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 #1

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

This is an interesting manuscript describing the formation of sulfate radical anions through heterogeneous oxidation and transformation of selected organosulfate model compounds (sodium methyl sulfate and sodium ethyl sulfate). The authors reported kinetics and mass spectrometric data to explain the potential chemical mechanisms for the observed composition change. Overall, this manuscript is concise and well written, and provides useful information for a better understanding of the chemical evolution of particle phase products that is thus far not very well understood. These findings are of great interest to the atmospheric chemistry community. I am in support of publication after the following comments being addressed in the revised manuscript.

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

<u>General Comments:</u>

Reviewer Comments #1

Have the authors observed any evidence for hydrolysis of organosulfates without OH exposures? Could the presence of bisulfate be also resulting from the acid-base equilibrium of sulfate ions in the aqueous droplet (via water dissociation) without radicals involved?

Author Response

In the literature, Hu et al. (2011) have investigated the thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates. They found that primary and secondary organosulfates are stable against hydrolysis under atmospherically relevant aerosol acidities and lifetimes, while tertiary organosulfates may undergo hydrolysis efficiently. Since the sodium methyl sulfate and sodium ethyl sulfate are primary organosulfates, we expect the hydrolysis would not be significant in our experiments and bisulfate is not likely originated from the acid-base equilibrium of sulfate ions in the aqueous droplet (via water dissociation).

Reviewer Comments #2

Page 3, Line 17: the estimated vapor pressure for sodium methyl sulfate is actually not low enough that can be considered as insignificant. Please provide more support to justify this statement. In *addition, is there any evidence showing that this compound may be present in the gas phase?*

Author Response

We agree with reviewer's comment. To our best knowledge, the vapor pressure of sodium methyl sulfate has not been experimentally measured. We would like to acknowledge that the value reported in the original manuscript is estimated using a model developed by the United States Environmental Protection Agency. In addition to heterogeneous OH oxidation experiments, 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 sodium methyl sulfate 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. As shown in the mass spectrum below (**Figure S1**), the parent peak is very small and is about 20 times less than that obtained before oxidation (**Figure 1**).

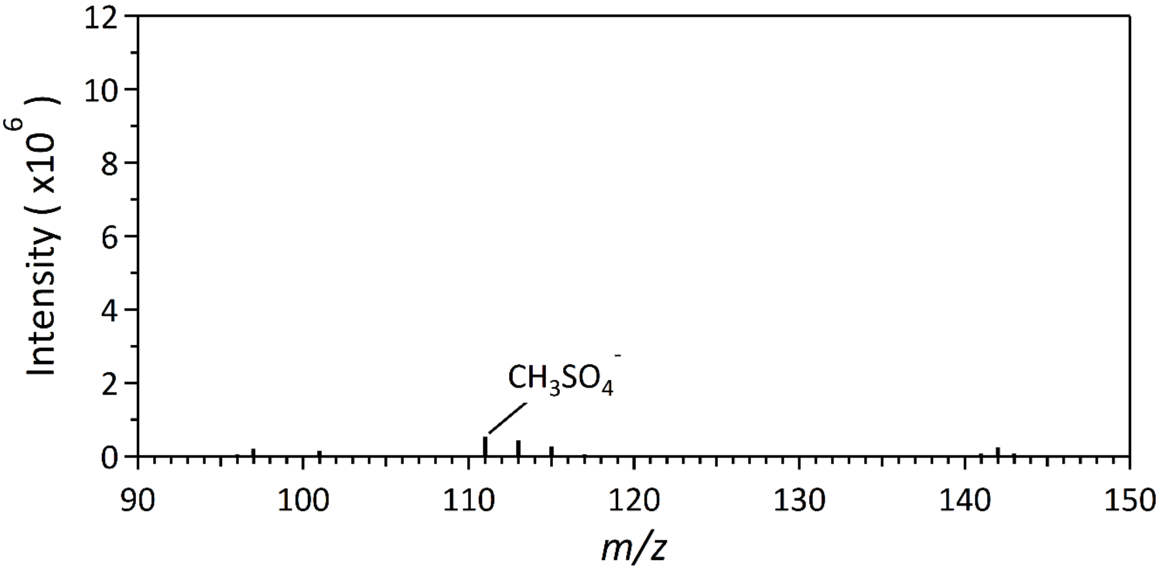


Figure S1. Mass spectrum without sodium methyl sulfate aerosols.

This suggests that there is insignificant amount of sodium methyl sulfate present in the gas phase. We would also like to mention that organosulfates and their salts are in general considered to have low volatilities and have not been detected in the gas phase in field studies. These results suggest that volatilization and gas phase oxidation of sodium methyl sulfate is not significant. To avoid confusion, we have removed the estimated vapor pressure of sodium methyl sulfate. We have added the following information in the revised manuscript to show that volatilization and gas phase oxidation of sodium methyl sulfate is likely not significant in this study.

Page 4, Lines 18-22

"We have run control experiments to investigate the potential volatilization of parent compound (i.e. sodium methyl sulfate), and the effect 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."

Reviewer Comments #3

Page 6, Lines 13-14: what are the bond dissociation energies for the C−O versus C−C bonds, respectively?

Author Response

We would like to acknowledge that the dissociation energies for C−O and C−C bonds of sodium methyl sulfate are not known. However, the dissociation energy of C−O bond is in general thought to be smaller than that of C−C bond (*Dean and Lang, 1992*). We have clarified this point in the revised manuscript.

Page 7, Lines 7-10

"Although the dissociation energies for C−O and C−C bonds of sodium methyl sulfate are not known, fragmentation processes could be enhanced since the decomposition of the alkoxy radical involves the cleavage of a C−O bond, which is in general thought to be weaker than a C−C bond (*Dean and Lang, 1992*)."

Reviewer Comments #4

Page 6, Lines 14-15: please provide more detailed explanation about why the authors think the bond dissociation energy of a C−O bond is likely to be lowered in the presence of a sulfur atom (C−O−S).

Author Response

Oae and Doi (1991) and Dean and Lange (1992) have reported that dissociation energies for different kinds of bonds and show the following trend: C−C > C−OC > C−SC > C−OS. The bond dissociation energy of a C−O bond is smaller in the presence of a sulfur atom or sulfur-oxygen bearing group compared to a carbon atom (C−OC > C−OS). One possible explanation is that sulfur atom or sulfur-oxygen bearing group (e.g. sulfate) is more electronegative than a carbon atom, reducing the electron density and bond strength of the C−O bond by inductive effect. We acknowledge that further investigation is required to better understand the effect of sulfate group on the dissociation energies of C−O bond for the sodium methyl sulfate. We have revised the sentences in the revised manuscript to reflect the unknown effect of sulfate group on the decomposition of the C−O bond in the sodium methyl sulfate.

Page 7, Lines 10-14

"The bond dissociation energy of a C−O bond might be lowered in the presence of a sulfur atom or sulfur-oxygen bearing group (*Oae and Doi, 1991; Dean and Lange, 1992*). One possibility is that sulfur atom or sulfur-oxygen bearing group (e.g. sulfate) is more electronegative than a carbon atom, reducing the electron density and bond strength of the C−O bond by inductive effect. Further investigation is required to better understand the effect of sulfate group on the dissociation energies of the C−O bond for the sodium methyl sulfate."

Reviewer Comments #5

Page 6, Line 23: "…… typically have an order of magnitude ranging from ……" This sentence reads incomplete. Please double check if something is missing.

Author Response

We have revised the sentence.

Page 7, Lines 20-22

"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*)."

Reviewer Comments #6

Page 6, Line 27: the acid dissociation constant (K_a) of the bisulfate ion is 1.2×10^{-2}. The authors might report this as "pK_a" by mistake.

Author Response

Thank you for pointing out the typo. We have corrected it in the revised manuscript.

Page 7, Lines 26-29

"For the OH reaction with sodium methyl sulfate, it is proposed that sulfate radical anion, once formed, can abstract a hydrogen atom from the neighboring, unreacted sodium methyl sulfate, yielding the bisulfate ion, which has a small acid dissociation constant in equilibrium with sulfate (SO_4^{2-}) and hydrogen (H^+) ions ($K_a = 1.2 \times 10^{-2}$) (*Brown et al., 2012*)."

References

Dean, J. and Lange, N.: Lange's handbook of chemistry (15th Edition). *New York: McGraw-Hill,* 4.42−4.43, **1992**.

Hu, K. S., Darer, A. I., Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, *Atmos. Chem. Phys.*, 11, 8307−8320, **2011**.

Oae, S. and Doi, J.: Organic Sulfur Chemistry: Structure and Mechanism, *CRC Press: Boca Raton, Florida*, **1991**.

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.

References

Block, E., Dane, A. J., Thomas, S., Cody, R. B.: Applications of Direct Analysis in Real Time Mass Spectrometry (DART-MS) in Allium Chemistry. 2-Propenesulfenic and 2-Propenesulfinic Acids, Diallyl Trisulfane S-Oxide, and Other Reactive Sulfur Compounds from Crushed Garlic and Other Alliums, *J. Agric. Food Chem.*, 58(8), 4617−4625, **2010**.

Chan, M. N., Zhang, H., Goldstein, A. H., Wilson, K. R.: The Role of Water and Phase in the Heterogeneous Oxidation of Solid and Aqueous Succinic Acid Aerosol by Hydroxyl Radicals, *J. Phys. Chem. C*, 118(50), 28978–28992, **2014**.

Cheng, C. T., Chan, M. N., Wilson, K. R.: The Role of Alkoxy Radicals in the Heterogeneous Reaction of Two Structural Isomers of Dimethylsuccinic Acid, *Phys. Chem. Chem. Phys.*, 17(38), 25309–25321, **2015**.

Cheng, C. T., Chan, M. N., Wilson, K. R.: Importance of Unimolecular HO_2 Elimination in the Heterogeneous OH Reaction of Highly Oxygenated Tartaric Acid Aerosol, *J. Phys. Chem. A*, 120(29), 5887–5896, **2016**.

Cody, R. B., Laramee, J. A., Durst, H. D.: Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions, *Anal. Chem.*, 77 (8), 2297−2302, **2005**.

Hajslova, J., Cajka, T., Vaclavik, L.: Challenging Applications Offered by Direct Analysis in Real Time (DART) in Food-Quality and Safety Analysis, Trends Anal. Chem., 30(2), 204−218, 2011.
Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P., Zellner, R.: CAPRAM2.3: A

Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, *J. Atmos. Chem.*, 36, 231−284, **2000**.

Hu, K. S., Darer, A. I., Elrod, M. J.: Thermodynamics and Kinetics of the Hydrolysis of Atmospherically Relevant Organonitrates and Organosulfates, *Atmos. Chem. Phys.*, 11, 8307−8320, **2011**.

