Reply to interactive comment on "Importance of Sulfate Radical Anion Formation and Chemistry in Heterogeneous OH Oxidation of Sodium Methyl Sulfate, the Smallest Organosulfate" by Kai Chung Kwong et al.

Anonymous Referee #2

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-905.

Kwong et al. present studies detailing the heterogeneous OH oxidation of sodium methyl sulfate (CH_3SO_4Na) and sodium ethyl sulfate ($C_2H_5SO_4Na$) particles. The particles were exposed to OH radicals in a well-characterized flow reactor that has been applied in many heterogeneous oxidation kinetic studies over the last 10 years or so. Ensemble aerosol mass spectra were obtained with DART. The organic sulfates were found to have effective rate constants ranging from (3.79 − 4.64) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and effective uptake coefficients ranging from 0.17 − 0.19. For both organic sulfates, HSO_4^- was detected as an oxidation product, implying the formation of aqueous sulfate radical. Proposed reaction schemes detailing functionalization and fragmentation-dominated reaction pathways are examined. Overall, the experiments seemed to have been done carefully and the results are presented concisely. However, in my opinion more effort needs to be made to place these results in atmospheric context before I could support publication in ACP.

We are grateful for the comments from the reviewer and sincerely thank him/her for suggestions. Please see our responses to the comments and suggestions below.

Major Comments:

Reviewer Comments #1

An effective OH rate constant of ~ $4*10^{-13}$ cm^3 $molec^{-1}$ s^{-1} corresponds to an OH oxidation lifetime of nearly 20 days assuming a 24-hour average OH mixing ratio of $1.5*10^6$ cm^{-3}. As far as I can tell, this timescale is too long to compete with other removal processes for organic sulfates such as wet or dry deposition. If anything, the results suggest to me that, to a first approximation, it is reasonable to treat organic sulfates as chemically stable over atmospherically relevant timescales. However, If the authors are aware of atmospheric measurements that suggest atmospheric degradation of organic sulfates, that would be a strong addition to the paper and further motivate the present work.

Author Response

We agree with the reviewer's comment. Assuming a 24-hour average OH mixing ratio of 1.5 × 10^6 cm^{-3}, the lifetime of sodium methyl sulfate against heterogeneous OH oxidation is about 20 days. This timescale is longer than other removal processes such as wet or dry deposition. To our best knowledge, laboratory studies have revealed that primary and secondary organosulfates are stable against hydrolysis under atmospheric-relevant aerosol acidities and lifetimes, while tertiary organosulfates may undergo hydrolysis efficiently (*Hu et al., 2011*). Since sodium methyl sulfate is a primary organosulfates, it is expected to be stable against hydrolysis. These results suggest that sodium methyl sulfate is likely chemically stable over atmospherically relevant timescales. We would also like to note that studying the heterogeneous reactivity of sodium methyl sulfate towards OH radicals provides a much needed fundamental understanding of the oxidation kinetics and pathways, and these data may be applied in the interpretation of the oxidation of more complex organosulfates, which may have a range of chemical lifetimes in the atmosphere. This information is added in the revised manuscript.

Page 5, Lines 13-21
"Assuming a 24-hour average OH concentration of 1.5×10^{6} cm^{-3}, the lifetime of sodium methyl sulfate against heterogeneous OH oxidation is about 20 days. This timescale is longer than other removal processes such as wet or dry deposition. Laboratory studies have revealed that primary and secondary organosulfates are stable against hydrolysis under atmospheric relevant aerosol acidities and lifetimes, while tertiary organosulfates may undergo hydrolysis efficiently (*Hu et al., 2011*). Since sodium methyl sulfate is a primary organosulfate, it is expected to be stable against hydrolysis. These results suggest that sodium methyl sulfate is likely chemically stable over atmospherically relevant timescales. Studying the heterogeneous reactivity of sodium methyl sulfate towards OH radicals provides a much needed fundamental understanding of the oxidation kinetics and pathways, and these data may be applied in the interpretation of the oxidation of more complex organosulfates, which may have a range of chemical lifetimes in the atmosphere."

