Reply to Interactive comment on "Chemical Transformation of α-Pinene derived Organosulfate via Heterogeneous OH Oxidation: Implications for Sources and Environmental Fates of Atmospheric Organosulfates" by Rongshuang Xu et al.

Anonymous Referee #1

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-953-RC1, 2022

The work by Xu et al. investigated the heterogeneous OH oxidation of one α-Pinene derived organosulfate (i.e., $C_{10}H_{17}O_5SNa$, αpOS-249), and both reaction kinetics and mechanisms are well studied and discussed. This is an interesting work that uses a structure–activity relationship (SAR) to assess which carbon site is more favorable for hydrogen abstraction in reactions of OH radical with αpOS-249, further confirmed by the products measured. The experiments, model predictions, results, and conclusions are sound and well described. Therefore, this work could be published nearly as is. Before the publish, there are several minor comments the authors may consider.

We thank the reviewer for his/her thoughtful comments. The referee's comments are below in italics followed by our responses in normal font.

General Comment:

Methanol is a common solvent used for MS analysis. However, it should be careful that many SOA constituents such as carbonyls and carboxylic acids undergo chemical reactions with methanol during extraction, storage, and possibly during the electrospray process (Bateman et al., 2008). The influence of methanol may be little on the results of this study, but it is better to give some explanations here.

Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A. and Nizkorodov, S. A.: The effect of solvent on the analysis of secondary organic aerosol using electrospray ionization mass spectrometry, Environ. Sci. Technol., 42(19), 7341–7346, doi:10.1021/es801226w, 2008.

Author Response:

Thanks for this insightful comment. We agree with the reviewer's comment that organic compounds such as carbonyls and carboxylic acids could undergo reactions with methanol during extraction, storage, and possibly during the electrospray process. For instance, as suggested in the literature, carboxylic acids could react with methanol to form esters and with carbonyls to hemiacetals and acetals. This would result in the *m/z* shifts in the mass spectra: 14.0156 ($+CH_3OH\text{-}H_2O$), 32.0262 ($+CH_3OH$), 46.0419 ($+2CH_3OH\text{-}H_2O$) (Bateman et al., 2008). Based on our proposed reaction pathways, we checked the presence and relative abundance of these potential reaction products (to that of our precursor, αpOS-249) in our mass spectra. At the maximum OH exposure, only a few products that could be potentially formed from the reactions of αpOS-249 with methanol were detected and they had negligible intensities (Please see the table below). This would suggest the influence of methanol is not significant on the identification of the major reaction products in our study.

Precursor		Theoretical mass	
αpOS-249, $C_{10}H_{17}O_5S^-$		249.0797	
m/z shift	Formula	Theoretical mass	Relative abundance
14.0156	$C_{11}H_{19}O_5S^-$	263.0953	0.06%
32.0262	$C_{11}H_{21}O_6S^-$	281.1059	0.09%
46.0419	$C_{12}H_{23}O_6S^-$	295.1216	0.01%

We have added the following information in the revised manuscript.

Page 8, Line 23: "We note that organic compounds such as carbonyls and carboxylic acids could undergo reactions with methanol during extraction, storage, and possibly during the electrospray process (Bateman et al., 2008). For instance, Batman et al (2008) suggested carboxylic acids could react with methanol to form esters and with carbonyls to hemiacetals and acetals. We checked the presence

and relative abundance of these potential products (to that of our precursor, αpOS-249) in our aerosol mass spectra. At the maximum OH exposure, only a few products that could be potentially formed from the reactions of αpOS-249 with methanol were detected and they had negligible intensities. This would suggest that the influence of methanol is not significant on the identification of the major reaction products."

The literature was also added into the reference list.

- Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A. and Nizkorodov, S. A.: The effect of solvent on the analysis of secondary organic aerosol using electrospray ionization mass spectrometry, Environ. Sci. Technol., 42, 7341–7346, doi:10.1021/es801226w, 2008.

Specific Comment #1:
Page 2 Line 16: Some supported references were suggested to be added here.

Author Response:
Thanks for the suggestion. We have added supported references in the manuscript and the references.
Page 2, Line 17: "Sulfur-containing aerosols are of particular significance for human health because of their high abundance and significant impacts on regional air quality and global climate (Bentley et al., 2004; Riva et al., 2015; Stadtler et al., 2018)."

Following references were also added into the references:

- Bentley, R.; Chasteen, T. G.: Environmental VOSCs – formation and degradation of dimethyl sulfide, methanethiol and related materials, Chemos., 55, 291−317, https://doi.org/10.1016/j.chemosphere.2003.12.017, 2004.
- Riva, M.; Tomaz, S.; Cui, T. Q.; Lin, Y. H.; Perraudin, E.; Gold, A.; Stone, E. A.; Villenave, E.; Surratt, J. D.: Evidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol, Environ. Sci. Technol, 49, 6654−6664, https://doi.org/10.1021/acs.est.5b00836, 2015.
- Stadtler, S.; Kühn, T.; Schröder, S.; Taraborrelli, D.; Schultz, M. G.; Kokkola, H.: Isoprene derived secondary organic aerosol in a global aerosol chemistry climate model, Geosci. Model Dev., 11, 3235−3260, https://doi.org/10.5194/gmd-11-3235-2018, 2018.

Specific Comment #2:
Page 5 Line 25: were → was

Author Response:
We have revised the sentence in the manuscript.
Page 5, Line 33: "Part of the remaining stream was introduced into a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the size distribution of the aerosols."

Specific Comment #3:
Page 18 Lines 13-14: Is it possible that inorganic sulfate was formed from the hydrolysis of organic products instead of a direct formation?

Author Response:
We agree with the reviewer that inorganic sulfate could also be generated from the hydrolysis of reaction products. This is because secondary and tertiary OS could readily undergo hydrolysis and may form upon OH oxidation based on our proposed reaction mechanisms. We have added this information in the manuscript.
Page 20, Line 22: "Furthermore, we cannot rule out the possibility of the formation of SO_4^{2-} could be from the hydrolysis of reaction products as some secondary and tertiary OS could readily undergo hydrolysis and may form upon oxidation."