Lelieveld, J., Crutzen, P. J.: The Role of Clouds in Tropospheric Photochemistry, *J. Atmos. Chem.*, 12, 229−267, **1991**.

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 #3

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

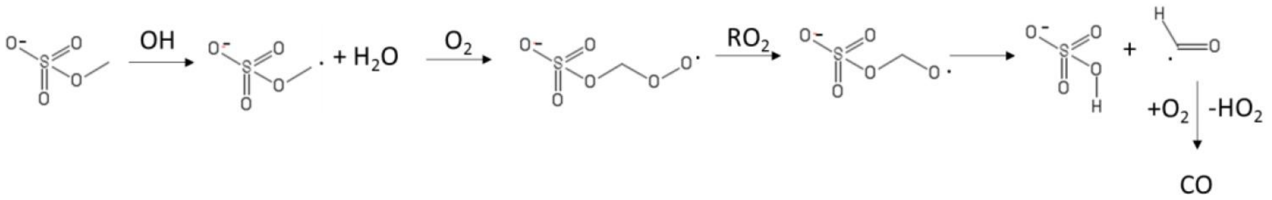
In this paper, titled “Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate” by Kwong et al., the authors present an interesting dataset focused on the heterogeneous chemical transformation of an organic sulfate compound. Organosulfates often have low saturation vapor pressure and have been identified in ambient aerosol particles, and therefore are considered important for SOA formation in the atmosphere. However, there is currently very little knowledge of the particle phase transformations of organosulfates, which could be important because variations in the organosulfate composition may influence particle volatility and SOA mass. Therefore, the topic is very much atmospherically relevant and suitable for Atmospheric Chemistry and Physics. The authors’ main finding is that OH oxidation primarily leads to bisulfate ion formation, and propose an H-atom abstraction pathway by the sulfate radical anion. The chemistry is plausible, but as described in my first comment, the authors could have discussed other mechanisms. In general, I think the manuscript is well written and should be published after addressing my comments.

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

The authors propose that bisulfate ion formation is primarily due to sulfate ion abstraction of hydrogen. First, it would help if the authors included a reaction mechanism in addition to the mechanisms shown in Scheme 1 and Scheme 2, showing the different products formed after hydrogen abstraction by the sulfate ion. However, in analogy to the OH-initiated oxidation of simple alkyl esters (see e.g., Sun et al., 2012), instead of H-atom abstraction by sulfate ion, might there be rearrangement of the hydrogen atom from the alkoxy radical carbon to the oxygen on the methoxy group, and decomposition of the O−C bond from the methoxy group to make formyl radical (HCO)? Subsequent reactions involving HCO would form CO and could explain the absence of additional products, besides HSO_4^-*, after oxidation of sodium methyl sulfate.*



Author Response

We agree with the reviewer’s suggestion on the reaction mechanisms for the OH oxidation of sodium methyl sulfate and the formation of bisulfate ion. This proposed mechanism is discussed in the main text and presented in the **Scheme 1** in the revised manuscript.

Page 6, Lines 18-21

“Alternatively, the decomposition of the alkoxy radical, in analogy to the OH radical-initiated oxidation of simple alkyl esters (*Sun et al., 2012*), could involve the rearrangement of the hydrogen atom from the alkoxy radical carbon to the oxygen on the methoxy group. The decomposition of the C−O bond from the methoxy group generates a bisulfate ion and a formyl radical (CHO). The subsequent reactions of the formyl radical can yield a carbon monoxide (CO) and HO_2. Like formaldehyde, carbon monoxide is volatile and partitions back to the gas phase.”

Reviewer Comments #2

These experiments were conducted in the absence of NO_x*, which may be more relevant for pristine, low NOx environments. Could the authors place this chemistry in context with varying ratios of* NO_x *and* RO_2*? How might the schemes differ under high/low NO?*

Author Response

We postulate that under high NOx environment (i.e. high NO), RO_2 + NO reactions might become more favorable compared to RO_2 + RO_2 reactions. Alkoxy radicals are more likely formed from the RO_2 + NO reactions and subsequently decompose to yield the volatile products (formaldehyde and carbon monoxide), sulfate radicals, and bisulfate ions as proposed in **Scheme 1**. Generally, the increase in NOx concentration likely favors the formation and decomposition of alkoxy radicals during the oxidation.

<u>Minor Comments:</u>

Reviewer Comments #3

The manuscript discussion seems equally focused on sodium methyl sulfate and sodium ethyl sulfate. The authors might think of including both in the title.

Author Response

We would like to thank the reviewer’s suggestion. We decide to keep the title unchanged because we would like to focus the discussion on the heterogeneous OH oxidation of sodium methyl sulfate, which has been detected in atmospheric aerosols (*Hettiyadura et al., 2015*).

Reviewer Comments #4

Section 2 (lines 17-19): I am not convinced that the following statement is true, "The sodium methyl sulfate has a low estimated vapor pressure of 4.65 × 10^{-2} mmHg (Chemistry Dashboard), and therefore, volatilization and gas-phase oxidation of sodium methyl sulfate are expected to be insignificant in these experiments." Such a vapor pressure is ~ 60 ppm. The authors should clarify that if gas phase oxidation takes place, what effect it could have on the results?

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 2, comments # 5). 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 #5

What potential effects are there, if any, from the exposure of sodium methyl sulfate to ozone and UV light from the O3 lamp?

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.

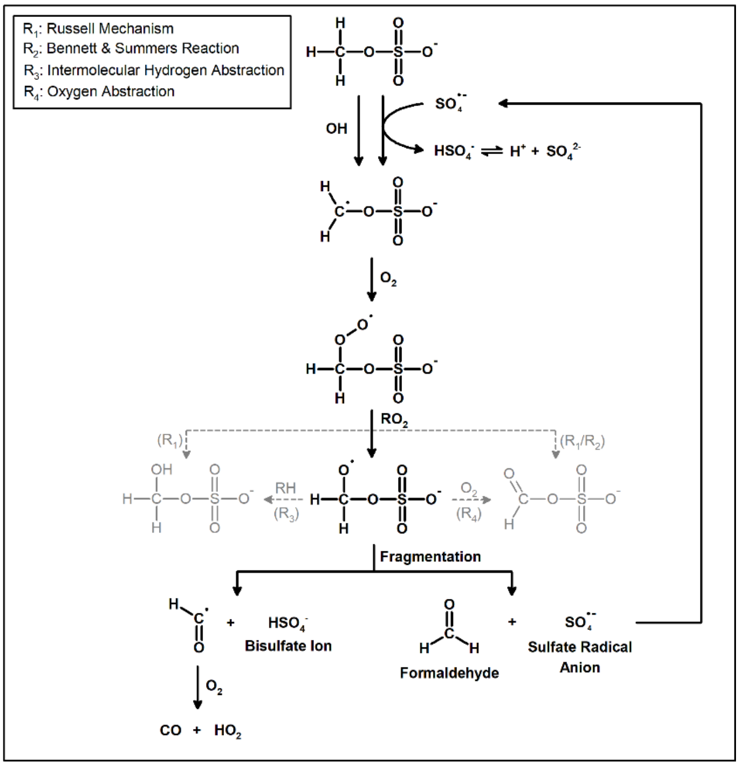
Page 4, Lines 18-26

"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.”

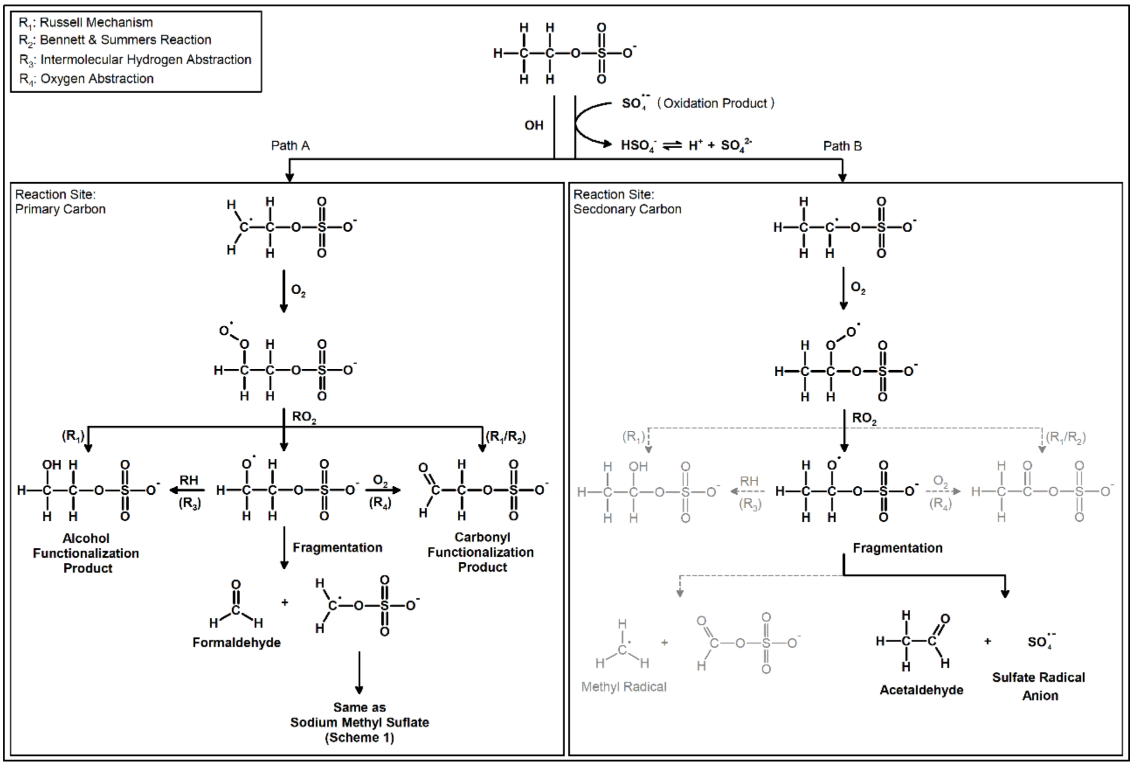
References

Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., Humphry, T.: Determination of Atmospheric Organosulfates using HILIC Chromatography with MS Detection, *Atmos. Meas. Tech.*, 8(6), 2347−2358, **2015**.

Sun, X., Hu, Y., Xu, F., Zhang, Q., Wang, W.: Mechanism and Kinetic Studies for OH Radical-initiated Atmospheric Oxidation of Methyl Propionate, *Atmos. Environ.*, 63, 14−21, **2012**.



