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 #3

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-989-RC1, 2018.

This manuscript describes the OH oxidation of small organosulfates derived from atmospheric oxidation of isoprene. Using advanced mass spectrometry of aerosol particles generated in an aerosol flow reactor, it is shown that loss of 3-methyltetrol sulfate ester is slow, with a lifetime for oxidation of more than 2 weeks under likely atmospheric conditions. This suggests that other loss processes (e.g. deposition) may be the main atmospheric loss process for similar organosulfate esters. Lack of detection of smaller oxidation products suggests formation of volatile products upon oxidation. These results are consistent with relatively high observed levels of organosulfates in atmospheric aerosol. This work is a solid contribution to the field, and I recommend this manuscript for publication pending minor revisions.

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

The experimental setup and data are fairly straightforward, generally giving clear, direct support of the key conclusion of a long atmospheric lifetime for small, oxidized organosulfates, but the detailed and long discussion of mechanistic details is not warranted. Without detection, in either gas or aerosol phase, of any reaction products other than bisulfate, the mechanistic discussion is largely speculative. Nearly all of this discussion should be removed. All reaction schemes presented should be moved to supplementary material and the mechanistic discussion must be reduced significantly. You cannot make such strong claims about a mechanism in which you more or less only observe loss of product with inability to detect products. Table 1 is the crucial result of this paper, not the speculation about the mechanism for oxidation.

Author Response:

We agree with the reviewer's comment. In the revised manuscript, we have reduced the mechanistic discussion and moved the detailed discussion and reaction schemes to the supplementary material. We also address that the reaction pathways (Schemes S1-S5) are tentatively proposed based on the observed aerosol-phase products detected by the DART. To better understand the reaction pathways, more studies are needed to characterize and quantify the reaction products in both aerosol and gas phases with different analytical techniques in order to cross check the aerosol composition data obtained by DART and verify the proposed reaction pathways in this work.

Page 5, Line 20,

" **3.3 Proposed Reaction Mechanisms**

Based on the aerosol mass spectra and well-known aerosol-phase reactions previously reported in the literature (George and Abbatt, 2010; Kroll et al., 2015), we tentatively propose reaction mechanisms for the heterogeneous OH oxidation of 3-methyltetrol sulfate ester. The reaction schemes proposed can be found in the supplementary materials (Schemes S1-S5). Briefly, potassium methyltetrol sulfate ester likely dissociates and exists in its ionic form in the droplets.

In the first oxidation step, the OH radical abstracts a hydrogen atom to form an alkyl radical which quickly reacts with oxygen to form a peroxy radical. We propose that the formation of alkoxy radical may be favored over the Russell mechanism (Russell, 1957) and Bennett–Summers reactions (Bennett and Summers, 1974) as functionalization products were not detected. Alkoxy radicals, once formed, may tend to undergo fragmentation due to the presence of vicinal hydroxyl groups, which lower the activation energy required for the decomposition of the alkoxy radicals (Cheng et al., 2015; Wiegel et al., 2015; Jimenez et al., 2009; Peeters et al., 2004; Vereecken and Peeters, 2009).

Formation of HSO_4^-. Sulfate radical anion ($SO_4^{\bullet-}$) can be formed through the decomposition of the alkoxy radical and is a strong oxidant in aqueous phase (Neta et al., 1988; Clifton and Huie, 1989; Padmaja et al., 1993). $SO_4^{\bullet-}$ can abstract a hydrogen atom from a neighboring organic molecule (e.g. unreacted 3-methyltetrol sulfate ester) to form HSO_4^- (R1) or react with particle-phase water to yield a HSO_4^- and an OH radical (R2) (Tang et al., 1988) as illustrated below. It is noted that $SO_4^{\bullet-}$ or OH radical recycled from R2 can react with 3-methyltetrol sulfate ester, contributing to the secondary chain reactions.

$$\mathrm{C_5H_{11}O_7}S^- + \mathrm{SO_4}^{\bullet-} \rightarrow \mathrm{C_5H_{10}O_7}S^{\bullet-} + \mathrm{HSO_4}^- \qquad (R1)$$

$$\mathrm{SO_4}^{\bullet-} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH}^{\bullet} + \mathrm{HSO_4}^- \qquad (R2)$$

Since 3-methyltetrol sulfate ester is unlikely to hydrolyze (Darer et al., 2011), the formation of the HSO_4^- upon OH oxidation could be best explained by the formation and subsequent reactions of $SO_4^{\bullet-}$.

Based on the proposed reaction mechanisms, the decomposition of alkoxy radicals can lead to formation fragmentation products (without sulfate group) and smaller organosulfates. We acknowledge that the ionization efficiency and detection limit of the reaction products are not fully understood. The absence of the potential products might attribute to the DART ionization and detection issues. More work is needed to investigate the formation and abundance of the reaction products formed in the aerosol and gas phases upon oxidation in order to better understand the reaction pathways. It is also noted that the formation of second or higher generation products are possible due to the high OH concentrations used in this study. While the potential secondary or higher generation products have not detected possibly due to their low concentrations and/or ionization issues, for clarify, the formation and oxidation of second or higher generation products are not further discussed."

Comment #2

You must comment on the potential for side-reactions, such as oxidation of second-generation products, due to the high OH levels used in this study.

