

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

Received and published: 17 December 2018

Review of “Heterogeneous OH Oxidation of Isoprene Epoxydiol-Derived Organosulfates: Kinetics, Chemistry and Formation of Inorganic Sulfate” (acp-2018-989).

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

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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.

General Comments:

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.

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.

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.

Specific Comments

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

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available in published literature.

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.

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.

Page 2, Line 2 Change to read “, the largest atmospheric source”

4,6 Change to read “The hygroscopicity”

7,9 Change to read “stable over its atmospheric lifetime.” 7, 12-13 Note that this is only a likely mechanism.

Figure 2 Y-axis should note m/z.

Figure 3 Y-axis should note m/z. Scheme 5. Only 1 pathway is shown, text seems to mention more than one.

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

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