denjean et al., 2014b), it is likely that the volatility of the condensed species also varies during this time period."

Conclusions It would be worthwhile noting that different VOC systems (other biogenic etc) could behave differently than alpha-pinene, such as other SOA systems that have shown different "glassy" properties in other studies.

Response: We completed the Conclusions as follows: "In addition, further experimental studies on SOA which exhibit different viscosity are required in order to evaluate the atmospheric implication of the oxidative processing and photochemistry."

References:

Bones, D. L., Henricksen, D. K., Mang, S. A., Gonsior, M., Bateman, A. P., Nguyen, T. B., Cooper, W. J., and Nizkorodov, S. A.: Appearance of strong absorbers and fluorophores in limonene-O3 secondary organic aerosol due to NH4+-mediated chemical aging over long time scales, Journal of Geophysical Research: Atmospheres, 115, D05203, 10.1029/2009JD012864, 2010.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys. Discuss., 14, 19791-19835, 10.5194/acpd-14-19791-2014, 2014.

Chen Qi, Ying J.L., Donahue N.M., Shilling J.E., Martin S.T. Particle-phase chemistry of secondary organic material : compared to measured O:C and H:C elemental ratios provide constraints. Environ. Sci.Technol., 45, 4763-4770, 2011.

Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111-4131, 10.5194/acp-10-4111-2010, 2010.

Denjean, C., Formenti, P., Picquet-Varrault, B., Pangui, E., Zapf, P., Katrib, Y., Giorio, C., Tapparo, A., Monod, A., Temime-Roussel, B., Decorse, P., Mangeney, C., and Doussin, J. F.: Relating hygroscopicity and optical properties to chemical composition and structure of secondary organic aerosol particles generated from the ozonolysis of α-pinene, Atmos. Chem. Phys. Discuss., 14, 10543-10596, 10.5194/acpd-14-10543-2014, 2014b.

Laskin, J., Laskin, A., Roach, P. J., Slysz, G. W., Anderson, G. A., Nizkorodov, S. A., Bones, D. L., and Nguyen, L. Q.: High-Resolution Desorption Electrospray Ionization Mass Spectrometry for Chemical Characterization of Organic Aerosols, Analytical Chemistry, 82, 2048-2058, 10.1021/ac902801f, 2010.

Nakayama, T., Matsumi, Y., Sato, K., Imamura, T., Yamazaki, A., and Uchiyama, A.: Laboratory studies on optical properties of secondary organic aerosols generated during the photooxidation of toluene and the ozonolysis of alpha-pinene, J. Geophys. Res.-Atmos., 115, 10.1029/2010jd014387, 2010.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., McKinney, K. A., and Martin, S. T.: Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of α-pinene, Atmos. Chem. Phys., 8, 2073-2088, 10.5194/acp-8-2073-2008, 2008.

Zhong, M., Jang, M., Oliferenko, A., Pillai, G. G., and Katritzky, A. R.: The SOA formation model combined with semiempirical quantum chemistry for predicting UV-Vis absorption of secondary organic aerosols, Physical Chemistry Chemical Physics, 14, 9058-9066, 10.1039/C2CP23906J, 2012.