Reviewer Comments #2

The authors propose that sulfate radicals generated from OH oxidation of organic sulfates could contribute to secondary condensed-phase chemistry, but the relevant oxidation timescales are not discussed. They state that sulfate rate constants range from $10^{6} - 10^{9}$ M^{-1} s^{-1}*, and imply that because these are comparable to OH rate constants (*10^{7} *to* 10^{11} M^{-1} s^{-1}*), secondary sulfate chemistry might be important. I disagree with this conclusion because this cited range of sulfate rate constants is one to two orders' magnitude lower than OH rate constants. Furthermore, it is not appropriate to make this conclusion without citing corresponding ranges of condensed phase sulfate vs OH radical concentrations, and calculating the corresponding oxidation lifetimes with respect to sulfate radicals vs OH radicals. If the authors are aware of atmospheric measurements that suggest influence of sulfate radical-initiated oxidation chemistry, that would be a strong addition to the paper and further motivate the present work.*

Author Response

We would like to thank the reviewer's comment and agree that the reported $SO_4^{\bullet-}$ rate constants and

OH rate constants are not comparable. In the literature, the typical aqueous phase radical concentration of OH and $SO_4^{\bullet-}$ are of 10^{-13} M and 10^{-14} M, respectively (*Lelieveld and Crutzen, 1991; Herrmann et al., 2000*). With the reported OH rate constants (10^7 – 10^{11} M^{-1} s^{-1}) and $SO_4^{\bullet-}$ rate constants (10^6 – 10^9 M^{-1} s^{-1}), the calculated lifetime toward aqueous phase oxidation with OH and $SO_4^{\bullet-}$ is about 2 minutes – 12 days and 1.2 days – 3 years, respectively. These results suggest that aqueous phase OH radical reactions with organic compounds are likely the dominant reaction pathways. Some organic compounds (e.g. alkanes and alkenes) are stable against $SO_4^{\bullet-}$ initiated oxidation, but some (e.g. alcohols and ethers) react with $SO_4^{\bullet-}$ at atmospherically relevant timescale. We would like to note that $SO_4^{\bullet-}$ reaction rate with sodium methyl sulfate is not known. Future works are needed to better understand the role of the $SO_4^{\bullet-}$ initiated oxidation chemistry in chemical transformation of sodium methyl sulfate and organic compounds in the atmospheric aerosols. We have clarified this point in the revised manuscript.

Page 7, Lines 20-26
"The second-order rate constants for $SO_4^{\bullet-}$ reactions with alcohols, ethers, alkanes, and aromatic compounds typically range in value from 10^6 to 10^9 M^{-1} s^{-1} (*Clifton and Huie, 1989; Neta et al., 1977; Neta et al., 1988; Padmaja et al., 1993*). With an aqueous phase $SO_4^{\bullet-}$ concentration of 10^{-14} M (*Herrmann et al., 2000*), the calculated lifetime toward aqueous phase oxidation with $SO_4^{\bullet-}$ ranges from 1.2 days to 3 years. These results suggest that some organic compounds (e.g. alkanes and alkenes) are stable against $SO_4^{\bullet-}$ initiated reactions, but some (e.g. alcohols and ethers) can react with $SO_4^{\bullet-}$ efficiently. Future works are needed to better understand the role of $SO_4^{\bullet-}$ initiated oxidation chemistry in chemical transformation of sodium methyl sulfate and organic compounds in the atmospheric aerosols."

Minor Comments:

Reviewer Comments #3

I did not notice discussion of control experiments detailing exposure to ozone or 254 nm photons to rule out the contributions of ozonolysis or photolysis to the degradation of organic sulfates.

Author Response

We have run control experiments to investigate the potential volatilization of parent compound (i.e. sodium methyl sulfate) and the effects of ozone and UV light on the composition of the aerosols before oxidation under the same experimental conditions. We found that there is no change in aerosol mass spectra in the presence of ozone without the UV light, suggesting that the reaction of sodium methyl sulfate with ozone is not significant. The aerosol mass spectrum is about the same as that obtained in the absence of ozone with the UV light, suggesting that the photolysis of sodium methyl sulfate aerosols is not likely. We have added this information in the revised manuscript.

Page 4, Lines 18-26

"We have run control experiments to investigate the potential volatilization of parent compound (i.e. sodium methyl sulfate), and the effects of ozone and UV light on the composition of the aerosols before oxidation under the same experimental conditions. To investigate the volatilization of sodium methyl sulfate, we have measured the mass spectrum by filtering out the aerosols, and the parent peak is very small, suggesting there is very small amount of sodium methyl sulfate present in the gas phase. Volatilization and gas-phase oxidation of sodium methyl sulfate is expected to be not significant. For the effect of ozone and UV light, we found that there is no change in aerosol mass spectra in the presence of ozone without the UV light, suggesting that the reaction of sodium methyl sulfate with ozone is not significant. The aerosol mass spectrum is about the same as that obtained in the absence of ozone with the UV light, suggesting that the photolysis of sodium methyl sulfate aerosols is not likely to occur."