Scheme 1. Proposed reaction mechanism for heterogeneous OH oxidation of sodium methyl sulfate (Gray arrows denote the minor pathways)



Scheme 2. Proposed reaction mechanism of heterogeneous OH oxidation of sodium ethyl sulfate (Gray arrows denote the minor pathways)

Importance of Sulfate Radical Anion Formation and Chemistry in Heterogeneous OH Oxidation of Sodium Methyl Sulfate, the Smallest Organosulfate

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Abstract. Organosulfates are important organosulfur compounds present in atmospheric particles. While the abundance, composition, and formation mechanisms of organosulfates have been extensively investigated, it remains unclear how they transform and evolve throughout their atmospheric lifetime. To acquire a fundamental understanding of how organosulfates chemically transform in the atmosphere, this work investigates the heterogeneous OH radical-initiated oxidation of sodium methyl sulfate (CH_3SO_4Na) droplets, the smallest organosulfate detected in atmospheric particles, using an aerosol flow tube reactor at a high relative humidity of 85 %. Aerosol mass spectra measured by a soft atmospheric pressure ionization source (Direct Analysis in Real Time, DART) coupled with a high-resolution mass spectrometer showed that neither functionalization nor fragmentation products are detected. Instead, the ion signal intensity of the bisulfate ion (HSO_4^-) has been found to increase significantly after OH oxidation. We postulate that sodium methyl sulfate tends to fragment into a formaldehyde (CH_2O) and a sulfate radical anion ($SO_4^{\bullet-}$) upon OH oxidation. The formaldehyde is likely partitioned back to the gas phase due to its high volatility. The sulfate radical anion, similar to OH radical, can abstract a hydrogen atom from neighboring sodium methyl sulfate to form the bisulfate ion, contributing to the secondary chemistry. Kinetic measurements show that the heterogeneous OH reaction rate constant, k, is $(3.79 \pm 0.19) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} with an effective OH uptake coefficient, γ_{eff}, of 0.17 ± 0.03. While about 40 % of sodium methyl sulfate is being oxidized at the maximum OH exposure (1.27×10^{12} molecule cm^{-3} s), only a 3 % decrease in particle diameter is observed. This can be attributed to a small fraction of particle mass lost via the formation and volatilization of formaldehyde. Overall, we firstly demonstrate that the heterogeneous OH oxidation of an organosulfate can lead to the formation of sulfate radical anion and produce inorganic sulfate. Fragmentation processes and sulfate radical anion chemistry play a key role in determining the compositional evolution of sodium methyl sulfate during heterogeneous OH oxidation.

1 Introduction

Organosulfur compounds have been found to contribute a significant mass fraction of atmospheric organic compounds. A maximum organosulfur contribution of 30 % to PM_{10} organic mass was estimated at a forest site in Hungary by calculating the difference between total sulfur and inorganic sulfate (*Surratt et al., 2008*). Using a similar approach, Tolocka and Turpin (2012) estimated that organosulfur compounds contribute up to 5 – 10 % of the total organic mass in southeastern United States, while Shakya and Peltier (2013) reported that organosulfur compounds account for about 1 – 2 % of organic carbon in Fairbanks, Alaska. Given their high atmospheric abundances, it is crucial to understand the composition, formation, and transformation of organosulfur compounds in the atmosphere.

Organosulfates have been identified as one of the major organosulfur compounds. The detection of organosulfates in laboratory studies have been complemented by a number of field observations, which confirm the presence of organosulfates in atmospheric particles (*Budisulistiorini et al., 2015; Chan et al., 2010; Darer et al., 2011; Frossard et al., 2011; Froyd et al., 2010; Hawkins et al., 2010; Hettiyadura et al., 2015; Huang et al., 2015; Iinuma et al., 2007; Kuang et al., 2016; Olson et al., 2011; Rattanavaraha et al., 2016; Riva et al., 2016; Shakya and Peltier, 2013; Stone et al., 2012; Surratt et al., 2007, 2008, 2010*). Various possible reaction pathways by which organosulfates form have been suggested. For instance, Iinuma et al. (2009) and Surratt et al. (2010) showed that organosulfates can be effectively formed via the reactive uptake of gas-phase epoxides, which are formed from the photooxidation of various biogenic volatile organic compounds (e.g. isoprene, α-pinene, and β-pinene), onto the acidic sulfate seed particles. Rudziński et al. (2009) and Nozière et al. (2010) suggested that the reactions between sulfate radical anion and reaction products of isoprene (e.g. methyl vinyl ketone and methacrolein) can yield a variety of organosulfates.

While the abundance, composition, and formation mechanisms have extensively been investigated, there is comparably little work understanding how organosulfates chemically transform in the atmosphere. Organosulfates are primarily present in the particle phase owing to their low volatility (*Huang et al., 2015; Estillore et al., 2016*). They can continuously react with gas-phase oxidants such as hydroxyl (OH) radicals, ozone (O_3), and nitrate (NO_3) radicals at or near the particle surface throughout their atmospheric lifetime. These heterogeneous oxidative processes have been found to change the size, composition, and physiochemical properties of both laboratory-generated organic particles and atmospheric particles (*Rudich et al., 2007; George and Abbatt, 2010; Kroll et al., 2015*). To gain a better understanding of how organosulfates chemically transform through heterogeneous oxidation in the atmosphere, this work investigates the heterogeneous OH radical-initiated oxidation of sodium methyl sulfate (CH_3SO_4Na) particles, the smallest organosulfate detected in atmospheric particles, using an aerosol flow tube reactor at a high relative humidity (RH) of 85 %. A soft atmospheric pressure ionization source (Direct Analysis in Real Time, DART) coupled with a high-resolution mass spectrometer was employed to characterize the molecular composition of the particles before and after OH oxidation in real time. Sodium methyl sulfate is detected in atmospheric particles with a concentration of 0.7 ng m^{-3} and 0.34 ng m^{-3} during daytime and nighttime, respectively in Centreville, Alabama (*Hettiyadura et al., 2015*). As shown in **Table 1**, the simple structure of sodium methyl sulfate allows us to gain a more fundamental understanding of the heterogeneous ~~oxidative~~ oxidation kinetics and chemistry. The sodium salt of methyl sulfate could be considered as atmospherically relevant since a positive correlation between sodium ion and organosulfates has been observed over the coastal areas (S*orooshian et al., 2015; Estillore et al., 2016*). The effects of salt (e.g. ammonium and potassium salt) on the heterogeneous oxidative kinetics and chemistry is also of atmospheric significance and warrants future study.

2 Experimental Method

An atmospheric pressure aerosol flow tube reactor was used to investigate the heterogeneous OH oxidation of sodium methyl sulfate droplets. Detail experimental procedures have been described previously (*Davies and Wilson, 2015; Chim et al., 2017*). Briefly, aqueous droplets were generated by a constant output atomizer, and mixed with humidified nitrogen (N_2), oxygen (O_2), ozone (O_3), and hexane (a gas-phase OH tracer) before introducing into the reactor. The RH inside the reactor was maintained at 85 % and at a temperature of 20 ˚C. Estillore et al. (2016) measured the hygroscopicity of sodium methyl sulfate particles and showed that the particles absorb or desorb water reversibly upon increasing or decreasing RH. These observations suggest that the particles likely exist as aqueous droplets over a range of RH (10 to 90 %). In our experiments, since the sodium methyl sulfate droplets are always exposed to a high RH, they are likely aqueous droplets prior to OH oxidation. ~~The sodium methyl sulfate has a low estimated vapor pressure of 4.65 × 10^{-2} mmHg (*Chemistry Dashboard*), and therefore, volatilization and gas-phase oxidation of sodium methyl sulfate are expected to be insignificant in these experiments.~~

Sodium methyl sulfate droplets were oxidized inside the reactor by gas-phase OH radicals that were generated by the photolysis of O_3 under ultraviolet light (254 nm) illumination in the presence of water vapor. The OH concentration was regulated by changing the O_3 concentration and determined by measuring the decay of hexane using gas chromatography coupled with a flame ionization detector. The OH exposure, defined as the product of OH concentration, [*OH*], and the particle residence time, *t*, was determined by measuring the decay of the gas-phase tracer, hexane (*Smith et al., 2009*).

$$OH\ Exposure = -\frac{ln([Hex]/[Hex]_0)}{k_{Hex}} = \int_o^t [OH]dt \qquad (1)$$

where [*Hex*] is the hexane concentration leaving the reactor, $[Hex]_0$ is the initial hexane concentration and k_{Hex} is the second order rate constant of the gas-phase OH-hexane reaction. The aerosol residence time was determined to be 1.3 minutes, and the OH exposure was varied from 0 to 1.27 × 10^{12} molecule cm^{-3} s. The particle stream leaving the reactor was passed through an annular Carulite catalyst denuder and an activated charcoal denuder to remove O_3 and gas-phase species, respectively.

A portion of the particle stream was sampled by a scanning mobility particle sizer (SMPS) for particle size distribution measurements. The remaining flow was delivered into a stainless-steel tube heater, where the particles were vaporized at 350 – 400 ˚C. Sodium methyl sulfate particles were confirmed to be fully vaporized upon heating at 300 ˚C or above by measuring the size distribution of the particles leaving the heater with the SMPS in a separate experiment. The resulting gas-phase species were directed to an ionization region, a narrow open space between the DART ionization source (IonSense: DART SVP), and the inlet orifice of the high-resolution mass spectrometer (ThermoFisher, Q Exactive Orbitrap).

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 °C 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*).

We have run control experiments to investigate the potential volatilization of parent compound (i.e. sodium methyl sulfate), and the effect 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.

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3 Results and Discussions

3.1 Aerosol Mass Spectra

Figure 1 shows the aerosol mass spectra before and after oxidation. Before oxidation (**Figure 1a**), there is one major peak and some minor background peaks. The largest peak at *m/z* 111 has a chemical formula of $CH_3SO_4^-$, which is corresponding to the negative ion (i.e. anionic form) of sodium methyl sulfate. For ionic compounds, 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 the ammonium pyruvate using the DART (*Block et al., 2010*). **Figure 1b** shows that the intensity of the parent compound decreases after oxidation. At the maximum OH exposure (1.27×10^{12} molecule cm^{-3} s), only one new peak at *m/z* 97 evolves, corresponding to the bisulfate ion (HSO_4^-). As shown in **Figure 2**, its intensity increases significantly after oxidation, suggesting that the bisulfate ion is likely generated during the oxidation. Based on the aerosol speciation data measured at different extents of OH oxidation, oxidation kinetics will be determined in section 3.2 and reaction mechanisms will be proposed in section 3.3 to explain the formation of major ions detected in the aerosol mass spectra.

