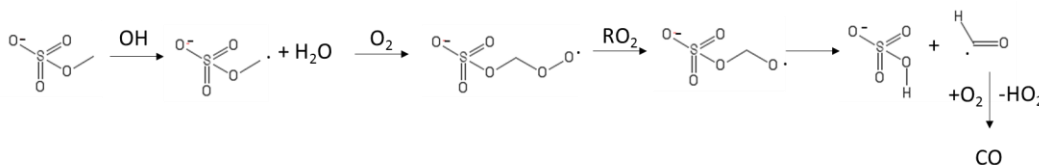


Overview

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.

Major 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.



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 RO_2 ? How might the schemes differ under high/low NO ?

Minor Comments

1. The manuscript discussion seems equally focused on sodium *methyl* sulfate and sodium *ethyl* sulfate. The authors might think of including both in the title.
2. 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?

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

References

Sun, Y. et al., “Mechanism and kinetic studies for OH radical-initiated atmospheric oxidation of methyl propionate”, *Atmos. Environ.*, **63**, 14-21, 2012.