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Comment

Interactive comment on “Simulation of aromatic SOA formation using the lumping model integrated with explicit gas-phase kinetic mechanisms and aerosol-phase reactions” by Y. Im et al.

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We thank reviewer 2 for valuable comments.

The manuscript by Im et al. reports on the development and application of the UNIPAR model for prediction of SOA produced in smog chamber experiments by oxidation of toluene and 1,3,5-trimethylbenzene. While advancements in SOA modeling clearly are needed, particularly in the representation of particle-phase and heterogeneous

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reactions, in its current state the manuscript does not stand to advance the field to a great degree. The model likely is too computationally expensive and is highly empirical, making its application in regional/global chemical transport models unlikely and potentially irrelevant. Possibly a better goal of the model would be to provide insight into the relative importance of particle-phase and heterogeneous reactions (in this case, generalized oligomer formation and (inorganic) acid-catalyzed organosulfate formation) for SOA formation under a variety of atmospherically-relevant conditions (based on new or published chamber studies). With a significant amount of the relevant material in the supplemental section, the manuscript is somewhat hard to follow. And again, the relevant conclusions and implications are lacking. It is recommended that the manuscript be reevaluated after significant revision.

Response:

The UNIPAR model can be easily implemented to the regional/global models because the development of the UNIPAR model follows a similar modularity employed in the CMAQ model. Although UNIPAR is developed with many sub models (e.g., MCM, UNIFAC, aerosol phase reaction, inorganic thermodynamics), it requires relatively few inputs at run time because the UNIPAR model itself is a self-contained FORTRAN module that needs inputs commonly available in regional/global air quality models. This module also includes built-in thermodynamic parameters (e.g., activity coefficients of lumped groups in inorganic phase and temperature dependency of partitioning coefficients) and a lumping matrix that is filled based on the VOC/NO_x ratio, which is necessary for the SOA prediction. In addition, the SOA production via aerosol phase reactions is simply approached with analytical solutions.

In order to respond to the reviewer's comment, section "5 Model uncertainty and implications" has been rewritten.

Scientific Comments:

1) Abstract-The authors mention the use of the SOA partitioning model in CMAQv5.0.1 (newest release); however, it is not clear what (if any) unique features of this model

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are being applied. The SOA model in CMAQv.5.0.1 has its own treatment of oligomer formation and non-volatile SOA formation via oxidation of aromatic compounds under low- NO_x conditions. Comparison with the CMAQ SOA model may be one way in which the manuscript could be improved. It rather appears that standard gas/particle partitioning theory is being applied.

Response:

In the UNIPAR model, the estimation of the organic matter (OM_P) by gas-particle partitioning of SVOCs was approached using the numerical method which had been used in CMAQV5.0.1, but aerosol phase reactions including oligomerization, acid catalyzed reaction, and organosulfate formation were approached by our own modules. Please find section 3.6 SOA formation by partitioning (OM_P)

“The estimation of OM_P is approached using the partitioning module derived by Schell et al. (2001), which has been employed in CMAQ. In UNIPAR, the partitioning module approached by Schell et al. has been modified by inclusion of OM_{AR} (Cao and Jang, 2010) and reconstructed into OM_P based on a mass balance of organic compounds between the gas and particle phases.”

2) p. 5845 line 10-The VBS model does not account for oxidation reactions in the condensed phase.

Response:

The VBS model empirically remaps volatility bins to describe the evolution of oxidation of products in both the gas and the condensed phase. (Donahue et al., 2006)

3) p. 5850 line 21- **(A)** The model assumes ideality for compounds condensing into the organic phase, while estimating partitioning coefficients for compounds partitioning into the inorganic/aqueous phase, citing Zuend and Seinfeld, (2012). However, Zuend and Seinfeld (2012) indicate that treating particles as two separate phases at high RH (which applies to the chamber experiments reported) is not justified-rather the particles likely exist as a single phase. **(B)** In addition, the O:C

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ratio is an important parameter for understanding mixing and phase separation (in the absence of detailed modeling). The manuscript does not address predicted/measured changes in O:C ratios (say as a function of oligomerization), which may have an impact on the assumed two-phase system, as well as the activity coefficients of condensing compounds (i.e., is the nature of the condensed phase very different if dominated by monomers vs. dimers and how is the partitioning of each affected). Zuend and Seinfeld conclude that assuming ideality at high RH (>60%) greatly overpredicts SOA mass (if the system has relatively low O:C ratios). It is recommended that the authors consider O:C ratios and the effects on partitioning/phase separation, and potentially the prediction of activity coefficients for partitioning into an organic phase (if not justified to assume phase separation and/or ideality in the organic phase).