3.2 Oxidation Kinetics

The normalized parent decay as a function of OH exposure is shown in **Figure 3** and the OH radical-initiated decay can be fitted using an exponential function:

$$ln\frac{I}{I_0} = -k\,[OH]\cdot t \qquad (2)$$

where I is the ion signal at a given OH exposure, I_0 is the ion signal before oxidation, k is the second order heterogeneous rate constant, and $[OH]\cdot t$ is the OH exposure. The exponential k is determined to be $(3.79 \pm 0.19) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. 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. The effective uptake coefficient, γ_{eff}, defined as the fraction of OH collisions that yield a reaction, is computed (*Davies and Wilson, 2015*),

$$\gamma_{eff} = \frac{2}{3}\frac{D_0\,\rho\,mfs\,N_A}{M_w\,\overline{c_{OH}}}\,k \qquad (3)$$

where D_0 is the mean surface-weighted particle diameter, ρ is the aerosol density before oxidation, *mfs* is the mass fraction of solute, N_A is the Avogadro's number, M_w is the molecular weight of sodium methyl sulfate, and $\overline{c_{OH}}$ is the average speed of gas-phase OH radicals. The mean surface-weighted particle diameter was 218 nm and decreased slightly to 211 nm (about 3 % decrease) at the maximum OH exposure (**Figure 4**). Before oxidation, the composition of the droplets (i.e. *mfs*) is derived from the hygroscopicity data reported by Estillore et al. (2016). The particle growth factor, G_f, defined as the ratio of the diameter at different RH to the dry particle at a reference RH (RH_1), is converted into *mfs* using the following equation (*Ansari and Pandis, 2000; Peng et al., 2001*),

$$G_f = \left(\frac{mfs_{RH,1}\,\rho_{RH,1}}{mfs_{RH,2}\,\rho_{RH,2}}\right)^{\frac{1}{3}} \tag{4}$$

where $mfs_{RH,i}$ and $\rho_{RH,i}$ are the mass fraction of solute and particle density at a given RH, respectively. It is assumed that sodium methyl sulfate exists as an anhydrous particle at the reference RH (RH < 10 %) (i.e. $mfs_{RH,1} = 1$). The particle density is estimated using the volume additivity rule with the density of water and sodium methyl sulfate (1.60 g cm^{-3}, *Chemistry Dashboard*) with an uncertainty of 20 – 30 %. The *mfs* is computed to be 0.34 at 85 %. 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 ($SO_4^{\bullet-}$).

3.3 Reaction Mechanisms: OH Reaction with Sodium Methyl Sulfate

Sodium methyl sulfate tends to dissociate and exist in its ~~an~~ionic form because of its high dissociation constant (pKa = −2.4). As shown in **Scheme 1**, the oxidation is initiated by hydrogen abstraction from the methyl group by the OH radical, forming an alkyl radical that quickly reacts with an oxygen molecule to form a peroxy radical. Based on the well-known particle-phase reactions (*George and Abbatt, 2010*), the self-reaction of two peroxy radicals can form a carbonyl functionalization product ($CHSO_5^-$) via the Bennett and Summers mechanism (*Bennett and Summers, 1974*), or form both alcohol ($CH_3SO_5^-$) and carbonyl functionalization products via the Russell reactions (*Russell, 1957*). Alternatively, alkoxy radicals can be produced through the peroxy–peroxy radical reactions. Once formed, alkoxy radical can react with an oxygen molecule to form the carbonyl functionalization product or abstract a hydrogen atom from the neighboring molecules to form the alcohol functionalization product. Furthermore, the alkoxy radical can undergo fragmentation to yield a formaldehyde (CH_2O) and a sulfate radical anion ($SO_4^{\bullet-}$). Alternatively, the decomposition of the alkoxy radical, in analogy to the OH radical-initiated oxidation of simple alkyl esters (*Sun et al., 2012*), could involve the rearrangement of the hydrogen atom from the alkoxy radical carbon to the oxygen on the methoxy group. The decomposition of the C−O bond from the methoxy group generates a bisulfate ion and a formyl radical (CHO). The subsequent reactions of the formyl radical can yield a carbon monoxide (CO) and HO_2. Like formaldehyde, carbon monoxide is volatile and partitions back to the gas phase.

As shown in **Figure 1**, neither functionalization nor fragmentation products are detected. Formaldehyde has a mass which is below the mass range of the mass spectrometer and, once formed, it is likely partitioned back to the gas phase due to its high volatility. On the other hand, it is expected that the two functionalization products can be detected by DART ionization source if they were formed in significant amount. Additional experiments were performed to verify whether the alcohol and carbonyl functionalization products can be detected by the DART ionization source. We have measured the heterogeneous OH radical-initiated oxidation of sodium ethyl sulfate ($C_2H_5SO_4Na$) under similar experimental conditions. As shown in **Figure 5**, the negative ions of the alcohol ($C_2H_5SO_5^-$) and carbonyl ($C_2H_3SO_5^-$) functionalization products are detected in the aerosol mass spectra. When the sodium ethyl sulfate is oxidized (**Figure 6**), the abundance of these two functionalization products increases with increasing OH exposure (**Figure 7**). Similar to sodium methyl sulfate, the bisulfate ion has been detected and its intensity increases after oxidation (**Figure 8**). These results suggest that if functionalization products are formed during the OH oxidation of sodium methyl sulfate, they could be detected by DART ionization source.

The absence of the functionalization products in the aerosol mass spectra suggests that the OH reaction with sodium methyl sulfate tends to undergo fragmentation processes rather than functionalization processes. One possibility is that, due to the presence of bulky sulfate group relative to the methyl group, reaction intermediates resulted from the self-reaction of two peroxy radicals may not be easily arranged into appropriate configurations (i.e. cyclic transition states), which are required for the formation of the functionalization products via Russell reaction or Bennett and Summers mechanism. Alternatively, alkoxy radicals are more likely formed, followed by fragmentation. Although the dissociation energies for C−O and C−C bonds of sodium methyl sulfate are not known, fragmentation processes could be enhanced since the decomposition of the alkoxy radical involves the cleavage of a C−O bond, which is in general thought to be weaker than a C−C bond (*Dean and Lang, 1992*). ~~Fragmentation processes could also be enhanced since the decomposition of the alkoxy radical involves the cleavage of a C−O bond, which is in general thought to be weaker than a C−C bond.~~ The bond dissociation energy of a C−O bond might be lowered in the presence of a sulfur atom or sulfur-oxygen bearing group (*Oae and Doi, 1991; Dean and Lange, 1992*). One possibility is that sulfur atom or sulfur-oxygen bearing group (e.g. sulfate) is more electronegative than a carbon atom, reducing the electron density and bond strength of the C−O bond by inductive effect. Further investigation is required to better understand the effect of sulfate group on the dissociation energies of the C−O bond for the sodium methyl sulfate.

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~~Although the effect of a sulfate group on the bond strength of the C−O bond is not well studied, the bond dissociation energy of a C−O bond is likely to be lowered in the presence of a sulfur atom (*i.e.* C−O−S) (*Oae and Doi, 1991*).~~

~~3.4 Formation and Reaction of Sulfate Radical Anion in the OH Reaction with Sodium Methyl Sulfate~~

3.4 Formation and Reaction of Sulfate Radical Anion in the OH Reaction with Sodium Methyl Sulfate

Scheme 1 shows that sulfate radical anion ($SO_4^{\bullet-}$) can be formed via the fragmentation processes. The sulfate radical anion is a strong oxidant in aqueous phase. For example, Huie and Clifton (1989) have reported that hydrogen abstraction by sulfate radical anions on the alkane can result in the formation of bisulfate ions. They also reported that the hydrogen abstraction rate is the highest on the tertiary carbon, and the rate is one order of magnitude smaller for the secondary carbon, and even smaller for the primary carbon. 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. ~~The second-order rate constants for $SO_4^{\bullet-}$ reactions with alcohol, ethers, alkanes, and aromatic compounds typically have an order of magnitude ranging 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*), which is comparable to that of OH radicals (10^7 to 10^{11} M^{-1} s^{-1}) (*Chen et al., 2014*).~~ For the OH reaction with sodium methyl sulfate, it is proposed that sulfate radical anion, once formed, can abstract a hydrogen atom from the neighboring, unreacted sodium methyl sulfate, yielding the bisulfate ion, which has a small acid dissociation constant in equilibrium with sulfate (SO_4^{2-}) and hydrogen (H^+) ions (~~p~~*Ka* = 1.2×10^{-2}) (*Brown et al., 2012*).

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$$SO_4^{\bullet-} + CH_3SO_4^- \rightarrow CH_2SO_4^{\bullet-} + HSO_4^- \tag{5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{6}$$

Moreover, the sulfate radical anion may react with particle-phase water to form a bisulfate ion and an OH radical (*Tang et al., 1988*).

$$SO_4^{\bullet-} + H_2O \rightleftharpoons OH^{\bullet} + HSO_4^- \tag{7}$$

As shown in **Figure 1b**, the bisulfate ion is the second largest peak detected in the aerosol mass spectrum and its intensity has found to increase significantly with increasing OH exposure (**Figure 2**). The detection of the bisulfate ion provides indirect evidence to support the formation and subsequent reactions of sulfate radical ions. When these reactions occur (**Eqn. 5 and 7**), additional sodium methyl sulfate is consumed by the sulfate radical ions and OH radicals, contributing to the secondary chemistry. It is also known that the self-reaction of two sulfate radical anions can yield a peroxydisulfate ion ($S_2O_8^{2-}$) (*Hayon et al., 1972; Tang et al., 1988; Huie et al., 1989; Huie et al., 1991; Das, 2001*):

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{8}$$

Based on its mass-to-charge ratio, the peroxydisulfate ion can be detected as SO_4^- at *m/z* 96 in the aerosol mass spectra (**Figure 1**). It is worth noting that the peak at *m/z* 96 ~~is~~ does not likely originate from the sulfate radical anions due to its high reactivity. The ion signal intensity of the SO_4^- is measured to be smaller than that of the bisulfate ion (**Figure 2**). However, the abundance of these two ions cannot be directly inferred from their intensities owing to their unknown ionization efficiencies in the DART ionization source.

3.5 Sodium Methyl Sulfate vs. Sodium Ethyl Sulfate: Kinetics and Chemistry

We here further examine the results of sodium methyl sulfate and sodium ethyl sulfate to gain more insights into how the carbon number affects the kinetics and chemistry for these two small organosulfates (C_1 and C_2). Kinetic measurements show that the heterogeneous rate constant and effective OH uptake coefficient of sodium ethyl sulfate are determined to be (4.64 ± 0.29) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and 0.19 ± 0.03, respectively (**Table 1** and **Figure 6**). These kinetic parameters are slightly larger than that of sodium methyl sulfate ($3.79 \pm 0.19 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and 0.17 ± 0.03). An additional carbon atom does not significantly change the heterogeneous OH reactivity. On the other hand, the composition of the sodium ethyl sulfate (**Figure 5**) is different from that of sodium methyl sulfate after oxidation (**Figure 1**). As discussed in section 3.3, the bisulfate ion (HSO_4^-) and SO_4^- have been observed for both organosulfates. However, the alcohol and carbonyl functionalization products are only detected in the OH oxidation of sodium ethyl sulfate. These observations suggest the potential reaction pathways may change with an increasing carbon number.

