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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Investigative modeling of new pathways for secondary organic aerosol formation” *by* B. K. Pun and C. Seigneur

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We would like to thank the anonymous reviewers for their input. Our responses to key issues raised are denoted using "R:" below. Editorial changes and clarifications to text and tables are also made as requested by the referees.

Anonymous Referee #1 ... The reader would greatly benefit from a clearer road map and indications early in the text of which topics will be re-visited and which sensitivities explored.

R: We have added a road map in the introduction to present the overall organization of information in terms of “model formulation” and “sensitivity investigations”.

p. 6: Since the Martin-Reviejo and Wirtz [2005] study was used to constrain benzene yields, it would helpful to see if the 0D model reproduces the experimental results

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obtained by those authors under varying initial conditions and as a function of time (for example comparing model with Figures 5, 7 and/or 8 of that paper).

R: This is an interesting exercise and the results have been added to the benzene subsection. The model predicts a range of SOA yields from 11-25% (vs. the observed yields of 8-25%) for individual experiments in Martin-Reviejo and Wirtz (2005). The average model bias is +5%, and the average error is approximately 20%. At present, there are significant uncertainties in the gas-phase chemical mechanisms for benzene leading to SOA formation. The investigative model focuses on reproducing the yield and the complex dependence on NOx is not represented. We do not present time-dependent results here as this would require simulation of the gas-phase chemistry of the experiment in addition to the SOA formation and partitioning.

Section 4.1 is lengthy and occasionally hard to follow. A clearer overall description of how oligomerization is to be treated is required up-front.

R: An overall description of the treatment of oligomerization is provided prior to the derivation.

Section 5: I suggest that the authors quantify the overall effect of including oligomerization for all precursors in terms of total yield (as a function of pH) and discuss which SOA precursor class is most enhanced by this additional mechanism. This is commonly not treated in models and would seem a key result of this work.

R: Acoording to our model formulation, the overall effect of oligomerization depends on the fraction of SOA that are aldehydes as well as the partition characteristics without oligomer formation at the given conditions (LWC, POC, total condensables, T). At conditions favoring the partition of the monomers to the particulate phase, e.g., low temperature, high LWC, high POC, high SOA concentrations, the effect of oligomerization is expected to be small. We have included an example of alpha-pinene + O3 to illustrate a range of enhancement of SOA due to oligomerization (5 - 54%) depending on the total SOA formed under experimental conditions of Griffin et al. (1999). We have

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added some discussion about the relative enhancement seen under a specific set of test condition for several compounds. Except under conditions of low LWC or POC that are less favorable to the particulate phase equilibrium, the effect of oligomerization is relatively small for monomer products that have low vapor pressure (e.g., humulene and alpha-pinene-O3 products) because the monomers already reside in the particulate phase. Oligomerization enhances SOA formation from precursors (e.g., a-pinene + OH; terpineol, terpinene) with large fractions of products subject to oligomerization, especially for relatively volatile monomers. SOA yields are also enhanced for aromatics because of oligomerization of glyoxal. This information is now included in the text.

Anonymous Referee #2

1) Benzene, isoprene, and oligomerization all receive separate treatments, but this seems unnecessary. A major product of benzene oxidation is glyoxal (and similar ringopening products); a major product of isoprene oxidation is methylglyoxal. Both dialdehydes are generally believed to contribute to SOA via oligomerization (at least at high RH). It is not clear why they require different treatments, which are also distinct from the treatment that other oligomerizing aldehydes receive. Is there any way to represent these three related systems using a single framework for partitioning?

R: The manuscript presents three aspects of model development, but they are not disjointed. As the reviewer points out, all aromatic compounds produce glyoxal, which undergoes oligomerization like the aldehyde fraction of the surrogate condensables. The only difference is that because of the availability of thermodynamic data, the gas-particle partitioning for glyoxal is characterized using a Henry's law constant as opposed to an experimentally derived partitioning constant for the surrogate SOA products.

Of specific concern is glyoxal and methylglyoxal; the two are extremely similar structurally (differing by only a CH2 group) and yet in this manuscript their partitioning involves fundamentally different physics (Henry's Law vs. APR). It would seem methyl-

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glyoxal, a water-soluble organic, should be well-described by a Henry's Law treatment (the same could be said for the other 2nd-generation isoprene products).

