

Interactive comment on “Enhancement of Secondary Organic Aerosol Formation and its Oxidation State by SO₂ during Photooxidation of 2-Methoxyphenol” by Changgeng Liu et al.

Anonymous Referee #3

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This manuscript presents results from a series of chamber experiments investigating the effect of SO₂ on the SOA yield for guaiacol oxidization in the presence of NO_x and seed aerosols. The authors report increased SOA yields for increasing amounts of SO₂ in the chamber and also observe an increased carbon oxidation state. This research is important for understanding the impact of gas-phase precursors on SOA formation, with relevance for severely polluted regions in China. This is a valuable set of experiments, however, the interpretation is not fully supported by the presented results. Before publication, I recommend the authors provide more detailed information on the results from the chamber experiments, as outlined below. These additional data sets will help support the conclusions made in the current manuscript.

1. The big question I have for this paper is what part of the observations is due to chemical differences (i.e. different SOA formation mechanisms) and what part is due to changes in the physical system (i.e. more seed surface area = more SOA). To understand these results, it would really help to be able to compare the data sets for the experiments. Can you show experimental traces (AMS and PTR-MS) for some of these experiments?

For the particle phase: When/how does the particulate sulfate from SO₂ grow in? What is the NH₄⁺ doing? Does it rise as well or is the pH of the particles dropping (forming H₂SO₄) or are you forming organic sulfate? What about the NO₃⁻ and NO₂⁻ ions? Do they grow in at the same rate for all experiments? When the lights are turned on for the different experiments, are there any differences in the induction period before SOA growth is observed? How do the chemical properties change with time (What is the time series for the O/C, H/C, and N/C)?

For the gas phase: What do the experimental traces from the PTR-MS look like? Does the decay in Guaiacol look the same in all experiments? Are any other VOC products observed during the experiments? If so, are there any differences between experiments and what do the time series for these products look like? What do the time traces for NO_x and SO₂ look like?

2. Error bars on the comparison plots (Figs 2, 4, 5, and 7) would really help with interpretation. Were replicate experiments at some of the same initial conditions run? How much variation was observed?

3. What is the motivation for the PMF analysis? The difference between the two factors appears to be dominated by the intensity difference for CO₂⁺. Do you expect a difference in chemical formation/aging when SO₂ is added? It looks like there is a difference in the chemical properties of the aerosol as a function of time for the different systems (Figure S4). Is this due to different chemistry or differences in partitioning of condensable vapors to the particles? Please also include more information on how the

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PMF analysis was carried out in the supplemental.

4. You claim that oligomerization reactions will decrease the oxidation state of the SOA (page 12, line 236). How does this occur (please either explain or provide references)? Oligomerization should lead to an increase in carbon number but little change in the net O/C or H/C values for the oligomer.

5. How are the spectra in Figures S5, S9, and S10 normalized? Are they normalized to the max intensity or to the sum of the intensities? It looks like there is very little negative ion intensity in many of the figures which I would not expect if these are normalized to the sum. When are these mass spectra taken from in terms of experiment time? Are they the average over the whole or the end only? Please also increase the size of this figure, it is very difficult to read which m/z values are negative.

6. Please briefly outline how organosulfate concentration was calculated (page 13, line 251). In figure S6, what is the system being shown? Is this methyl sulfate alone or is it a mixture? If it is methyl sulfate alone, why are there so many oxidized and reduced nitrogen peaks fit under the curve? When fitting AMS data, it is best to use the smallest number of ions to fit the curve as you can always improve the fit by adding more ions.

7. You note on line 267, page 13 that you do not see evidence of H₂SO₄ formation. Is this conclusion drawn from a lack of the ion(s) observed in the AMS? Have you run acidified ammonium sulfate particles? How do the mass spectra of the sulfate peaks from acidified ammonium sulfate measured in your AMS compare to the sulfate peaks observed here?

In Table 2 you note that the sulfate concentration formed via SO₂ oxidation increases with more SO₂ in the chamber (~10-20 ug/m³). You also note that the organosulfate concentration was in the range of 2.1-4.3 ng/m³ (page 13, line 250). What is the identity of the remaining sulfate in the particles (ammonium sulfate, sulfuric acid)? Going back to the first question, what does its time trace look like?

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8. Even if the surface area of the aerosol particles is much smaller than that of the smog chamber (page 14 line 276) I would still expect that small increases in the surface area of particles for condensation would have an effect on SOA yield. Your data for surface area and SOA yield appears to follow a relatively linear trend. Can you run an experiment with the same initial surface area with and without SO₂? (i.e. start with higher initial seed in the experiment without SO₂). This will help interpret the influence of SO₂ on SOA yield.

9. In Figure 6, the intensity of CO⁺ does not match the intensity of CO₂⁺. What fragmentation tables are being used to calculate the CO⁺ ion? Usually, that is set at the same value as CO₂⁺ because of interference from atmospheric N₂⁺. When (during the experiment) are these mass spectra collected? Are they an average over the whole or the end of the experiments? How reproducible are these differences? Is the difference spectra shown in Figure 6c observed for all the combinations of NaCl and ammonium sulfate seeds (at the same SO₂ concentrations)?

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