**Reviewer 2**

**Interactive comment on** "Simulation of SOA Formation from the Photooxidation of Monoalkylbenzenes in the Presence of Aqueous Aerosols Containing Electrolytes under Various $NO_x$ Levels" by Chufan Zhou et al.

Chufan Zhou, Myoseon Jang, and Zechen Yu
mjang@ufl.edu

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We appreciate the reviewer for the valuable comments.

**Major comments:**

**(1)** It is unclear which experiments were conducted in sunlight, and how this important factor affected the results. The paper mentions that the sunlight from one experiment performed near summer solstice was used in gas-phase simulations, apparently for all experiments, even those conducted in mid-winter. Were all experiments performed on clear days? How might using more intense sunlight in simulations of winter experiments affect the uncertainties of the results?

**Response:**

Please also find the response to the major comment from reviewer 1. All the simulations were performed by using natural sunlight. As described in Section 3.1 in the manuscript, the aging scale factor is defined as $f_A(t) = log\frac{[HO_2]+[RO_2]}{[HC]_0}$. In order to set the aging scale factor for the fresh ($f_A(fresh)$) and highly aged processing ($f_A(higly\ aged)$) of hydrocarbon oxidation, we utilized the sunlight intensity near summer solstice (on 06/14/2018 with a clear sky in Gainesville, Florida (29.64185° N, 82.347883° W)). The aging factor ($f_A'(t)$) at time = t is estimated by using the equation below,

$$f_A'(t) = \frac{f_A(highly\ aged)\ -\ f_A(t)}{f_A(highly\ aged)\ -\ f_A(fresh)}$$

Then, the $\alpha_i$ set is dynamically reconstructed by a weighted average method (Eq. (2) in the manuscript) using fresh $\alpha_i$ set, highly aged $\alpha_i$ set and $f_A'$(t).

**(2)** p. 6 line 10: Was oligomerization in both the organic phase and the aqueous (inorganic) phase based on self-dimerization of individual products, or lumped products? In other words, were cross-reactions possible between molecules lumped into a single bin?

**Response:**

In UNIPAR model, oligomerization of organic compounds is processed in both the organic and the inorganic phases based on the self-dimerization reaction of lumped products. The cross-reactions between lumped species are complex. If highly reactive organic species react with weakly reactive species, this oligomerization may be less than the reaction of highly reactive organic species in a single bin but greater than the reaction of weakly reactive organic species in a single bin. Ultimately, they can be compensated in the production of organic matter. Thus, oligomerization in UNIAPR was treated as self-dimerization of lumped products within a single bin (Jang et al., 2005;Jang et al., 2006).

**(3)** p. 10 line 32: The authors identify a large temperature effect on SOA yields, as seen in other studies. However, the authors are uniquely positioned to identify whether this effect is due only to partitioning, as typically assumed, or is also due to temperature dependent reactions that either destroy condensable species or produce other species that hinder gas-to-particle transfers. Partitioning seems to be such a minor SOA source in this study that it is surprising that the observed temperature effects are so pronounced. Could the authors probe the cause of the temperature effect?

**Response:**

Gaseous lumped species first partitions onto aerosols based on a traditional gas-particle partitioning theory. In UNIAPR, the oligomerizations rate is processed by a second order reaction as follows.

$$\frac{dC_{or,i}}{dt} = -k_{o,i}{C'_{or,i}}^2\left(\frac{MW_i OM_T}{\rho_{or}\,10^3}\right), \qquad \text{(Eq. 6 in the manuscript)}$$

$$\frac{dC_{in,i}}{dt} = -k_{AC,i}{C'_{in,i}}^2\left(\frac{MW_i M_{in}}{\rho_{in}\,10^3}\right), \qquad \text{(Eq. 7 in the manuscript)}$$

The oligomerization rate constants (L mol$^{-1}$ s$^{-1}$) in the organic (*or*) phase and inorganic (*in*) phase are $k_{o,i}$ and $k_{AC,i}$, respectively. The bracketed terms in the equations are the conversion factors from aerosol-base concentrations ($C'_{or,i}$ and $C'_{in,i}$: mol L$^{-1}$) into air-base concentrations (μg m$^{-3}$) (Section S5). $\rho_{or}$ and $\rho_{in}$ represent the density of the *or* and *in* aerosol. The concentrations (μg m$^{-3}$ of air) of species *i* in the gas phase ($C_{g,i}$), *or* phase ($C_{or,i}$) and *in* phase ($C_{in,i}$) are estimated using partitioning coefficients in the multiphase: i.e., $K_{or,i}$ (m$^3$ μg$^{-1}$, *g* /*or*) and $K_{in,i}$ (m$^3$ μg$^{-1}$, *g* /*in*). $K_{or,i}$ and $K_{in,i}$ are calculated (by Pankow(Pankow, 1994)) by using estimated activity coefficients in the *or* and *in* phase ($\gamma_{or,i}$ and $\gamma_{in,i}$), the mass concentration of media ($OM_T$ and $M_{in}$), and vapor pressure ($p_l^{\circ}$) (See Section 3.3 SOA formation: aerosol-phase reactions). If $C_{or,i}$ and $C_{in,i}$ increase, the formation of oligomerization also increases. Numerous studies have shown that a large fraction of SOA is oligomers (Tolocka et al., 2004;Loeffler et al., 2006;Hoffer, 2004;Baltensperger et al., 2005;Hastings et al., 2005;Riva et al., 2019).

