

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

Received and published: 23 December 2018

General Comments:

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

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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.

Specific Comments:

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.

Page 5, line 20: The authors should justify their decision to ignore decomposition of a-hydroxyperoxy radicals to carbonyl + HO₂, 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)].

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?

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?

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Technical Comments:

Page 3, line 15: Should be “chromatograph”.

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