Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-99-RC1, 2020

Atmospheric Chemistry and Physics
Open Access
Discussions

Interactive comment on "The Aarhus Chamber Campaign on Highly Oxidized Multifunctional Organic Molecules and Aerosols (ACCHA): Particle Formation and Detailed Chemical Composition at Different Temperatures" *by* Kasper Kristensen et al.

Anonymous Referee #1

Received and published: 7 March 2020

Kristensen et al. conducted dark ozonolysis of alpha pinene at different temperatures. They found at low temperatures the particle formation rates, particle number and mass concentrations were enhanced. The effects of temperature on particle-phase organic acids and dimer esters were also evaluated. They found the formation of less oxidized dimer esters increased at lower temperatures while the formation of the more oxidized species was suppressed. The link between the dimer ester and HOMs was also discussed. Though the topic of this study is timely and highly demanded in the area of

new particle formation, the manuscript is well written, and the results are interesting, I have some major concerns to be addressed before the recommendation of publication. The first major concern is the experiments were conducted at not dry conditions but the effects of RH on results were missing when the authors interpreted the results. The second major concern is the formation pathway of esters proposed by the authors is not fully convincing and other possible formation pathways found by other research groups are not mentioned.

Major comments: (1) Some statements in the Introduction section are not comprehensive and some related important references are missing, for example: Page 2, Line 50-51, Line 59-61: "higher yields with lower temperatures". This may not be absolutely right, as relative humidity, phase state, and the involved multiphase reactions all affect the SOA mass yields at different temperatures. For instance, von Hessberg et al. (2009) found the oscillatory negative temperature dependence under dry conditions while the positive temperature dependence under humid conditions when examining the SOA yield from the ozonolysis of beta pinene. Pathak et al. (2007) showed that the alpha pinene SOA yields showed a weak dependence on temperature in the 15°C to 40°C range, implying that the negative dependence of the partitioning on the temperature is counteracted by a positive dependence of the chemical mechanism (Tillmann et al., 2010). Page 2, Line 58: for organic compound partitioning, besides volatility and total particle mass, particle size and particle phase state also affect the partitioning and the gas-particle equilibration timescale significantly (Shiraiwa & Seinfeld, 2012; Liu et al., 2016; Li & Shiraiwa, 2019; Zaveri et al., 2014, 2020). Page 2, Line 72: Add Lawler et al. (2018). As far as I know, it is the first paper showing newly formed 20–70 nm particles showed enhancement in alkanoic acids from the perspective of ambient observations.

(2) Experiment section, Page 5, Line 187: As important results of this study are related to dimer esters and organic acids, what are the uncertainties in the estimations of the functional groups within SOA? The authors stated that due to lack of authentic

standards, the dimer esters were quantified using DTAA as surrogate standard. What is the effect of using DTAA other than another surrogate, e.g., bis(2-ethylhexyl) sebacate (Ranney & Ziemann, 2016; Claflin et al., 2018)?

(3) It is nice to show the various relative humidity values in Table 1 but the role of RH in the particle phase state, gas-particle partitioning, multiphase reactions (refer to the papers listed in Major Comment 1) and the concentrations of OH and HO2 radicals is not discussed in the manuscript, which could affect the interpretation of the experimental results. For example, Line 221, would the phase state also play a role (maybe a minor role though) making the maximum SOA mass reached slower at the lower temperature? Would the RH affect the detected concentrations of functional groups (Claflin et al., 2018) in Sec. 3.3? As the OH scavenger seems not used, would the RH affect the HO2 concentrations and thus the competition with the RO2-RO2 reaction (Claflin et al., 2018; Simon et al., 2020)?

(4) Figure 9: Is the reaction with RO2 radicals the only termination step? As far as I know, additional termination reactions of CI include their reactions with aldehydes (RC = O), alcohols (ROH), carboxylic acids (ROOH) to form hydroperoxy esters and secondary ozonides and water vapor to form hydroxy hydroperoxides (Claflin et al., 2018; Zeng et al., 2020). Claflin et al. (2018) stated that the only known gas-phase mechanism for forming esters in their experiments was the reaction of CI with carboxylic acids under dry conditions. Claflin et al. (2018) showed that particle-phase oxidation of carbonyl groups may contribute significantly to the formation of both carboxyl and ester groups in the SOA. Müller et al. (2008) have suggested that the esters they identified by mass spectrometry in SOA formed by α-pinene ozonolysis might be formed by an unknown gas-phase radical mechanism. Could the authors give the reasons why other pathways can be excluded in Fig. 9? As the formation of esters via particle-phase decarboxylation of diacyl peroxides as proposed by Zhang et al. (2015) requires an ionic aerosol matrix such as aqueous ammonium sulfate, could the authors convince the readers the mechanisms proposed by Zhang et al. (2015) indeed happen in their

experiments without the presence of inorganic seeds?

Minor comments:

(1) P2, Line 55: Cite a review paper (e.g., Nizkorodov et al., 2011; Noziere et al., 2015) after "…peroxides and peroxy-acids". (2) P5, Line 163: Does the temperature gradually and continuously change or the system stay for some time at each temperature? In Figure S1, for the panel for Exp. 1.5, move "Temp" closer to the temperature line instead of the RH line. (3) Was OH scavenger used in the experiments? (4) Reference list: P19, Line 547: The title of Jensen et al. (2020) is Temperature and VOC concentration as controlling factors for chemical composition of alpha-pinene derived secondary organic aerosol: https://www.atmos-chem-phys-discuss.net/acp-2020-100/. P21, Line 613-614: Peräkylä et al. has been published in ACP.