Author Response:

We agree with the reviewer that first generation products can be further oxidized to form second or higher generation products due to the high OH levels in this study. However, the potential secondary or higher generation products have not detected possibly due to their low concentration and/or ionization efficiency. For clarity, the formation and oxidation of second or higher generation products are addressed but will not be discussed in details.

Page 6, Line 9, "It is also noted that the formation of second or higher generation products are possible due to the high OH concentrations used in this study. While the potential secondary or higher generation products have not detected possibly due to their low concentrations and/or ionization issues, for clarity, the formation and oxidation of second or higher generation products are not further discussed."

Comment #3

Supplementary materials must include a figure showing time dependent variables during an experiment including: aerosol size distributions, hexane concentration, and product signal. This may be nearly a step function, but it should be clearly shown that your system clearly responds to initiation of oxidation.

Author Response:

We would like to note that oxidation experiments were carried out in a flow tube reactor. We have measured the composition and size of the aerosols leaving the reactor before and after OH oxidation with a fixed reaction time (aerosol residence time is about 1.5 minutes in this study. Hence, the time dependent data (e.g. the time evolved data of aerosol size distributions and product signal) are not available in our study.

Comments #4

It should be noted that volatile products formed in the aerosol used here might remain in other aerosol if the Henry's law constant changes dramatically with composition, particularly if the volatile products are highly reactive with other types of aerosol species not present in your study (e.g. reactive nitrogen species). Comment on precedents available in published literature.

Author Response:

We agree with the reviewer that based on the proposed reaction mechanisms, volatile fragmentation products likely contain polar functional groups. They might partition back to the aerosols, for instance aqueous droplets because of their high water solubilities or Henry's law constants. Additionally, these fragmentation products could be reactively uptaken by the aerosols which contain reactive nitrogen or oxygen species through reactions. We have added this information in the revised manuscript.

Page 6, Line 29, "It is also noted that volatile fragmentation products likely contain polar functional groups. They may partition back to the aerosols, for instance aqueous droplets because of their high water solubilities or Henry's law constants. Additionally, they could be reactively uptaken by aerosols which contain reactive nitrogen or oxygen species through reactions."

Comments #5

Due to the open ionization region, is it possible that you lose volatile products as a result of detection method? This would mean that non-detection of products might be caused by the method of detection rather than evaporation under reasonable atmospheric conditions.

The non-detection of products (particularly from functionalization) using DART would be good information to add to the abstract.

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 2 Line 22). We have clarified this point.

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."

Comments #6

Section 3.3 This should be reduced to a single paragraph that only mentions the proposed mechanism and does not go into details concerning issues such as the sterics of the reaction intermediates.

Author Response:

The reviewer has raised the same concern in **Comment #1.** We agree with the reviewer's comment. In the revised manuscript, we have reduced mechanistic discussion and moved the reaction schemes to the supplementary materials. We also address that the reaction pathways (Schemes S1-S5) are tentatively proposed based on the observed products detected by the DART. Please see our response to **Comment #1**. We have also removed the content about the steric effects on the formation of reaction products from the Abstract.

Comments #7

Page 2, Line 2 Change to read ", the largest atmospheric source"

Author Response:

We have revised the sentence in the manuscript.

Page 2, Line 2, "Isoprene (2-methyl-1,3-butadiene, C_5H_8), emitted from terrestrial vegetation to the atmosphere, is the largest atmospheric source of non-methane volatile organic compounds."

Comments #8

Page 4, Line 6, Change to read "The hygroscpocity"

Author Response:

We have revised the sentence in the manuscript.

Page 4, Line 5, "The hygroscopicity of potassium 3-methyltetrol sulfate ester aerosols has not been experimentally determined."

Comments #9

Page 7, Line 9, Change to read "stable over its atmospheric lifetime."

Author Response:

We have revised the sentences in the manuscript.

Page 6, Line 19, "3-methyltetrol sulfate ester is potentially chemically stable over its atmospheric lifetime."

Comments #10

7,12-13 Note that this is only a likely mechanism.

In the revised manuscript, we have reduced the mechanistic discussion and do not go into detailed reaction pathways such as the steric effects of functional groups on the formation of the reaction intermediates. We have removed the sentences in the revised manuscript.

Comments #11

Figure 2 Y-axis should note m/z.

Author Response:

Figure 2 illustrates the change in ion intensity detected as a function of OH exposure while *m/z* refers to the mass-to-charge-ratio of ions detected. We have modified the caption of Figure 2.

Figure 2, "The evolution of the ion intensity of bisulfate ion (HSO_4^-) as a function of OH exposure during the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at 70.8% RH."

Comments #12

Figure 3 Y-axis should note m/z.

Author Response:

Figure 3 illustrates the parent decay, which is the ion signal of 3-methyltetrol sulfate ester at a given OH exposure divided by the ion signal of 3-methyltetrol sulfate ester before oxidation, as a function of OH exposure. Hence, there would be no unit for the parent decay.

Comments #13

Scheme 5. Only 1 pathway is shown, text seems to mention more than one.

Author Response:

Scheme S5 shows the proposed reaction pathway of methyl sulfate anion decomposing into sulfate radical anion, as an extension of both Schemes S1 and S2 (as noted in Schemes S1 and S2).