Reply to Interactive comment on "Heterogeneous OH Oxidation of Isoprene Epoxydiol-Derived Organosulfates: Kinetics, Chemistry and Formation of Inorganic Sulfate" by Hoi Ki Lam et al.

Anonymous Referee #1

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-989-RC2, 2018.

In this paper the authors describe results of a laboratory study of the heterogeneous oxidation of 3-methyltetrol sulfate ester by OH radicals in aqueous aerosol particles. This compound served as a surrogate for organosulfate esters formed from particle-phase reactions of isoprene oxidation products. Understanding the atmospheric fate of these compounds is important because of their potential importance as aerosol components. The reactions were conducted in a flow tube and the concentrations of the parent compound and products were monitored using DART mass spectrometry. The rates of oxidation were quantified using relative rate methods and the measured rate constant used to estimate the lifetime of these and similar compounds in the atmosphere due to this reaction. The only major product observed was bisulfate, and a mechanism was proposed to explain its presence. The paper is clearly and concisely written and the experiments are straightforward. The interpretation is reasonable, although it is challenging to build a believable mechanism when only one of the proposed products was detected. I think the paper should be publishable after some comments are addressed, but there is clearly work to be done to provide more convincing evidence for the proposed mechanism.

We would like to sincerely thank the reviewer for his/her thoughtful comments and suggestions. Please see our responses to reviewer's comments and suggestions below.

Comment #1

Page 2, line 34: The kinetics method assumes that the particles are uniformly mixed, which is probably true here. But in the atmosphere where particles contain numerous compounds with a range of surface-active properties there will be significant inhomogeneities in surface concentrations where the OH reaction occurs, thus affecting estimated lifetimes. Some comments on this are warranted.

Author Response:

We agree with the reviewer that the chemical lifetime could be affected by surface-active compounds in the particle. If surface-active compounds are present, the chemical lifetime will likely be longer due to a lower surface concentration of parent molecules. This reduces the collision probability between gas-phase OH radicals and parent molecules at particle surface, leading to a smaller overall oxidation rate. We have added the following information in the revised manuscript.

Page 6, Line 20, "In the atmosphere where particles may contain compounds with different surface-active properties, the chemical lifetime could be affected due to the inhomogeneity in surface concentration. If surface-active compounds are present, the chemical lifetime will likely be longer due to a lower surface concentration of the parent molecules. This reduces the collision probability between gas-phase OH radicals and parent molecules at the particle surface, leading to a smaller overall oxidation rate."

Comment #2

Page 5, line 20: The authors should justify their decision to ignore decomposition of a-hydroxyperoxy radicals to carbonyl + HO_2, which is the dominant pathway in the gas phase. This should be based on kinetics arguments since the absence of product peaks in the mass spectrum could be influenced by ionization. Relevant rate constants are available [Neta et al., J. Phys. Chem. Ref. Data, 19, 413-513 (1990)].

Author Response:

Thanks for the comment. As suggested by the reviewer, the decomposition of α-hydroxylperoxy radical to carbonyl and HO_2 is a dominant pathway in gas phase. In our previous study, we have also found that this intramolecular HO_2 elimination process is an important reaction pathway during the heterogeneous OH oxidation of tartaric acid (Cheng et al., 2016). We do not include this reaction in this study because the carbonyl functionalization products have not been detected. Since the similarity in structures as compared to the parent compound (i.e. methyltetrol sulfate), we thought that the ionization issue might not be the primary reason for the absence of carbonyl products peak. However, as pointed by the reviewer, we agree that the detection of reaction products originated by the intramolecular HO_2 elimination process could be influenced by the ionization since the ionization efficiency and detection limit of the potential products are not fully understood. Further investigations on the ionization efficiency and detection limit of potential reaction products are needed to better understand the reaction pathways and the significance of the decomposition of α-hydroxyperoxy radicals through the HO_2 elimination process. In the revised manuscript, we have discussed and included this reaction pathway in the proposed reaction mechanisms in the supplementary material.

