

Reviewer #2

This manuscript (which is a companion paper to one submitted by Wu et al.) describes results of a laboratory study of the effect of aging in the dark on the mass and composition of SOA formed from the reaction of NO₃ radicals with a-pinene for a few different concentrations of a-pinene and N₂O₅, which was the source of NO₃ radicals. Experiments were conducted in a Teflon chamber, SOA mass and size were monitored with an SMPS, and gas and particle composition were monitored with a FIGAERO-CIMS and EESI-TOF. The observations are thoroughly discussed, and various possible explanations, such as evaporation, oxidation, and monomer-dimer reactions are proposed. In general, however, given the complexity of the system, the lack of information on the molecular structures of the SOA components (only elemental formulas are available), and the non-quantitative MS analyses, it was not possible to draw convincing conclusions about the physical or chemical processes that might have altered the SOA in the dark. Nonetheless, the data set is interesting, and future studies may provide more detailed data that can help to explain the results. I think the manuscript can be published after the following comments are addressed.

We would like to thank the reviewer for their questions and comments.

Specific Comments

1. Line 205: The reaction RO₂ + NO₃ forms RO + NO₂ + O₂, not peroxy nitrates (ROONO₂). I assume you meant RO₂ + NO₂ → ROONO₂.

Thank you for this comment, we have changed the RO₂ + NO₃ to RO₂ + NO₂.

2. How do you propose that peroxy nitrates are converted to nitrates? The only ROONO₂ reactions I am aware of are reversible formation of RO₂ + NO₂ and decomposition to R(O) + HNO₃. It seems more likely that the additional nitrates observed in the excess N₂O₅ experiments 1 and 3 are formed by reactions of alcohols with N₂O₅: ROH + N₂O₅ → RONO₂ + HNO₃, which is a well-known reaction that is used to synthesize organic nitrates from the corresponding alcohols.

We assume the reviewer is referring to the fact that peroxy nitrates are likely unstable and have a lifetime that is very short in the aerosol phase. Overall, we cannot distinguish the difference between organonitrates and peroxy nitrates with our current measurement techniques, so there is a possibility we observe molecules formed from both RO₂ + NO₂ and ROH + N₂O₅. Though, Zhao et al. (2020) suggests that the route via RO₂ + NO₂ is an important driver to form trinitrates in chamber experiments studying isoprene + NO₃, which will also be a valid pathway in the experiments shown here. (Highlighted on line 210).

Once in the particle phase, we propose that peroxy nitrates can undergo unimolecular scission, which would create an NO₃ radical and an alkoxy radical. After this condensed phase radical chemistry is not clear, at least this is true in bulk polymer chemistry (Smith et al., 2018). The suggested route to form a carbonyl is unlikely because the formation of C₂₀H₃₀NO_x molecules is not significant, which would occur with the conversion of a nitrate to a carbonyl. But once radicals are formed, presumably cascading H-abstraction reactions will continue through the aerosol until finally terminating.

3. Line 255: Because the RO₂ + RO₂ and RO₂ + NO₃ reactions both lead to the same alkoxy radicals, and these can go on to form monomers that then form dimers in particles, an alternative explanation for the similarity in SOA dimer composition in the two radical regimes is that most of the dimers are formed in the particles and that gas-phase dimers are minor. Since these MS methods are not quantitative, it is not possible to draw conclusions on the importance of gas-phase dimers.

This comment is in stark contrast to reviewer #1, which suggests that we can use the current data to infer the rates of reactions of RO₂+RO₂ reactions. We agree with reviewer #2 in that we are unable to assess exact rates of reactions (e.g. rates of RO₂ + RO₂ reactions) for gas-phase dimer formation without well calibrated measurements of gas-phase concentrations.

Although the alkoxy pathway would be the same for both of the radical pathways (RO₂ + RO₂/NO₃), the ultimate branching can be remarkably different between the two, since RO₂+RO₂ has other termination pathways (e.g. dimers, alcohol, or carbonyl). Besides the difference in the branching pathways, the alkoxy pathway (RO₂ + NO₃) is predicted to proceed mostly to pinonaldehyde. Based on saturation vapor concentration estimates, this molecule would not participate significantly in the formation of SOA or the formation of dimers. In contrast to this, many recent studies have demonstrated the importance of RO₂ + RO₂ reactions to the formation of dimers. (Berndt et al., 2018a;Berndt et al., 2018b;Zhao et al., 2018;Ng et al., 2008;Molteni et al., 2019;Rissanen et al., 2015;Simon et al., 2020;Heinritzi et al., 2020)

Additionally, the idea that both reaction pathways could lead to the same products and ultimately be just as important in the formation of SOA does not agree with other results that show SOA yields are smaller for both isoprene + NO₃ and α -pinene + NO₃ when dominated by RO₂ + NO₃ chemistry(Bates et al., 2021;Ng et al., 2008).