As shown in **Scheme 2**, at the first OH oxidation step of sodium ethyl sulfate, the hydrogen abstraction can occur either on the primary (**Scheme 2, Path A**) or the secondary carbon site (**Scheme 2, Path B**). Depending on the initial OH reaction site, two structural isomers of alcohol ($C_2H_5SO_5^-$) and carbonyl ($C_2H_3SO_5^-$) functionalization products can be formed. However, these isomers cannot be differentiated by exact mass measurements. Although the preferential OH reaction site is not well understood, we postulate that the formation of the alcohol and carbonyl functionalization products are likely originated from the hydrogen abstraction occurred at the primary carbon (**Scheme 2, Path A**). One likely explanation is that based on the knowledge of the OH reaction with sodium methyl sulfate (**Scheme 1**), when the hydrogen abstraction occurs at a carbon atom adjacent to the sulfate group, an alkoxy radical is likely formed from the self-reaction of two peroxy radicals and tends to decompose. It is hypothesized that when the hydrogen atom of the secondary carbon is abstracted by the OH radical (**Scheme 2, Path B**), similar to the sodium methyl sulfate, an alkoxy radical is likely generated and fragments into a sulfate radical anion and an acetaldehyde, which is volatile and likely partitions back to the gas phase. The sulfate radical anion can subsequently react with an unreacted sodium ethyl sulfate, leading to the formation of a bisulfate ion (HSO_4^-, *m/z* 97). Alternatively, the self-reactions of two sulfate radical anions can yield a peroxydisulfate ion ($S_2O_8^{2-}$), which can be detected as SO_4^- at *m/z* 96 in the aerosol mass spectra. Future works are needed to verify these hypotheses.

3.6 Aerosol Mass Lost via Volatilization

While the fragmentation and volatilization processes are likely the dominant reaction pathways of OH oxidation of sodium methyl sulfate, the diameter of the particles decreases slightly from 218 nm to 211 nm at the maximum OH exposure (**Figure 4**). As shown in **Scheme 1,** when the fragmentation processes occur, one methyl group is lost via volatilization in the form of formaldehyde. The methyl group (CH_3, M_w = 15 g mol^{-1}) contributes about 11 % of the total molecular mass (CH_3SO_4Na, M_w = 134 g mol^{-1}). At the maximum OH exposure, about 40 % of sodium methyl sulfate is reacted (**Figure 3**). If we assume that only fragmentation processes occur during OH oxidation, this will lead to a 4.4 % loss in particle mass via volatilization. The result of this simple analysis is consistent with the experimental observation that only a small decrease in particle size (~ 3 %) is measured after oxidation. For the sodium ethyl sulfate (**Figure 9**), the particle diameter decreases slightly from 203 nm to 195.5 nm at the maximum OH exposure (~ 4 % decrease in particle diameter). According to **Scheme 2**, formaldehyde and acetaldehyde are the volatile fragmentation products, which are likely partitioned back to the gas phase. Following the above analysis, if we assume the fragmentation only leads to the formation and volatilization of the acetaldehyde, this will lead to a maximum 9 % loss in the particle mass at the highest OH exposure. Similar to sodium methyl sulfate, the formation and volatilization of fragmentation products do not cause a significant decrease in particle mass (and diameter) during OH oxidation.

4 Conclusions and Atmospheric Implications

This work investigates the heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate found in atmospheric particles. During oxidation, sodium methyl sulfate tends to fragment into a formaldehyde and a sulfate radical anion. The formation and chemistry of sulfate radical anions in the heterogeneous OH oxidation of organosulfates could be of atmospheric interest. This is because sulfate radical anion, like OH radical, can abstract a hydrogen atom from unreacted sodium methyl sulfate, contributing to the secondary reactions. The formation of bisulfate and likely sulfate ions from sulfate radical anion reactions suggest that OH reaction with sodium methyl sulfate or other organosulfates can possibly lead to the formation of inorganic sulfate. Moreover, sulfate radical anions can react with organic compounds to regenerate organosulfates. Compared to sodium methyl sulfate, the OH reaction with sodium ethyl sulfate occurs at a similar reaction rate. The oxidation of both compounds can lead to the formation of bisulfate ions, but different distribution of reaction products is observed. These observations suggest that the carbon number plays a significant role in governing the reaction mechanisms for these two small organosulfates. Given a variety of organosulfates have been detected in atmospheric particles, the role of molecular structure (e.g. carbon chain length, position and nature of functional groups (e.g. hydroxyl and carbonyl)) in the heterogeneous OH oxidation kinetics, chemistry, and sulfate radical anion formation and reactions of organosulfates remains unexplored and warrants further study.

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References

1. Ansari, A. S. and Pandis, S. N.: Water Absorption by Secondary Organic Aerosol and Its Effect on Inorganic Aerosol Behavior, *Environ. Sci. Technol.*, 34(1), 71−77. **2000**.
2. Bennett, J. E. and Summers, R.: Product Studies of the Mutual Termination Reactions of sec-Alkylperoxy Radicals: Evidence for Non-Cyclic Termination, *Can. J. Chem.*, 52(8), 1377−1379, **1974**.

3. Block, E., Dane, A. J., Thomas, S., Cody, R. B.: Applications of Direct Analysis in Real Time Mass Spectrometry (DART-MS) in Allium Chemistry. 2-Propenesulfenic and 2-Propenesulfinic Acids, Diallyl Trisulfane S-Oxide, and Other Reactive Sulfur Compounds from Crushed Garlic and Other Alliums, *J. Agric. Food Chem.*, 58(8), 4617−4625, **2010**.

4. Brown, T. L., Lemay JR, H. E., Bursten, B. E., Murphy, C. J., Woodward, P. M.: Chemistry: The Central Science, *Pearson Education*, 12 Edition, Appendix D, 1062, **2012**.

5. Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., Surratt, J. D.: Examining the Effects of Anthropogenic Emissions on Isoprene-Derived Secondary Organic Aerosol Formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee Ground Site, *Atmos. Chem. Phys.*, 15(15), 8871−8888, **2015**.

6. Chan, M. N., Surratt. J. D., Claeys, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., Eddingsaas, N. C., Wennberg, P. O., Seinfeld, J. H.: Characterization and Quantification of Isoprene-Derived Epoxydiols in Ambient Aerosol in the Southeastern United States, *Environ. Sci. Tech.*, 44(12), 4590−4596, **2010**.

7. Chan, M. N., Zhang, H., Goldstein, A. H., Wilson, K. R.: The Role of Water and Phase in the Heterogeneous Oxidation of Solid and Aqueous Succinic Acid Aerosol by Hydroxyl Radicals, *J. Phys. Chem. C*, 118(50), 28978–28992, **2014**.

8. Chemistry Dashboard, Sodium Methyl Sulfate, 512-42-5 | DTXSID0042406, *United States Environmental Protection Agency*, Retrieved fromhttps://comptox.epa.gov/dashboard/dsstoxdb/results?search=Sodium+methyl+sulfate

9. Cheng, C. T., Chan, M. N., Wilson, K. R.: The Role of Alkoxy Radicals in the Heterogeneous Reaction of Two Structural Isomers of Dimethylsuccinic Acid, *Phys. Chem. Chem. Phys.*, 17(38), 25309–25321, **2015**.

10. Cheng, C. T., Chan, M. N., Wilson, K. R.: Importance of Unimolecular HO_2 Elimination in the Heterogeneous OH Reaction of Highly Oxygenated Tartaric Acid Aerosol, *J. Phys. Chem. A*, 120(29), 5887–5896, **2016**.

~~6.~~

~~7. Chen, Z., Yu, X., Huang, X., Zhang, S.: Prediction of Reaction Rate Constants of Hydroxyl Radical with Organic Compounds, *J. Chil. Chem. Soc.*, 59(1), **2014**.~~

~~8.~~11. Chim, M. M., Chow, C. Y., Davies, J. F., Chan, M. N.: Effects of Relative Humidity and Particle Phase Water on the Heterogeneous OH Oxidation of 2−Methylglutaric Acid Aqueous Droplets, *J. Phys. Chem. A*, 121(8), 1666−1674, **2017**.

12. Clifton, C. L. and Huie, R. E.: Rate Constant for Hydrogen Abstraction Reactions of the Sulfate Radical, SO_4^-. Alcohol, *Int. J. Chem. Kinet.*, 21(8), 677−687, **1989**.

~~9.~~ Cody, R. B., Laramee, J. A., Durst, H. D.: Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions, *Anal. Chem.*, 77 (8), 2297−2302, **2005**.

13.

~~10.~~14. Darer, A. I., Cole-Filipiak, N. C., O'Connor, A. E., Elrod, M. J.: Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates, *Environ. Sci. Tech.*, 45(5), 1895−1902, **2011**.

~~11.~~15. Das, T. N.: Reactivity and Role of $SO_5^{\bullet-}$ Radical in Aqueous Medium Chain Oxidation of Sulfite to Sulfate and Atmospheric Sulfuric Acid Generation, *J. Phys. Chem. A*, 105(40), 9142−9155, **2001**.

16. Davies, J. F. and Wilson, K. R.: Nanoscale Interfacial Gradients Formed by the Reactive Uptake of OH Radicals onto Viscous Aerosol Surfaces, *Chem. Sci.*, 6(12), 7020−7027, **2015**.

~~12.~~17. Dean, J. and Lange, N.: Lange's handbook of chemistry (15th Edition). *New York: McGraw-Hill*, 4.42−4.43, **1992**.

~~13.~~18. Estillore, A. D., Hettiyadura, A. P. S., Qin, Z., Leckrone, E., Wombacher, B., Humphry, T., Stone, E. A., Grassian, V. H.: Water Uptake and Hygroscopic Growth of Organosulfate Aerosol, *Environ. Sci. Technol.*, 50(8), 4259−4268, **2016**.

~~14.~~19. Frossard, A. A., Shaw, P. M., Russell, L. M., Kroll, J. H., Canagaratna, M. R., Worsnop, D. R., Quinn, P. K., Bates, T. S.: Springtime Arctic Haze Contributions of Submicron Organic Particles from European and Asian Combustion Sources, *J. Geophys. Res.*, 116(D5), **2011**.

~~15.~~20. Froyd, K. D., Murphy, S. M., Mruphy, D. M., Gouw, J. A. de, Eddingsaas, N. C., Wennberg, P. O.: Contribution of Isoprene-Derived Organosulfates to Free Tropospheric Aerosol Mass, *Proc. Natl. Acad. Sci. U.S.A.*, 107(50), 21360−21365, **2010**.