Supplementary material, Page 3, Line 27, "It is noted that decomposition of α-hydroxylperoxy radical to carbonyl and HO_2 is a dominant pathway in gas phase (Neta et al., 1990). In our previous study, we have also found that this intramolecular HO_2 elimination process is an important reaction pathway during the heterogeneous OH oxidation of tartaric acid (Cheng et al., 2016). However, the carbonyl functionalization products have not detected in the aerosol mass spectra. Given the similarity in structures as compared to the parent compound (i.e. methyltetrol sulfate), the ionization issue might not be the primary reason for the absence of carbonyl products in the mass spectra. However, further investigations on the ionization efficiency and detection limit of reaction products are needed to better understand the reaction pathways and the significance of the decomposition of α-hydroxyperoxy radicals through HO_2 elimination process during oxidation."

References

Cheng, C.T., Chan, M. N., Wilson, K.R.: Importance of unimolecular HO2 elimination in the heterogeneous OH reaction of highly oxygenated tartaric acid aerosol", J. Phy. Chem. A, 118, 28978–28992, 2016.

Neta, P., Huie, R. E., and Ross, A. B.: Rate constants for reactions of peroxyl radicals in fluid solutions, J. Phys. Chem. Ref. Data, 19, 413–513, 1990.

Comment #3

Page 6, lines 13–18: I am not yet convinced by the argument that because the authors were able to detect small organosulfates in a previous study that they would have seen them here if they were present. How sensitive is the DART method to matrix effects, concentrations, and other conditions?

Author Response:

We agree with the reviewer's concern. We acknowledge that the detection limits and possible matrix effects are not yet well understood. Further studies on the sensitivity of DART-MS to smaller organosulfates under different conditions are warranted. We have added this information in the revised manuscript.

Supplementary material, Page 2, Line 36, "In our previous study, we have demonstrated that small organosulfates, such as sodium methyl sulfate (CH_3SO_4Na) and sodium ethyl sulfate ($C_2H_5SO_4Na$), the alcohol and carbonyl functionalization products of sodium ethyl sulfate can be detected by the DART ionization source (Kwong et al., 2018). If these small organosulfates are formed in a significant amount during the oxidation of methyltetrol sulfate, the DART ionization technique will likely be able to detect them. We acknowledge that the detection limits and possible matrix effects are not yet well understood. Further studies on the sensitivity of DART-MS to smaller organosulfates under different conditions are warranted."

Comment #4

Page 7, lines 1–2 and elsewhere: Why wouldn't compounds that evaporate also be detected by DART, since the method for analyzing the particles involves first evaporating them at high temperature?

Author Response:

As mentioned in the experimental section, the volatile fragmentation products or gas-phase species were removed by an activated charcoal denuder before entering the heater as well as ionization region, leaving only the particle-phase products (see Page 3, Line 22). We have clarified this point in the revised manuscript.

Page 3, Line 22, "An annular Carulite catalyst denuder and an activated charcoal denuder were used to remove ozone and gas-phase species from the aerosol stream leaving the reactor, respectively. As a result, only particle-phase products are detected. A fraction of the aerosol stream was sampled by a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the aerosol size and number distribution. The surface-weighted diameter of the aerosols was measured to be 225.9 ± 1.4 nm before oxidation. The remaining flow was then directed into a stainless steel tube heater at 380–400°C, where the temperature and aerosol residence time in the heater were sufficient to completely vaporize the aerosols."

Technical Comments

Page 3, line 15: Should be "chromatograph".

Author Response:

We have revised the sentence.

Page 3, Line 15, "By measuring the decay of hexane using a gas chromatograph coupled with a flame ionization detector, the OH exposure, which is an integral of gas-phase OH radical concentration and reaction time, can be calculated (Smith et al., 2009):"