Response:

(A)
In the study of Zuend and Seinfeld (2012), high RH referred to conditions greater than 90%. However, the chamber experiments of this study were conducted under RH of less than 90%. Generally RH greater than 90% is unusual in the ambient condition except during the nighttime and early morning. For 135-TMB SOA, RH was higher than 90% in the early morning but the SOA formation from this period of the experiment was negligible.

(B)
Zuend and Seinfeld (2012) estimated the activity coefficients of organic compounds for a non-ideal mixture of organic/inorganic salt solution using the thermodynamic model (AIOMFAC) integrated with vapor pressure calculation. They proposed that gas-particle partitioning of organic compounds were better-predicted under the assumption of a complete organic/electrolyte phase separation below a certain RH in systems. They applied the model to the ozone- α -pinene SOA/ammonium sulfate particle system, in which the average oxygen-to-carbon (O:C) ratio is lower than 0.6, with assumption of complete LLPS under ambient RH. The predicted ozone- α -pinene SOA mass yields agreed well with experimental data with the assumption of non-ideal

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mixing while SOA yields were over-predicted under the assumption of ideal mixing (activity coefficient =1).

For the discussion on the relation between O:C ratios and phase separation, please find the responses to questions 3 and 4 from reviewer 1 and section “3.3 Product concentrations among the gas, organic and inorganic aerosol phases” in the revised manuscript. In recent chamber studies, Nakao et al. (2011) measured O:C ratios of various aromatic SOAs. In their study, O:C ratios of toluene SOA were up to 0.65 and those of m-xylene were up to 0.45. In our study, the O:C ratio of SOA from photooxidation of toluene and 135-TMB were not measured. To response to the reviewer’s comment, we have attempted to estimate the O:C ratio using the product compositions predicted from the UNIPAR model. The predicted O:C ratio of toluene SOA and 135-TMB SOA were around 0.62 and 0.37 and close to the reported O:C ratios by Nakao et al. (2011).

In the study of Bertram et al. (2011), the LLPS of organic/ammonium sulfate particle has been semi-empirically predicted using elemental O:C ratio and relative humidity. Based on our O:C ratio (0.62 for toluene SOA and 0.37 for 135-TMB SOA), the predicted RH values of LLPS using the semiempirical equation derived by Bertram et al. (2011) are 65% for toluene SOA and 90% for 135-TMB SOA. Thus, the assumption of phase separation for aromatic SOA in the UNIPAR model can be justified by the fact that current chamber experiments are conducted under lower than 65% RH for toluene SOA and lower than 90% RH for 135-TMB SOA, except for short period at the beginning of each experiment. The SOA formation is negligible during that beginning of experiment (less than 1 hour).

When we constructed the SOA model, we also considered the phase separation issue. Although we did not thoroughly discuss our efforts in handling the assumption regarding phase separation, we have built our SOA model based on two possible assumptions including phase separation and single phase. For toluene SOA and 135-TMB SOA, we have approached the model based on assumption of phase separation, which is supported by both the estimated and reported O:C ratios. However, for other

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hydrophilic SOA systems or high humidity conditions, which are operated by single phase, the different model approach will be necessary.

4) S6-If I understand correctly, the possible list of products is the same (albeit differently weighted-different alpha values) under low vs. high NO_x conditions. Is this consistent with chamber studies in which products have been measured?