**(4)** In Figure 5, dialkyl organosulfates (diOS) concentrations seem to track ammonium concentrations. In one experiment, the authors comment that diOS formation ceases when the aerosol effloresces. Is there any causative relationship between diOS and ammonium concentrations in wet aerosol?

**Response:**

When acidity is high in wet aerosol, both the diOS formation and the neutralization of acidic sulfate with ammonia can occur. When the inorganic phase is effloresced (no aqueous phase), organic compounds cannot be dissolved in the inorganic phase. Generally, the neutralization of acidic sulfate with ammonia in wet aerosol is faster than OS formation. When the gaseous ammonia concentration is high, sulfuric acid will be consumed by ammonia and thus the formation of diOS can be less. The formation of diOS depends on the concentrations of both acidic sulfate and reactive organic species in the aerosol phase. The prediction of the diOS formation ($[diOS]_{model}$) is performed using the semiempirical equation derived previously for several SOA systems such as aromatic and isoprene SOA (Im et al., 2014;Beardsley and Jang, 2016) as follows,

$$\frac{[diOS]_{model}}{[SO_4^{2-}]_{free}} = 1 - \frac{1}{1 + f_{diOS}\frac{N_{diOS}}{[SO_4^{2-}]_{free}}}, \qquad \text{(Eq. 9 in the manuscript)}$$

$N_{diOS}$ represents the numeric parameter originating from the quantity of reactive chemical species available to form diOS. This parameter is near-explicitly predicted in the model. $f_{diOS}$ represents the semi-empirically determined diOS conversion factor using various chamber data. At each time step, acidic free sulfate ($[SO_4^{2-}]_{free}$), which is the sulfate that is unassociated with ammonium ($[NH_4^+]$), is estimated as ($[SO_4^{2-}] - 0.5\,[NH_4^+]$) and applied to estimate $[diOS]_{model}$. As seen in the equation above, diOS formation ($\frac{[diOS]_{model}}{[SO_4^{2-}]_{free}}$) is not linearly related to $[SO_4^{2-}]_{free}$. Generally, the high proton concentration ([H$^+$]) in the aerosol indicates the high concentration of $[SO_4^{2-}]_{free}$

available for diOS formation. In the morning when humidity is high (>80%), gaseous ammonia concentrations are low because they are condensed on the chamber wall. The ammonia concentrations rise in daytime when humidity is low because ammonia is off-gassing from the chamber wall. Hence, the formation rate of diOS decreases by the two reasons: (1) the consumption of $[SO_4^{2-}]_{free}$ due to diOS formation and (2) the neutralization of $[SO_4^{2-}]_{free}$ with gaseous ammonia as shown in Figure 5 (flat diOS curve in the afternoon).

**(5)** Figure 7 implies that in most experiments, aqueous-phase SOA production is much greater than SOA production via traditional partitioning mechanisms, but the authors don't seem to make this comparison or comment on it. Is it a fair comparison?

**Response:**

The traditional partitioning-based SOA models such as two products model (Odum et al., 1996) or several semivolatile surrogates model (e.g., volatility basis set (VBS)) (Donahue et al., 2006) utilizes semiempirical parameters (e.g., the product stoichiometric coefficient ($\alpha$) and gas-particle partitioning coefficient ($K_p$)) for each HC system under a given $NO_x$ condition. The parameters in traditional partitioning-base models are apparently fit to observed SOA mass. Although the theory facilitates the predicting of SOA mass in the absence of inorganic seed, the SOA mass from the traditional surrogate-based partitioning models is not truly partitioning mass. In UNIAPR, $OM_P$ is predicted solely by the partitioning theory using a near-explicit molecular structure with their activity coefficient and vapor pressure and thus $OM_P$ will be less than the mass prediction using a traditional surrogate-based partitioning models.

**(6)** Figure S1 indicates that ozone is generated too quickly in the model, sometimes by a factor of 2 or 3. Can the authors comment on the implications of this overprediction? Is it related to the "artificial OH radicals" added to the model in certain experiments?