~~16.~~21. George, I. J. and Abbatt, J. P. D.: Heterogeneous Oxidation of Atmospheric Aerosol Particles by Gas-Phase Radials, *Nat. Chem.*, 2(9), 713−722, **2010**.

~~17.~~22. Hajslova, J., Cajka, T., Vaclavik, L.: Challenging Applications Offered by Direct Analysis in Real Time (DART) in Food-Quality and Safety Analysis, *Trends Anal. Chem.*, 30(2), 204−218, **2011**.

~~18.~~23. Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., Bates, T. S.: Carboxylic Acids, Sulfates, and Organosulfates in Processed Continental Organic Aerosol over the Southeast Pacific Ocean during VOCALS-REx 2008, *J. Geophys. Res.*, 115(D13), **2010**.

~~19.~~24. Hayon, E., Treinin, A., Wilf, J.: Electronic Spectra, Photochemistry, and Autoxidation Mechanism of the Sulfite-Bisulfite-Pyrosulfite System. The SO_2^{-}, SO_3^{-}, SO_4^{-} and SO_5^{-} Radicals, *J. Am. Chem. Soc.*, 94(1), 47−57, **1972**.

25. Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P., Zellner, R.: CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, *J. Atmos. Chem.*, 36, 231−284, **2000**.

26. Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., Humphry, T.: Determination of Atmospheric Organosulfates using HILIC Chromatography with MS Detection, *Atmos. Meas. Tech.*, 8(6), 2347−2358, **2015**.

~~20.~~27. Hu, K. S., Darer, A. I., Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, *Atmos. Chem. Phys.*, 11, 8307−8320, **2011**.

~~21.~~28. Huang, D. D., Li, Y. J., Lee, B. P., Chan, C. K.: Analysis of Organic Sulfur Compounds in Atmospheric Aerosols at the HKUST Supersite in Hong Kong Using HR-ToF-AMS, *Enviro. Sci. Technol.*, 49(6), 3672−3679, **2015**.

~~22.~~29. Huie, R. E., Clifton, C. L.: Rate Constants for Hydrogen Abstraction Reactions of the Sulfate Radical, SO_4^{-}. Alkanes and Ethers, *Int. J. Chem. Kinetics*, 21(8), 611−619, **1989**.

~~23.~~30. Huie, R. E., Clifton, C. L., Altstein, N.: A Pulse Radiolysis and Flash Photolysis Study of the Radicals SO_2^{-}, SO_3^{-}, SO_4^{-} and SO_5^{-}, *Radiat. Phys. Chem.*, 33(4), 361−370, **1989**.

~~24.~~31. Huie, R. E., Clifton, C. L., Neta, P.: Electron Transfer Reaction Rates and Equilibria of the Carbonate and Sulfate Radical Anions, *Radiat. Phys. Chem.*, 38(5), 477−481, **1991**.

~~25.~~32. Iinuma, Y., Müller, C., Berndt, T., Böge, O., Claeys, M., and Herrmann, H.: Evidence for the Existence of Organosulfates from β-pinene Ozonolysis in Ambient Secondary Organic Aerosol, *Environ. Sci. Tech.*, 41(19), 6678−6683, **2007**.

~~26.~~33. Iinuma, Y., Böge, O., Kahnt, A., and Herrmann, H.: Laboratory Chamber Studies on the Formation of Organosulfates from Reactive Uptake of Monoterpene Oxides, *Phys. Chem. Chem. Phys.*, 11(36), 7985−7997, **2009**.

~~27.~~34. Kroll, J. H., Lim, C. Y., Kessler, S. H., Wilson, K. R.: Heterogeneous Oxidation of Atmospheric Organic Aerosol: Kinetics of Changes to the Amount and Oxidation State of Particle-Phase Organic Carbon, *J. Phys. Chem. A*, 119(44), 10767−10783, **2015**.

~~28.~~35. Kuang, B. Y., Lin, P., Hu, M., Yu, J. Z.: Aerosol Size Distribution Characteristics of Organosulfates in the Peral River Delta Region, China, *Atmos. Environ.*, 130, 23−35, **2016**.

~~29.~~36. Neta, P., Madhavan, V., Zamel, H., Fessenden, R. W., Rate Constants and Mechanism of Reaction of $SO_4^{\bullet-}$ with Aromatic Compounds, *J. Am. Chem. Soc.*, 99(1), 163−164, **1977**.

~~30.~~37. Neta, P., Huie, R. E., Ross, A. B.: Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution, *J. Phys. Chem. Ref. Data*, 17, 1027, **1988**.

~~31.~~38. Nozière, B., Ekström, S., Alsberg, T., Holmström, S.: Radical‐Initiated Formation of Organosulfates and Surfactants in Atmospheric Aerosols, *Geophys. Res. Lett.*, 37(5), **2010**.

~~32.~~39. Oae, S. and Doi, J.: Organic Sulfur Chemistry: Structure and Mechanism, *CRC Press: Boca Raton, Florida*, **1991**.

~~33.~~40. Olson, C. N., Galloway, M. M., Yu, G., Hedman, C. J., Lockett, M. R., Yoon, T., Stone, E. A., Smith, L. M., Keutsch, F. N.: Hydroxycarboxylic Acid-Derived Organosulfates: Synthesis, Stability, and Quantification in Ambient Aerosol, *Environ. Sci. Tech.*, 45(15), 6468−6474, **2011**.

~~34.~~41. Padmaja, S., Alfassi, Z. B., Neta, P., Huie, R. E.: Rate Constants for Reactions of $SO_4^{\bullet-}$ Radicals in Acetonitrile, *Int. J. Chem. Kinet.*, 25(3), 193−198, **1993**.

~~35.~~42. Peng, C., Chan, C. K.: The Water Cycle of Water-Soluble Organic Salts of Atmospheric Importance, *Atmos. Environ.*, 35(7), 1183−1192, **2001**.

~~36.~~43. Rattanavaraha, W., Chu, K., Budisulistiorini S. H., Riva, M., Lin, Y. H., Edgerton, E. S., Baumann, K., Shaw, S. L., Guo, H., King, Laura., Weber, R. J., Neff, M. E., Stone, E. A., Offenberg, J. H., Zhang, Z., Gold, A., Surratt, J. D.:

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Assessing the Impact of Anthropogenic Pollution on Isoprene-Derived Secondary Organic Aerosol Formation in $PM_{2.5}$ Collected from the Birmingham, Alabama, Ground Site during the 2013 Southern Oxidant and Aerosol Study, *Atmos. Chem. Phys.*, 16(8), 4897−4914, **2016**.

~~37.~~44. Riva, M., Barbosa, T. D. S., Lin, Y. H., Stone, E. A., Gold, A., Surratt, J. D.: Chemical Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Alkanes, *Atmos. Chem. Phys.*, 16(17), 11001−11018, **2016**.

~~38.~~45. Rudich, Y., Donahue, N. M., Mentel, T. F.: Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies, *Annu. Rev. Phys. Chem.*, 58, 321−352, **2007**.

~~39.~~46. Rudziński, K. J., Gmachowski, L., Kuznietsova, I.: Reactions of Isoprene and Sulphoxy Radical-Anions: A Possible Source of Atmospheric Organosulphites and Organosulphates, *Atmos. Chem. Phys.*, 9(6), 2129–2140, **2009**.

~~40.~~47. Russell, G. A.: Deuterium-Isotope Effects in the Autoxidation of Aralkyl Hydrocarbons. Mechanism of the Interaction of Peroxy Radicals, *J. Am. Chem. Soc.*, 79(14), 3871−3877, **1957**.

~~41.~~48. Smith, J. D., Kroll, J. H., Cappa, C. D., Che, D. L., Liu, C. L., Ahmed, M., Leone, S. R., Worsnop, D. R., Wilson, K. R.: The Heterogeneous Reaction of Hydroxyl Radicals with Sub-Micron Squalane Particles: A Model System for Understanding the Oxidative Aging of Ambient Aerosols, *Atmos. Chem. Phys.*, 9(9), 3209−3222, **2009**.

~~42.~~49. Shakya, K. M. and Peltier, R. E.: Investigating Missing Sources of Sulfur at Fairbanks, Alaska, *Environ. Sci. Technol.*, 47(16), 9332−9338, **2013**.

~~43.~~50. Sorooshian, A., Crosbie, E., Maudlin, L. C., Youn, J. S., Wang, Z., Shingler, T., Ortega, A. M., Hersey, S., Woods, R. K.: Surface and Airborne Measurements of Organosulfur and Methanesulfonate over the Western United States and Coastal Areas, *J. Geophys. Res. Atmos.*, 120(16), 8535–8548, **2015**.

51. Stone, E. A., Yang, L., Yu, L. E., Rupakheti, M.: Characterization of Organosulfates in Atmospheric Aerosols at Four Asian Locations, *Atmos. Environ.*, 47, 323−329, **2012**.

~~44.~~52. Sun, X., Hu, Y., Xu, F., Zhang, Q., Wang, W.: Mechanism and Kinetic Studies for OH Radical-initiated Atmospheric Oxidation of Methyl Propionate, *Atmos. Environ.*, 63, 14−21, **2012**.

~~45.~~53. Surratt, J. D., Kroll, J. H., Kleindienst T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., Seinfeld, J. H.: Evidence for Organosulfates in Secondary Organic Aerosol, *Enviro. Sci. Technol.*, 41(2), 517−527, **2007**.

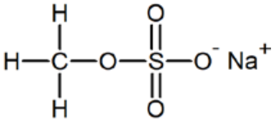
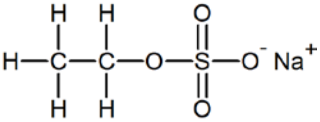
~~46.~~54. Surratt, J. D., González, Y. G., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., Seinfeld, J. H.: Organosulfate Formation in Biogenic Secondary Organic Aerosol, *J. Phys. Chem. A*, 112(36), 8345−8378, **2008**.

~~47.~~55. Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., Seinfeld, J. H.: Reactive Intermediates Revealed in Secondary Organic Aerosol Formation from Isoprene, *Proc. Natl. Acad. Sci. U.S.A.*, 107(15), 6640−6645, **2010**.

~~48.~~56. Tang, Y., Thorn, R. P., Mauldin III, R. L., Wine, P. H.: Kinetics and Spectroscopy of the SO_4^- Radical in Aqueous Solution, *J. Photochem. Photobiol., A*, 44(3), 243−258, **1988**.

~~49.~~57. Tolocka, M. P. and Turpin, B.: Contribution of Organosulfur Compounds to Organic Aerosol Mass, *Enviro. Sci. Technol.*, 46(15), 7978−7983, **2012**.