Reviewer Comments #4

A short description of the DART technique should be added to the experimental section for readers that are not familiar with the method (including this reviewer).

Author Response

We have added a brief description of DART in the revised manuscript.

Page 4, Lines 8-16

"The details of the DART operation have been described elsewhere (*Cody et al., 2005*). The DART ionization source was operated in the negative-ion mode. Helium was chosen as the ionizing gas and entered an ionization chamber, where a high electric potential of 4 kV was applied. This generates a glow discharge containing ions, electrons, and metastable helium atoms. A potential of 200 V was applied to two electrostatic lenses to remove ions and only the metastable helium atoms exited the chamber. The gas stream was heated to 500 ℃ before leaving the ionization source. The metastable helium atoms are responsible for ionizing the gas-phase species in the ionization region (*Chan et al., 2014; Cheng et al., 2015, 2016*). For ionic compounds like sodium methyl sulfate, negative ions can be formed via direct ionization in the negative ion mode (*Hajslova et al., 2011*); for instance, pyruvate ions have been detected from ammonium pyruvate using the DART (*Block et al., 2010*)."

Reviewer Comments #5

*P3, L17: I calculate that a vapor pressure of 0.0465 torr corresponds to a saturation concentration of 3.3E5 ug/m^3 at 20 deg C and 1 atm. If that vapor pressure is accurate, this statement is likely not true: "volatilization and gas-phase oxidation of sodium methyl sulfate are expected to be insignificant in these experiments." (The range of mass concentration is not provided, but I am assuming it is far less than 3*10^5 ug/m3, although this should be clarified). Some other more* *plausible evidence is needed to support the claim that volatilization/gas-phase oxidation is unimportant.*

Author Response

We agree with reviewer's comment and would like to note that the other two reviewers have raised the same comment on the potential volatilization and gas phase oxidation of sodium methyl sulfate (reviewer 1, comments #2 and reviewer 3, comments # 4). To be concise and address the volatility issue clearly once in the response, please kindly refer to our response to reviewer 1 (reviewer 1, comments #2) on this topic.

Reviewer Comments #6

P3, L30: Please clarify how the was the residence time of 1.3 min was determined, i.e., calculated from reactor volume and flow rate or obtained from a measured residence time distribution.

Author Response

We obtained this value from measured aerosol residence time distribution.

Reviewer Comments #7

P5, L13: typo ("occur" → "occurring")

Author Response

Thank you for pointing out the typo. We have revised the sentence.

Page 6, Lines 4-6

"Using **Eqn. 3**, the γ_{eff} is calculated to be 0.17 ± 0.03. Although the γ_{eff} is less than 1, as will be discussed in the section 3.3, secondary reactions are likely occurring, leading to the formation and subsequent reactions of sulfate radical anions ($SO_4^{\bullet-}$)."

Reviewer Comments #8

P6, L23: change "have an order of magnitude ranging" to "values"

Author Response

Thank you for the suggestion. We have revised the sentence.

Page 7, Lines 20-22

"The second-order rate constants for $SO_4^{\bullet-}$ reactions with alcohol, ethers, alkanes, and aromatic compounds typically range in value from 10^6 to 10^9 M^{-1} s^{-1} (*Clifton and Huie, 1989; Neta et al., 1977; Neta et al., 1988; Padmaja et al., 1993*)."

Reviewer Comments #9

Figures 1 and 5, 2 and 8, 3 and 6, and 4 and 9, and corresponding discussion, could easily be merged/consolidated to decrease the number of figures.

Author Response

We would like to thank the reviewer's suggestion but would like to keep the figures and corresponding discussion separately for the following reasons. First, we would like to focus the discussion on sodium methyl sulfate, which is the smallest organosulfate detected in atmospheric aerosols (as sodium ethyl sulfate has not been found in the atmosphere). Second, the results of sodium ethyl sulfate are primarily used to confirm the detectability of functionalization products using the DART ionization source coupled with a high-resolution mass spectrometer. Third, as the ionization efficiency and the relative abundance of two alkyl sulfates and their reaction products are not known, we would like to present the results of these two organosulfates in separate figures.

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