References:

Claflin, M. S., Krechmer, J. E., Hu, W., Jimenez, J. L. and Ziemann, P. J.: Functional Group Composition of Secondary Organic Aerosol Formed from Ozonolysis of α-Pinene Under High VOC and Autoxidation Conditions, ACS Earth and Space Chemistry, 2, 1196-1210, 10.1021/acsearthspacechem.8b00117, 2018.

Lawler, M. J., Rissanen, M. P., Ehn, M., Mauldin, R. L., Sarnela, N., Sipilä, M., & Smith, J. N. (2018). Evidence for diverse biogeochemical drivers of boreal forest new particle formation. Geophysical Research Letters, 45, 2038– 2046. https://doi.org/10.1002/2017GL076394

Li, Y. and Shiraiwa, M.: Timescales of secondary organic aerosols to reach equilibrium at various temperatures and relative humidities, Atmos. Chem. Phys., 19, 5959-5971, 10.5194/acp-19-5959-2019, 2019.

Liu, P., Li, Y. J., Wang, Y., Gilles, M. K., Zaveri, R. A., Bertram, A. K. and Martin, S. T.: Lability of secondary organic particulate matter, Proc. Natl. Acad. Sci. U.S.A., 113, 12643-12648, 10.1021/acscentsci.7b00452, 2016.

Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A., Riipinen, I., Hong, J., Donahue, N. M., Hallquist, M. and Petäjä, T.: Molecular identification of organic vapors driving atmospheric nanoparticle growth, Nature communications, 10, 1-7, 2019.

Müller, L., Reinnig, M.-C., Warnke, J., and Hoffmann, Th.: Unambiguous identification of esters as oligomers in secondary organic aerosol formed from cyclohexene and cyclohexene/α-pinene ozonolysis, Atmos. Chem. Phys., 8, 1423–1433, https://doi.org/10.5194/acp-8-1423-2008, 2008.

Nizkorodov, S. A., Laskin, J. and Laskin, A.: Molecular chemistry of organic aerosols through the application of high resolution mass spectrometry, Physical Chemistry Chemical Physics, 13, 3612-3629, 10.1039/c0cp02032j, 2011.

Noziere, B., Kaberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgic, I., Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahno, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R. and Wisthaler, A.: The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges, Chem. Rev., 115, 3919-3983, 10.1021/cr5003485, 2015.

Pathak, R. K., Stanier, C. O., Donahue, N. M., and Pandis, S. N. (2007), Ozonolysis of αâĂŘpinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), J. Geophys. Res., 112, D03201, doi:10.1029/2006JD007436.

April P. Ranney & Paul J. Ziemann (2016) Microscale spectrophotometric methods for quantification of functional groups in oxidized organic aerosol, Aerosol Science and Technology, 50:9, 881-892, DOI: 10.1080/02786826.2016.1201197

Shiraiwa, M. and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, 10.1029/2012GL054008, 2012.

Simon, M., et al.: Molecular understanding of new-particle formation from alpha-pinene between -50âĂĹ°C and 25âĂĹ°C, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1058, 2020.

Tillmann, R., Hallquist, M., Jonsson, Å. M., Kiendler-Scharr, A., Saathoff, H., Iinuma, Y., and Mentel, Th. F.: Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of α-pinene, Atmos. Chem. Phys., 10, 7057–7072, https://doi.org/10.5194/acp-10-7057-2010, 2010.

von Hessberg, C., von Hessberg, P., Pöschl, U., Bilde, M., Nielsen, O. J. and Moortgat, G. K.: Temperature and humidity dependence of secondary organic aerosol yield from the ozonolysis of β-pinene, Atmos. Chem. Phys., 9, 3583-3599, 10.5194/acp-9-3583-2009, 2009.

Zaveri, R. A., Easter, R. C., Shilling, J. E. and Seinfeld, J. H.: Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction, Atmos. Chem. Phys., 14, 5153-5181, 10.5194/acp-14-5153-2014, 2014.

Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Zawadowicz, M. A., Suski, K., China, S., Bell, D. M., Veghte, D. and Laskin, A.: Particle-Phase Diffusion Modulates Partitioning of Semivolatile Organic Compounds to Aged Secondary Organic Aerosol, Environmental Science & Technology, 54, 2595-2605, 10.1021/acs.est.9b05514, 2020.

Zeng, M., Heine, N. and Wilson, K. R.: Evidence that Criegee intermediates drive autoxidation in unsaturated lipids, Proceedings of the National Academy of Sciences, 117, 4486-4490, 10.1073/pnas.1920765117, 2020.

Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. F., Aumont, B., Flagan, R. C. and Seinfeld, J. H.: Formation and evolution of molecular products in α-pinene secondary organic aerosol, Proceedings of the National Academy of Sciences, 112, 14168-14173, 10.1073/pnas.1517742112, 2015.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-99,

2020.