Table 1. Chemical structures, properties, rate constant, and effective OH uptake coefficient of sodium methyl sulfate and sodium ethyl sulfate

Compounds	**Sodium Methyl Sulfate**	**Sodium Ethyl Sulfate**
Chemical Formula		
Molecular Formula	CH_3SO_4Na	$C_2H_5SO_4Na$
Molecular Weight	134.0867	148.1147
Density (g cm^{-3})	1.60	1.46
~~Vapor Pressure (mmHg)~~	~~4.65×10^{-2}~~	~~6.90×10^{-3}~~
Mass Fraction of Solute, *mfs* at 85 % RH	0.34	0.38
Heterogeneous OH Rate Constant, *k* ($\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1})	3.79 ± 0.19	4.64 ± 0.29
Effective OH Uptake Coefficient, γ_{eff}	0.17 ± 0.03	0.19 ± 0.03

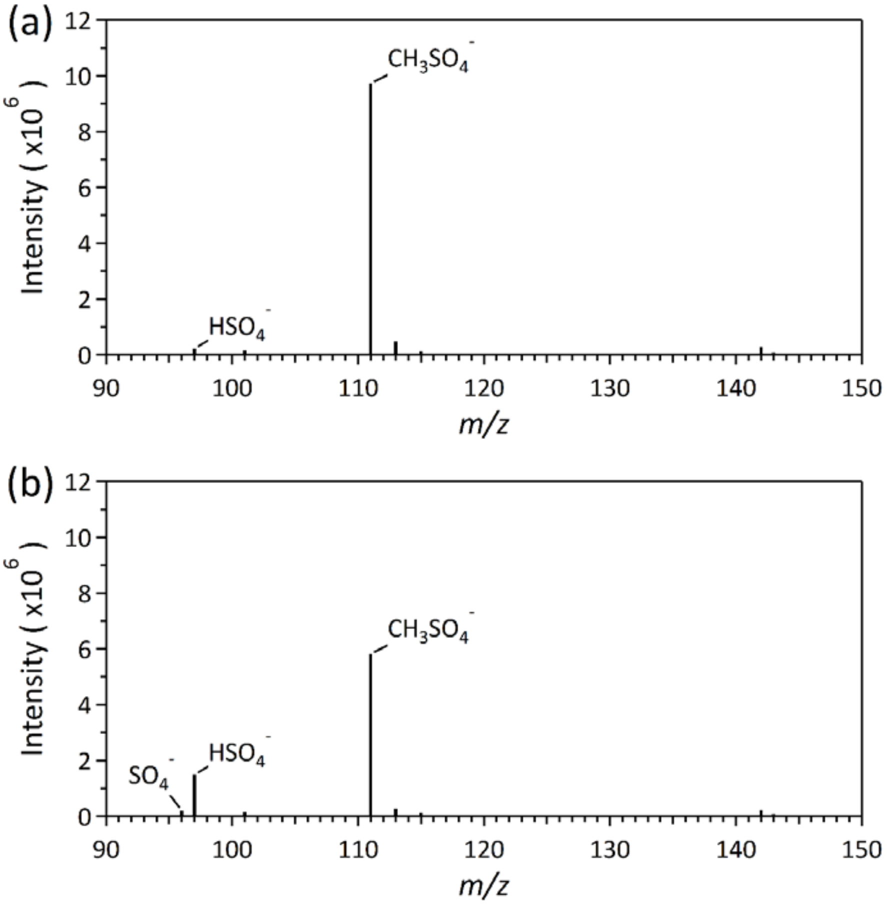


Figure 1. Aerosol mass spectra of sodium methyl sulfate before (a) and after (b) oxidation

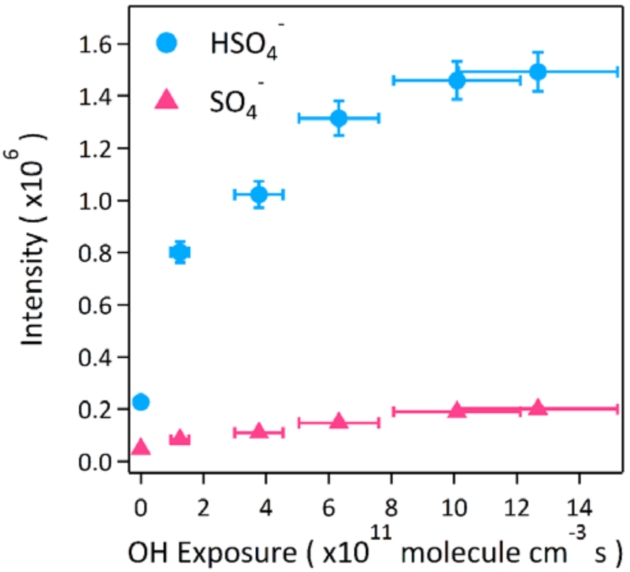


Figure 2. The kinetic evolution of HSO_4^- and SO_4^- as a function of OH exposure during the heterogeneous OH oxidation of sodium methyl sulfate. The small uncertainty in ion intensity measurement for SO_4^- is not visualized in the figure.

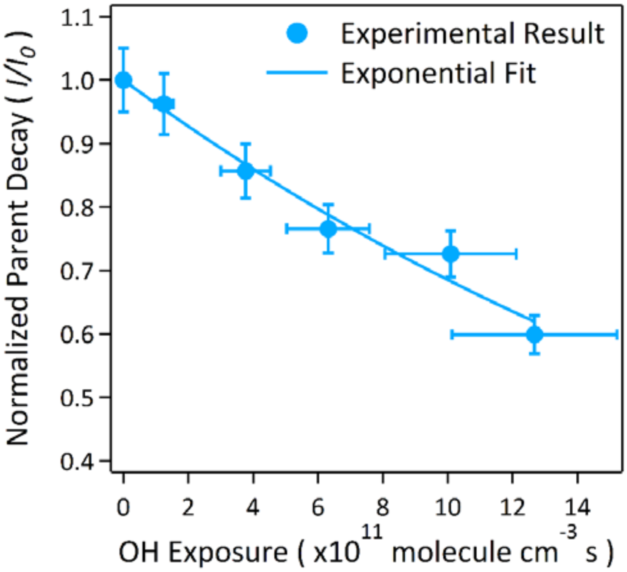


Figure 3. The normalized decay of sodium methyl sulfate as a function of OH exposure during the heterogeneous OH oxidation

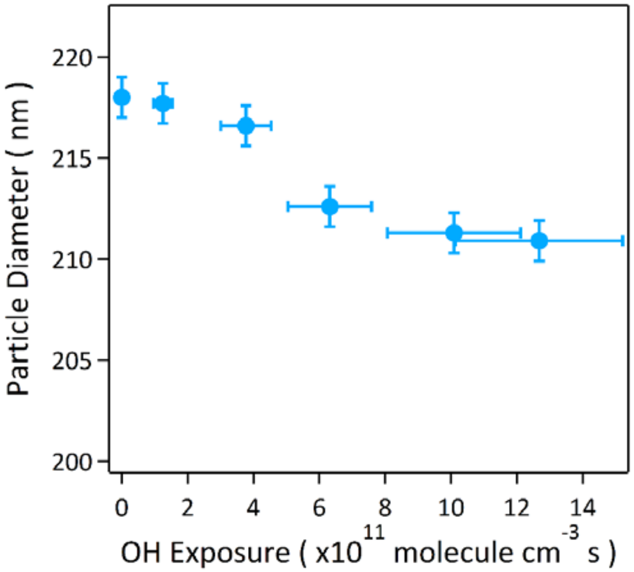


Figure 4. The surface-weighted particle diameter of sodium methyl sulfate as a function of OH exposure during heterogeneous OH oxidation

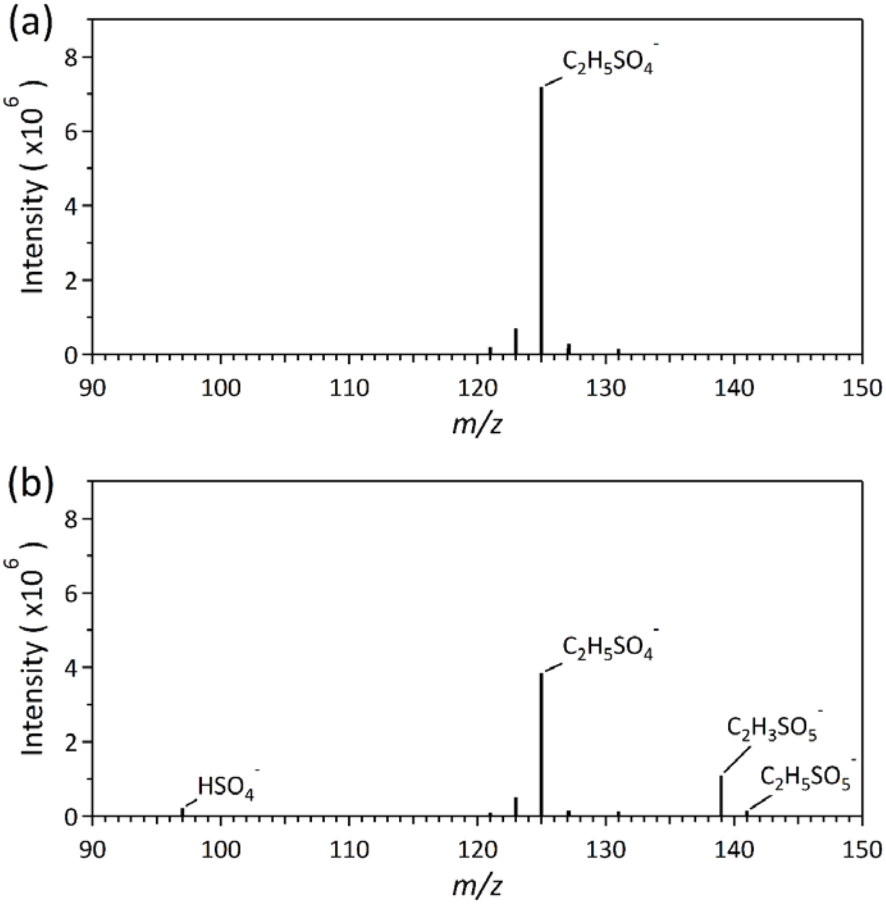


Figure 5. Aerosol mass spectra of sodium ethyl sulfate before (a) and after (b) oxidation