Along these lines, we added to the manuscript beginning on line 263: “These findings are consistent with the importance of dimers formed from RO₂ + RO₂ reactions in other systems (Berndt et al., 2018a;Berndt et al., 2018b;Zhao et al., 2018;Ng et al., 2008;Molteni et al., 2019;Rissanen et al., 2015;Simon et al., 2020;Heinritzi et al., 2020), and with higher SOA yields from NO₃ initiated oxidation during dominant RO₂ + RO₂ chemistry (Ng et al., 2008;Bates et al., 2021).”

4. Line 329: Since the EESI is not calibrated, how can you measure a mass flux?

Lines 130 – 138 of the manuscript detail the conversion from counts sec⁻¹ to attogram sec⁻¹. The conversion is based on assuming that all species are detected equally well and converting the mass observed at the detector of the EESI-MS. A comparison of the measured ag sec⁻¹ against the measured mass by the SMPS is presented in Figure S2, and demonstrates there is a good agreement. We have added our levoglucosan calibration points to demonstrate the same linearity from these experiments.

5. Since neither the EESI-TOF or the FIGAERO-CIMS signals have been calibrated, the authors cannot assume that all compounds have the same sensitivity. This makes it difficult to draw conclusions from the changes observed in MS signals over time. For example, if reversible (non-oxidative) monomer exchange reactions were occurring in the particles to form dimers with different structures and detection sensitivities, then this could appear as oxidation when it is not. One can imagine a variety of such scenarios that confuse an interpretation of the MS observations.

The response of the EESI-ToF has been shown to vary by ~ 1 order of magnitude when comparing oxidation products from different types of volatile organic compounds (Wang et al., 2021). Also, the EESI agrees very well with predicted SOA composition and mass based on measured components in the gas-phase by the PTR-3 for other SOA systems (Surdu et al., 2021). Additionally, we demonstrate the good agreement between the measured mass by the SMPS and the corresponding EESI signal (ag sec⁻¹) for the experiments presented here. Together, these results suggest even if there are differences in sensitivity, the EESI is capturing the chemical evolution.

In the proposed scenario, the formation of reversible dimers comes from non-observed monomers (or observed in a limited way). In order for this scenario to result in agreement with the observed SMPS mass, then the formation / consumption would have to perfectly equal out because in the scenario the monomers are not observed. Also, both the EESI and the FIGAERO-CIMS would have to be biased

in the same exact way in order to observe similar processes without observed reversible (non-oxidative) monomer exchange reactions.

The following has been added to the text as a paragraph at line 316:

“The argument from the preceding paragraph assumes that the sensitivity of the EESI-ToF holds equally for all molecules. On a molecule-by-molecule basis there is roughly a spread of 1 order of magnitude in the sensitivity of the EESI-ToF toward different ions (Wang et al., 2021; Lopez-Hilfiker et al., 2019), but when comparing bulk SOA composition there is good agreement with measured mass here (Fig. S2) and during measurements performed in Zurich, Switzerland (Qi et al., 2019; Stefenelli et al., 2019). Additionally, the SOA composition measured by the EESI-ToF compares well to the predicted particle composition based on gas-particle partitioning, using gas-phase measurements performed by the PTR3 (Surdu et al., 2021). This provides confidence that the EESI-ToF is not missing specific molecules here. However, even if the EESI-ToF were not sensitive to the species that are forming the higher oxygenated molecules (i.e. monomer exchange reactions), then the formation of more highly oxygenated dimers ($C_{20}H_{32}N_2O_{9-11}$) would have to be nearly equally balanced by the consumption / disappearance of $C_{20}H_{32}N_2O_8$ (in order for the SMPS mass and EESI to agree in Fig. S2). Further, the FIGAERO-CIMS would have to be biased in the exact same way as the EESI-ToF. Considering the agreement presented here and in previous studies it is more likely that the combination of the EESI and FIGAERO are capturing the change in chemical composition.”

Technical Comments

1. Please define ag s⁻¹.

Line 136: “EESI-ToF signal (attograms per second - ag s⁻¹)”

Bates, K. H., Burke, G. J. P., Cope, J. D., and Nguyen, T. B.: The nitrate radical (NO₃) oxidation of alpha-pinene is a significant source of secondary organic aerosol and organic nitrogen under simulated ambient nighttime conditions, *Atmos. Chem. Phys. Discuss.*, 2021, 1-24, 10.5194/acp-2021-703, 2021.