Response:

Very few SOA products have been identified, although much effort has been expended in aromatic SOA product identification. For example, in a recent study by Sato et al. (2007) using liquid chromatography-mass spectrometry (LC-MS), only $\sim 1\text{wt}\%$ of the total mass of aerosol products from the photooxidation of toluene were identified. In this study, major products predicted by MCM were glyoxal and methylglyoxal for toluene and methylglyoxal and 2-Methyl-4-oxo-2-pentenal for 135-TMB. Those products have been experimentally observed in many studies. For example, in product characterization of toluene SOA using the proton transfer reaction mass spectrometry (PTR-MS), Alvarez et al. (2007) have reported glyoxal, methylglyoxal, 4-oxo-2-pentenal, butenedial as the most abundant aldehyde products. In the study of Smith et al. (1999), methylglyoxal, 3-methyl-5-methylidene-5(2H)-furanone, 3,5-dimethyl-3(2H)-2-furanone, 3,5-dimethyl-5(2H)-2-furanone biacetyl, and 2-methyl-4-oxo-2-pentenal were observed for 1,3,5-TMB photooxidation. In order to respond to the reviewer, the current status for product characterization of aromatic SOA has been discussed in the beginning of “section 5. Model uncertainty and implications”.

5) Is the initial product distribution determined from a low- NO_x MCM run and then fitting done with decreasing VOC/NO_x ratio? Assuming that is the case, what happens if initial predictions are done for high- NO_x conditions and then fitting with increasing VOC/NO_x ratio?

Response:

Product distributions ($\alpha_{i,j}$ matrix) were simulated for series of initial VOC/NO_x ratios,

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and then each $\alpha_{i,j}$ value was mathematically fitted as a function of initial VOC/ NO_x ratio using a regression equation (described in detail in Supplement Section S6). The resulting regression equations for each lumping group were built-in in the UNIPAR model. When the initial condition (VOC/ NO_x ratio) is input into the model, the $\alpha_{i,j}$ matrix is computed from the model and used for simulating SOA mass.

6) Figure S9-The model simulations show that for toluene, the oligomer fraction decreases as NO_x decreases. However, Ng et al. (2007) report that under low- NO_x conditions, the SOA that forms is effectively non-volatile (suggesting a greater extent of oligomer formation). This is not discussed anywhere in the manuscript.

Response:

In the study of Ng et al. (2007), the higher SOA formation was observed in the lower NO_x condition (actually H_2O_2 experiment without addition of NO_x) for toluene photooxidation. They suggested that less volatile products formed in the lower NO_x condition due to RO_2 radical chemistry. However, there was no discussion about oligomer formation by aerosol phase reaction (no suggestion of greater extent of oligomer formation in low NO_x conditions). In their study, SOA yields were measured without product analysis, which means that the extent of oligomer fraction could not be evaluated. Overall, the NO_x effect on total SOA yields (OM_T) in this study (green line in Fig. S9) is consistent with the Ng et al.'s study. We cited other studies at the end of the 1st paragraph of section 4.2 Effect of NO_x on aromatic SOA formation.

Editorial Comments:

7) p. 5846 line 10-Need reference(s) for CMAQ model.

Response:

The reference was added as is shown below:

“regional air quality model (CMAQ 5.0.1, <http://www.cmaq-model.org/>, 2013)”

8) p. 5850 line 14-Not sure why OM_T is used instead of M_{or} (since M_{in} is

used for total inorganic mass).

Response:

In this model the total OM (OM_T) is formed by partitioning (OM_P) and aerosol phase reactions (OM_{AR}): $OM_T = OM_P + OM_{AR}$. Symbol " OM_T " would be much simpler than " M_{or} ". If M_{or} is used, OM_P and OM_{AR} need to be substituted with $M_{or,P}$ and $M_{or,AR}$, respectively, which looks more complicated.

9) p. 5852 line 20-The authors state that if $RH < ERH$, the particle is crystallized and acid-catalyzed reactions can't occur. However, they go on to state that the inorganic phase reaction was restricted to the dry condition ($RH < ERH$).

Response:

The author used "restricted" as a meaning of "excluded"

"the inorganic aerosol phase reaction was excluded in the dry condition ($RH < ERH$)"

10) It is suggested that the authors reconsider the order of the supplement material (e.g., section S5 should go before S4).

Response:

The section S4 is referred earlier than section S5 in main manuscript. Thus, it would be better to keep the current order.

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