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**).

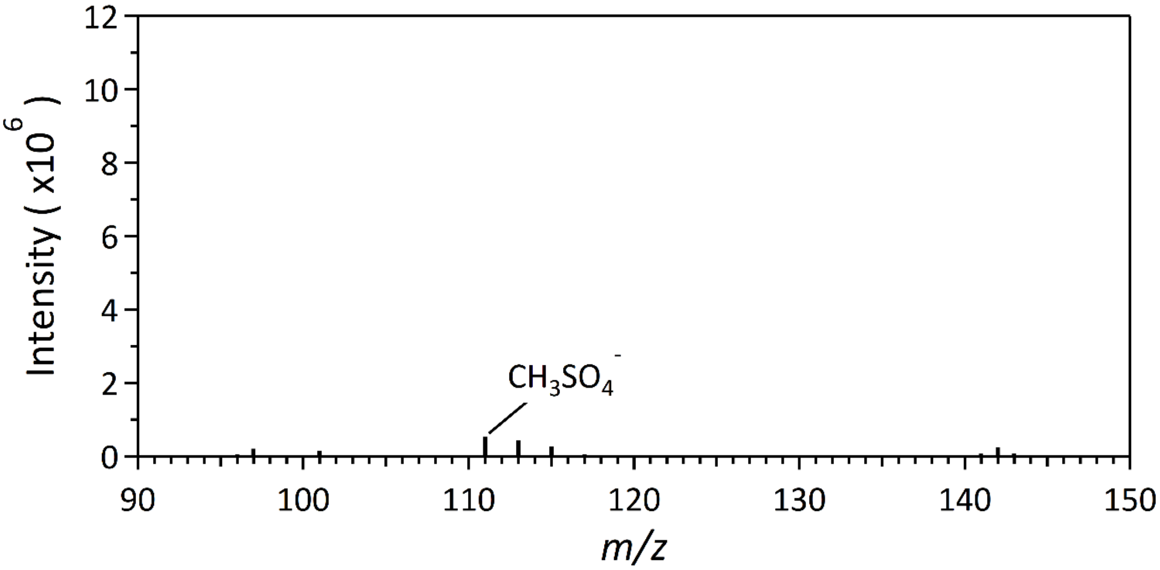

Figure S1. Mass spectrum without sodium methyl sulfate aerosols.

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**.