R: The treatment for MGLY using the APR approach is a special case. The observed APR should account for the effects of particulate-phase reactions (e.g., hydration and oligomerization) of MGLY. We selected the simple APR approach instead of following the approach for GLY because the effective Henry's law constant for MGLY is lower than GLY, and there are conflicting theories regarding the role of acid-catalyzed oligomerization (Kroll et al., 2005; Zhao et al., 2006).

2) Given that the various systems examined in this work are generally poorly understood, and this work represents one of the first attempts to describe them within a model, it would be extremely useful to test these new modeling approaches against observations. This strikes me as an important step to take prior to the sensitivity studies (which are also very useful), as much could be learned about the various systems.

R: Comparisons with experimental data have been added in the discussions for benzene, isoprene, and oligomerization. We appreciate the reviewer's suggestion, and agree that this step is a useful check for the model formulation.

For example: - how well does the APR approach reproduce the Kroll et al (2005) or Dommen et al (2006) chamber isoprene data?

R: The experiments of Kroll et al. (2006) are performed at low relative humidity; all but one experiments of Dommen et al. (2006) are performed at relative humidity below 60%. Both groups performed isoprene photo-oxidation experiments, where OH is expected to be the dominant oxidant. The APR approach results in a maximum SOA yield of approximately 7% when RH $<$ 60%, if the isoprene + OH reaction is allowed to go to completion. This SOA yield value is slightly higher than the range reported by Kroll et al. (2006) (0.9-5.5%) and the range reported by Dommen et al. (0.2-5.3%).

- how well does the approach towards benzene oxidation (with glyoxal partitioning) reproduce the Martin-Reviejo and Wirtz (2005) data?

R: Because the Martin-Reviejo and Wirtz (2005) data are used to constrain the derivation of the partitioning parameter, we expect the model to be able to reproduce the SOA yields of individual experiments fairly well. The model predicts a range of 11-25% SOA yield under the experimental conditions, as opposed to the 8-25% range observed. The average bias is +5% and the average error is approximately 20%.

- there is substantial evidence that aldehydes undergo oligomerization in the presence of ammonium sulfate seed; how well does this treatment of oligomerization reproduce chamber data from terpene or aromatic oxidation (from which aldehydes are major products)? The acidity-dependent studies of Jang et al or Gao et al (2004) may be particularly useful for testing the predicted pH dependence. Making each one of these comparisons is probably not necessary; but some comparison with laboratory data would serve as an excellent diagnostic for the appropriateness of the various approaches towards partitioning (APR, Henry's Law, Kp) described in this work.

R: We applied the oligomerization algorithm to a set of alpha-pinene + O3 chamber experiments reported by Griffin et al. (1999) from which the partitioning parameters (alpha, Kp) for this model are obtained. Because these experiments were conducted with ammonium sulfate seed, we applied the oligomerization algorithm to estimate the enhancement of SOA yields due to the use of ammonium sulfate-sulfuric acid seed and compare the relative yield difference (RYD) with the values seen in Gao et al. (2004). For a range of VOC values from 17 to 65 ppb , the RYDs range from 0.5 to 0.05. The range of values is in good agreement with the range seen by Gao et al. when different mixing ratios are used. The decreasing RYD trend with increasing precursor concentrations is properly reproduced. Gao et al. performed two experiments using ammonium sulfate seed, one of which is comparable in concentration with two of Griffin's experiments. For those experiments, the model predicts an RYD of 5-6%, which is in good agreement with the observed RYD (5%) from Gao et al.

3) For context, in the sensitivity studies, it would be useful if typical values of LWC and pH were given for both atmospheric and chamber conditions, preferably with citations.

R: Liquid water content is a function of ambient RH. At 90% RH, LWC can range from $<$100 to 250 microg/m3 (Jacobson, 1999 p.514). LWC of ˜5-90 microg/m3 was measured at 80-85% RH in Claremont, CA (Finlayson-Pitts and Pitts, 2000 p.411). Aerosol pH depends on the inorganic components. Alkaline particles can be formed near coastal areas, but can be as low as -1 to 2 (Jacobson, 1999 p.515). Under typical urban and coastal conditions, Zhang et al. (1999) simulated 0 - 400 microg/m3 LWC (with significant discrepancies among models) and corresponding pH of -1.2 to 6.4.

4) The treatment of oligomerization (section 4.1) is quite hard to follow, and a general explanation of the overall approach used would be helpful.

R: An overall description of the treatment of oligomerization is provided prior to the derivation.

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