Berndt, T., Mentler, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Ozonolysis and OH Radical Reaction of α -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene, *Environmental Science & Technology*, 52, 11069-11077, 10.1021/acs.est.8b02210, 2018a.

Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Self- and Cross-Reactions of RO₂ Radicals in the Atmosphere, *Angewandte Chemie International Edition*, 57, 3820-3824, 10.1002/anie.201710989, 2018b.

Heinritzi, M., Dada, L., Simon, M., Stolzenburg, D., Wagner, A. C., Fischer, L., Ahonen, L. R., Amanatidis, S., Baalbaki, R., Baccarini, A., Bauer, P. S., Baumgartner, B., Bianchi, F., Brilke, S., Chen, D., Chiu, R., Dias, A., Dommen, J., Duplissy, J., Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Granzin, M., El Haddad, I., He, X., Helm, J., Hofbauer, V., Hoyle, C. R., Kangasluoma, J., Keber, T., Kim, C., Kürten, A., Lamkaddam, H., Laurila, T. M., Lampilahti, J., Lee, C. P., Lehtipalo, K., Leiminger, M., Mai, H., Makhmutov, V., Manninen, H. E., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Molteni, U., Müller, T., Nie, W., Nieminen, T., Onnela, A., Partoll, E., Passananti, M., Petäjä, T., Pfeifer, J., Pospisilova, V., Quéléver, L. L. J., Rissanen, M. P., Rose, C., Schobesberger, S., Scholz, W., Scholze, K., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Vazquez-Pufleau, M., Virtanen, A., Vogel, A. L., Volkamer, R., Wagner, R., Wang, M., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P., Zha, Q., Zhou, X., Amorim, A., Baltensperger, U., Hansel, A., Kulmala, M., Tomé, A., Winkler, P. M., Worsnop, D. R., Donahue, N. M., Kirkby, J., and Curtius, J.: Molecular understanding of the suppression of new-particle formation by isoprene, *Atmos. Chem. Phys.*, 20, 11809-11821, 10.5194/acp-20-11809-2020, 2020.

Lopez-Hilfiker, F. D., Pospisilova, V., Huang, W., Kalberer, M., Mohr, C., Stefenelli, G., Thornton, J. A., Baltensperger, U., Prevot, A. S. H., and Slowik, J. G.: An extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) for online measurement of atmospheric aerosol particles, *Atmos. Meas. Tech.*, 12, 4867-4886, 10.5194/amt-12-4867-2019, 2019.

Molteni, U., Simon, M., Heinritzi, M., Hoyle, C. R., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Dias, A., Duplissy, J., Frege, C., Gordon, H., Heyn, C., Jokinen, T., Kürten, A., Lehtipalo, K., Makhmutov, V., Petäjä, T., Pieber, S. M., Praplan, A. P., Schobesberger, S., Steiner, G., Stozhkov, Y., Tomé, A., Tröstl, J., Wagner, A. C., Wagner, R., Williamson, C., Yan, C., Baltensperger, U., Curtius, J., Donahue, N. M., Hansel, A., Kirkby, J., Kulmala, M., Worsnop, D. R., and Dommen, J.: Formation of highly oxygenated organic molecules from α -pinene ozonolysis: chemical characteristics, mechanism, and kinetic model development, *ACS Earth Space Chem.*, 3, 873-883, 10.1021/acsearthspacechem.9b00035, 2019.

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), *Atmos. Chem. Phys.*, 8, 4117-4140, 10.5194/acp-8-4117-2008, 2008.

Qi, L., Chen, M., Stefenelli, G., Pospisilova, V., Tong, Y., Bertrand, A., Hueglin, C., Ge, X., Baltensperger, U., Prévôt, A. S. H., and Slowik, J. G.: Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) –

Part 2: biomass burning influences in winter, *Atmospheric Chemistry and Physics*, 19, 8037-8062, 10.5194/acp-19-8037-2019, 2019.

Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kausiala, O., Garmash, O., Kjaergaard, H. G., Petäjä, T., Worsnop, D. R., Ehn, M., and Kulmala, M.: Effects of Chemical Complexity on the Autoxidation Mechanisms of Endocyclic Alkene Ozonolysis Products: From Methylcyclohexenes toward Understanding α -Pinene, *The Journal of Physical Chemistry A*, 119, 4633-4650, 10.1021/jp510966g, 2015.