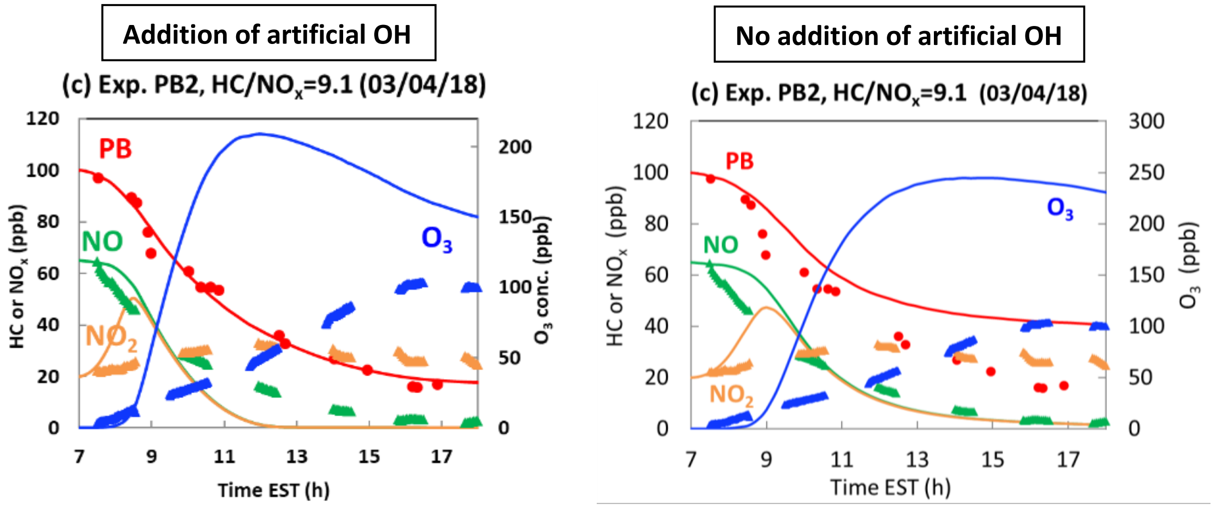
**Response:**

The over-prediction of ozone is not due to an artificial OH radical. As shown in the Figure below, ozone is over-predicted by removing make-up of artificial OH radicals. However, both the addition of artificial OH radicals and overestimation of ozone indicate potential problems in MCM for oxidation of monoalkylbenzenes. The MCM developers and other researchers also reported over-prediction of ozone for aromatic photooxidation (Bloss et al., 2005;Wagner et al., 2003). We have performed numerous chamber experiments. The overestimation of ozone using MCM appears in monoalkylbenzene series, while a good agreement between predictions and observations is found in xylenes, and trimethylbenzenes, terpenes and isoprene. We propose several explanations for the deviation of predicted ozone formation from the observations.

(a) $RO_2$ chemistry in MCM mechanisms is still uncertain. Numerous products and reactions are involved to form $RO_2$. The cross-reactions between $RO_2$ and the reaction of various $RO_2$ with $HO_2$ are complex (Villenave et al., 1998;Jokinen et al., 2014). Oversimplified surrogate coefficients for the diverse $RO_2$ chemistry could trigger the discrepancy between the modeled and the measured OH radical concentration.

(b) In the gas kinetic mechanism, the photolysis rate constants of organic compounds were also oversimplified using surrogate compounds and can cause uncertainty in ozone prediction and production distributions.

(c) The recent laboratory investigation shows the significance of gas-wall partitioning of organic compounds. The loss of oxygenated products to the chamber wall can lead the lower ozone measurements than the model prediction.



**Minor comments:**

**(1)** p. 2 line 5: Unclear comparison: "… fewer global emissions" that what?

**Response:**

We changed the sentence to "…, despite fewer global emissions compared with biogenic VOCs."

**(2)** p. 2 line 11: When the authors refer to "regional weather" do they really mean climate change?

p. 4 line 9: unclear comparison with literature: What system was "the reported value of 2" measured for? Is it a toluene oxidation study?

**Response:**

p. 2 line 11: We referred to climate change. We changed the sentence to "SOA formation has attracted substantial interest from scholars because of its vital role in affecting climate change, …"

p. 4 line 9: It is measure from a series of toluene oxidation study. We changed the sentence to "The ratio of organic matter (OM) to OC was experimentally determined to be 1.9 (Table 1, EB4), the reported value of 2 in a series of toluene-$NO_x$ oxidation study (Kleindienst et al., 2007)."

**(3)** p. 6 line 18: another unclear comparison with literature: What system was "the reported value of 1.4 $g/cm^3$" measured for?

**Response:**

We changed the sentence to "$\rho_{or}$ and $\rho_{in}$ represent the density of the aerosol of *or* and *in* aerosol. $\rho_{or}$ was experimentally determined (EB4 in Table 1) to be 1.38 g $cm^{-3}$, which was similar to the reported value of 1.4 $g/cm^3$ for aromatic SOA (Ng et al., 2007;Nakao et al., 2011;Chen et al., 2017)."

**(4)** p. 7 line 2: It appears that "irreversibility and nonvolatility" should be "irreversibly formed and nonvolatile".

**Response:**

This has been corrected in the revised manuscript.

**(5)** p. 9 line 12: The meaning of the phrase "contributed to" is unclear in this sentence.

**Response:**

We changed the sentence to "… The formation of aromatic SOAs is attributed to a few highly reactive species, such as GLY…"

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