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Atmospheric Chemistry and Physics
Discussions
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Interactive comment on "Formation of secondary aerosols from gasoline vehicle exhausts when mixing with SO_2" *by* T. Liu et al.

Anonymous Referee #3

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Liu et al present a series of smog chamber experiments where secondary organic aerosol (SOA) was generated from the photo-oxidation of gasoline vehicle exhaust. Data are presented from three vehicles. For each vehicle, an experiment was conducted both with and without the addition of SO2 to the smog chamber. In all cases, adding SO2 increased SOA production.

Overall the manuscript is topically relevant to Atmospheric Chemistry and Physics and should eventually be published. However, in my opinion the manuscript requires major revisions before it is ready for final publication.

I agree with Reviewer #2 that a thorough copy edit of the manuscript is required. There are many instances where the wording is awkward. My concerns about the manuscript

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run deeper than simple copy editing. Even after multiple readings, I am still left scratching my head regarding the major conclusions of this work. In many ways the manuscript reads as a long list of observations with very little in the way of interpretation. The authors need to make a stronger case for the new knowledge gained from these experiments and the atmospheric relevance or insight that these results provide.

Specific comments:

1. Section 2.4 - Toluene is used to determine the average [OH] in each experiment. While this is a common method for estimating [OH], it seems inappropriate to assume a constant [OH] for the entire experiment. [OH] is likely to change over the course of photo-oxidation, and therefore it would be more appropriate for the authors to calculate [OH] over shorter time scales (e.g., 1-hr or 30-min averages). Additionally, the authors do not specify if [OH] estimates only account for the portion of the experiment when the UV lamps are on. While [OH] likely drops rapidly to zero once the UV lamps are turned off, If sufficient O3 is formed during photo-oxidation, it would be possible for [OH] to remain non-zero during the dark period at the end of the experiment.

2. Section 2.4 describes how the average [OH] was calculated, but the values are not reported. Average [OH] needs to be reported, especially since the authors argue that OH oxidation alone is insufficient to explain the observed SO2 loss in these experiments.

3. The factor phi in the numerator of equation 5 is not defined.

4. Section 2.5-It is not clear how the concentrations of stabilized CI were calculated with the master chemical mechanism. Lines 19-21 of page 23621 suggest that the full chemical mechanism was used to determine concentrations of sCI. However, lines 1-7 of page 23622 suggest that all sCI were treated as CH2OO, CH3CHOO, or (CH3)2CHOO. However, the lumping scheme used to reduce the possible set of CIs to these three is not described. Additionally, the yields of the three possible CIs used in the model sum to a number greater than unity.

5. Page 23623, Line 4: “NO was fast oxidized” needs to be edited.

6. Vehicle 1 and 2 (Fig 2 and 3) both generate particulate nitrate in the no-SO2 experiment, and in each case the nitrate mass falls after an initial peak (I am assuming that Figs 1-3 show wall loss corrected masses of PM components). Nitrate formation is suppressed in the with-SO2 experiments for both vehicles. The nitrate is not discussed at all in the text. This needs to be remedied. Is the nitrate dominated by inorganic or organic nitrates? If the nitrate is organic, and adding SO2 causes a large loss of organic nitrates in the SOA, this would be an extremely interesting finding.

7. A major theme of the manuscript is described in Figure 6 - SO2 losses cannot be explained by OH oxidation alone. The authors attribute additional OH loss to reactions with stabilized CI. I do not find their argument convincing. Part of my skepticism arises from comments 3 and 4 above, and the author’s generally cursory description of their use of the MCM in this work.

8. I fundamentally disagree with the author’s assertions (summarized in the Conclusions) that gasoline exhaust has sufficient alkenes to be a major source of sCI in the atmosphere and that these sCI could play a major role in SOA formation. I simply don’t see the evidence presented in this manuscript to properly justify this claim. Gasoline exhaust is dominated by alkanes and aromatics (e.g., May et al 2014; Schauer et al 2002), not alkenes, and there are many other, larger sources of atmospheric alkenes (e.g., isoprene and monoterpenes).

9. I cannot tell what I am supposed to learn from Figure 5. The figure is very hard to read and interpret. It either needs to be edited for clarity or removed.

10. Is it possible that some of the SO2 loss, and some of the resultant PM mass during photo-oxidation, is in the form of organosulfates? Organosulfates have been observed in the ambient atmosphere using AMS, so marker ions should be available to investigate this possibility.

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11. Figure 8 is nearly uninterpretable. What does the intensity on the vertical axis indicate? It seems to first order that m/z 88 is more abundant in the SO2 experiment, but there is a lot of scatter in the data.

12. What does Figure 9 add to the manuscript that is not present in Fig 7? Its presence in the manuscript seems redundant.

13. Fig 10 should include the composition of the POA

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