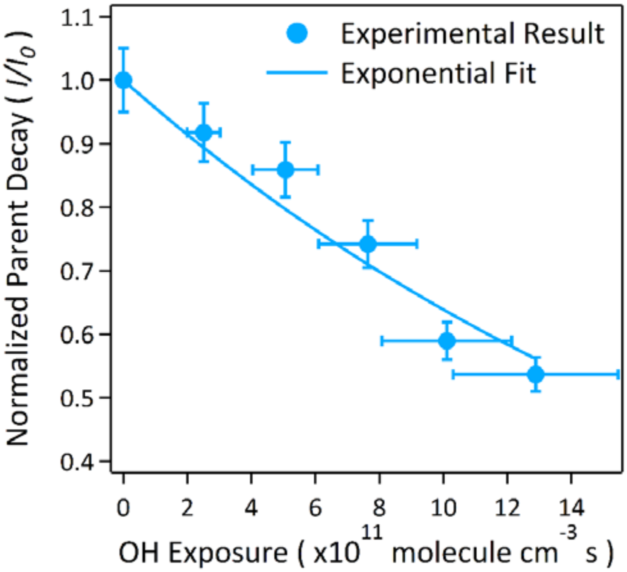


Figure 6. The normalized parent decay of sodium ethyl sulfate as a function of OH exposure in the heterogeneous OH oxidation

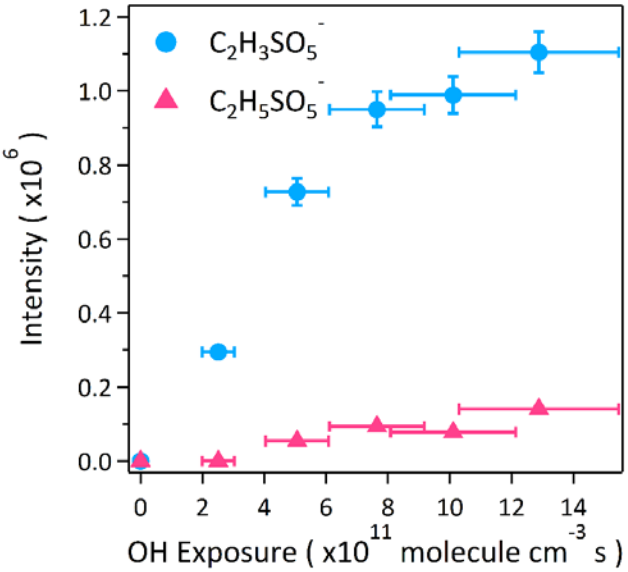


Figure 7. The kinetic evolution of carbonyl ($C_2H_3SO_5^-$) and alcohol ($C_2H_5SO_5^-$) functionalization products as a function of OH exposure in the heterogeneous OH oxidation of sodium ethyl sulfate. The small uncertainty in ion intensity measurement for $C_2H_5SO_5^-$ is not visualized in the figure.

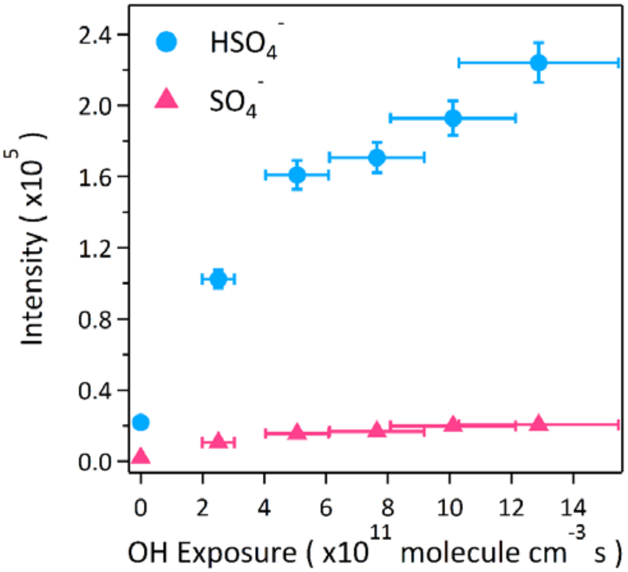


Figure 8. The kinetic evolution of HSO_4^- and SO_4^- as a function of OH exposure in the heterogeneous OH oxidation of sodium ethyl sulfate. The small uncertainty in ion intensity measurement for SO_4^- is not visualized in the figure.

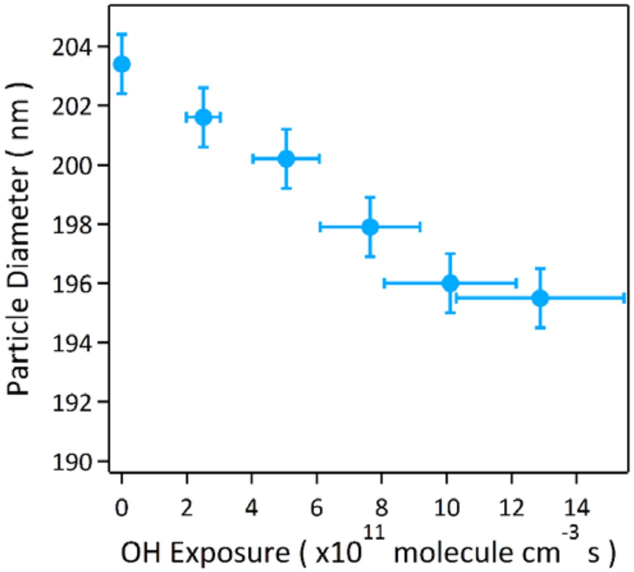
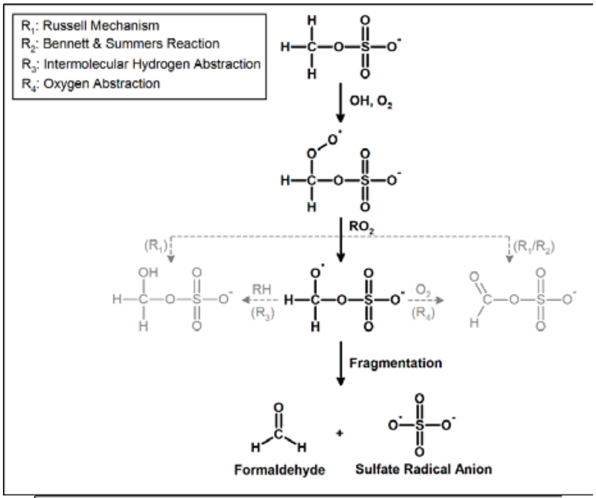
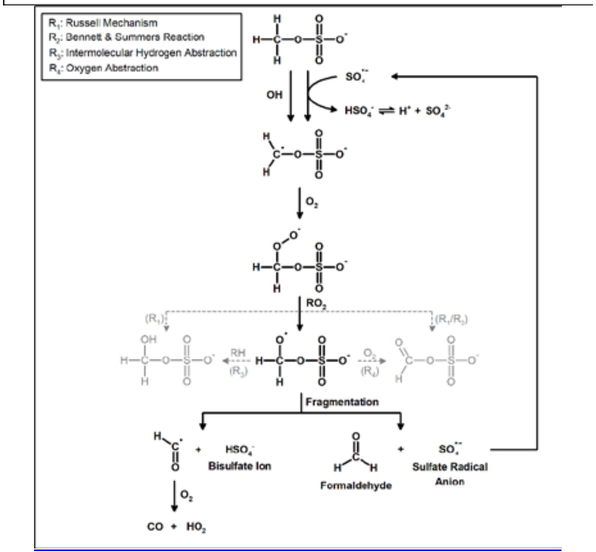
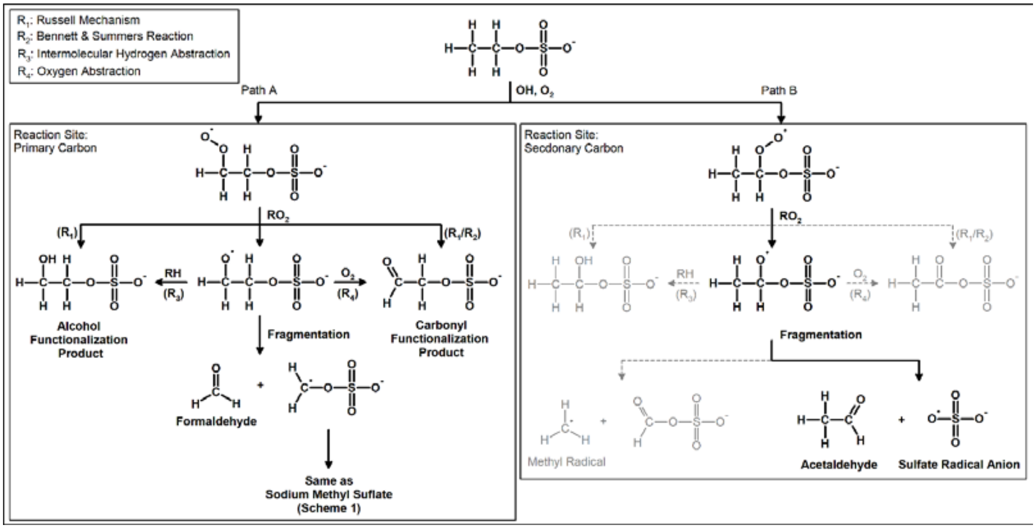


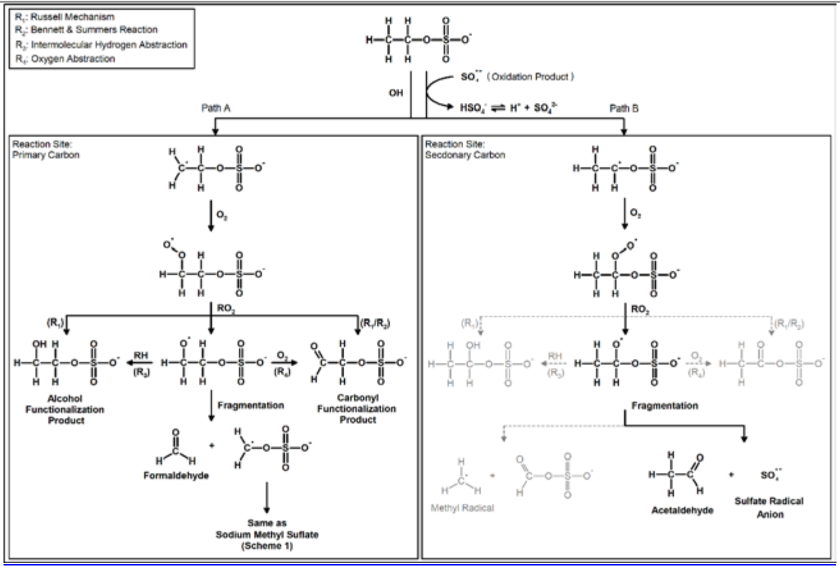
Figure 9. The surface-weighted particle diameter of sodium ethyl sulfate as a function of OH exposure during heterogeneous OH oxidation





Scheme 1. Proposed reaction mechanism for heterogeneous OH oxidation of sodium methyl sulfate (Gray arrows denote the minor pathways)





Scheme 2. Proposed reaction mechanism of heterogeneous OH oxidation of sodium ethyl sulfate (Gray arrows denote the minor pathways)