

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>.

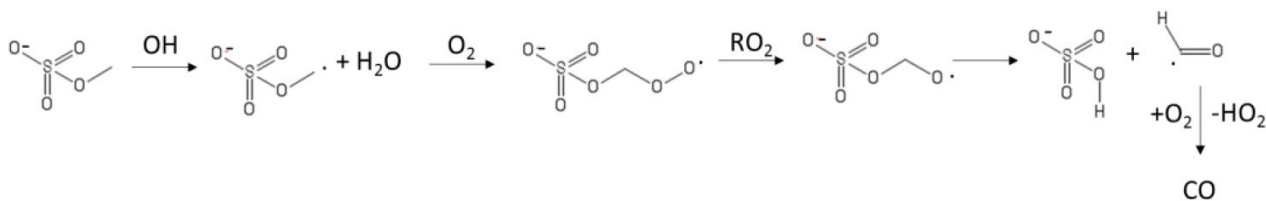
In this paper, titled “Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate” by Kwong et al., the authors present an interesting dataset focused on the heterogeneous chemical transformation of an organic sulfate 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.

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“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 HO₂. 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 NO_x environments. Could the authors place this chemistry in context with varying ratios of NO_x and RO₂? How might the schemes differ under high/low NO?

Author Response

We postulate that under high NO_x environment (i.e. high NO), RO₂ + NO reactions might become more favorable compared to RO₂ + RO₂ reactions. Alkoxy radicals are more likely formed from the RO₂ + 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 NO_x concentration likely favors the formation and decomposition of alkoxy radicals during the oxidation.

Minor Comments:

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.

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“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**.