Simon, M., Dada, L., Heinritzi, M., Scholz, W., Stolzenburg, D., Fischer, L., Wagner, A. C., Kürten, A., Rörup, B., He, X. C., Almeida, J., Baalbaki, R., Baccarini, A., Bauer, P. S., Beck, L., Bergen, A., Bianchi, F., Bräkling, S., Brilke, S., Caudillo, L., Chen, D., Chu, B., Dias, A., Draper, D. C., Duplissy, J., El Haddad, I., Finkenzeller, H., Frege, C., Gonzalez-Carracedo, L., Gordon, H., Granzin, M., Hakala, J., Hofbauer, V., Hoyle, C. R., Kim, C., Kong, W., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Mai, H., Manninen, H. E., Marie, G., Marten, R., Mentler, B., Molteni, U., Nichman, L., Nie, W., Ojdanic, A., Onnela, A., Partoll, E., Petäjä, T., Pfeifer, J., Philippov, M., Quéléver, L. L. J., Ranjithkumar, A., Rissanen, M., Schallhart, S., Schobesberger, S., Schuchmann, S., Shen, J., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Tomé, A. R., Vazquez-Pufleau, M., Vogel, A., Wagner, R., Wang, M., Wang, D. S., Wang, Y., Weber, S. K., Wu, Y., Xiao, M., Yan, C., Ye, P., Ye, Q., Zauner-Wieczorek, M., Zhou, X., Baltensperger, U., Dommen, J., Flagan, R. C., Hansel, A., Kulmala, M., Volkamer, R., Winkler, P. M., Worsnop, D. R., Donahue, N. M., Kirkby, J., and Curtius, J.: Molecular understanding of new-particle formation from alpha-pinene between -50 °C and 25 °C, *Atmos. Chem. Phys. Discuss.*, 2020, 1-42, 10.5194/acp-2019-1058, 2020.

Smith, L. M., Aitken, H. M., and Coote, M. L.: The Fate of the Peroxyl Radical in Autoxidation: How Does Polymer Degradation Really Occur?, *Accounts of Chemical Research*, 51, 2006-2013, 10.1021/acs.accounts.8b00250, 2018.

Stefenelli, G., Pospisilova, V., Lopez-Hilfiker, F. D., Daellenbach, K. R., Hüglin, C., Tong, Y., Baltensperger, U., Prévôt, A. S. H., and Slowik, J. G.: Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) – Part 1: Biogenic influences and day–night chemistry in summer, *Atmos. Chem. Phys.*, 19, 14825-14848, 10.5194/acp-19-14825-2019, 2019.

Surdu, M., Pospisilova, V., Xiao, M., Wang, M., Mentler, B., Simon, M., Stolzenburg, D., Hoyle, C. R., Bell, D. M., Lee, C. P., Lamkaddam, H., Lopez-Hilfiker, F., Ahonen, L. R., Amorim, A., Baccarini, A., Chen, D., Dada, L., Duplissy, J., Finkenzeller, H., He, X.-C., Hofbauer, V., Kim, C., Kürten, A., Kvashnin, A., Lehtipalo, K., Makhmutov, V., Molteni, U., Nie, W., Onnela, A., Petäjä, T., Quéléver, L. L. J., Tauber, C., Tomé, A., Wagner, R., Yan, C., Prevot, A. S. H., Dommen, J., Donahue, N. M., Hansel, A., Curtius, J., Winkler, P. M., Kulmala, M., Volkamer, R., Flagan, R. C., Kirkby, J., Worsnop, D. R., Slowik, J. G., Wang, D. S., Baltensperger, U., and Haddad, I. e.: Molecular characterization of ultrafine particles using extractive electrospray time-of-flight mass spectrometry, *Environmental Science: Atmospheres*, 10.1039/D1EA00050K, 2021.

Wang, D. S., Lee, C. P., Krechmer, J. E., Majluf, F., Tong, Y., Canagaratna, M. R., Schmale, J., Prévôt, A. S. H., Baltensperger, U., Dommen, J., El Haddad, I., Slowik, J. G., and Bell, D. M.: Constraining the response factors of an extractive electrospray ionization mass spectrometer for near-molecular aerosol speciation, *Atmos. Meas. Tech. Discuss.*, 2021, 1-24, 10.5194/amt-2021-125, 2021.

Zhao, Y., Thornton, J. A., and Pye, H. O. T.: Quantitative constraints on autoxidation and dimer formation from direct probing of monoterpene-derived peroxy radical chemistry, *Proceedings of the National Academy of Sciences*, 115, 12142, 10.1073/pnas.1812147115, 2018.