Comment on acp-2021-605

Anonymous Referee #1

Referee comment on "Development and evaluation of a new compact mechanism for aromatic oxidation in atmospheric models" by Kelvin H. Bates et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-605-RC1, 2021

Bates et al. have developed a new gas-phase chemical mechanism to simulate the oxidation chemistry for benzene, toluene, and xylenes in box and 3D models. They evaluated their model against chamber measurements as well as benchmarked it against other competing mechanisms. They find that their reduced mechanism performs well while noting that their mechanism alone models radical recycling from phenoxy-phenylperoxy that has modest effects on concentrations of smaller oxygenated products and oxidants. They also present interesting results from simulations performed separately with a boundary layer and 3D model.

Aromatics are an important class of organic compounds relevant for both anthropogenic (e.g., traffic) and biogenic (e.g., biomass burning) sources. Hence, the focus on aromatics and the development of a compact mechanism to simulate its atmospheric chemistry is well motivated. The manuscript was very easy to read and follow and I commend the authors for putting together a superb paper. I am less conversant with the chemical reactions described in the methods section so I am going to let the other reviewer(s) and editor to directly assess that section of the manuscript. However, I was able to follow the dominant chemical pathways and oxidation products and how they helped explain the results presented later. I recommend this paper for publication to ACP noting that the authors should consider my comments below before final submission.

Comments (major highlighted with asterisk):

- *Beyond BTX: My sense is that the impacts described here are likely to be biased (mostly underestimated) for the following reasons. First, how are aromatic species other than benzene, toluene, and xylenes accounted for in the modeling? My sense is that C8 and higher aromatics are lumped into xylenes. Or are they parsed by reactivity with OH? What about the treatment of multi-ring aromatics (e.g., naphthalene)? **This attribution (or lumping) of non-BTX species to BTX surrogates needs to be**

made clear throughout this work, in addition to how this attribution is justified and/or adds to the uncertainty. Furthermore, what would be good to consider here would be to document the relative magnitude of non-BTX species to BTX. Also, are the authors concerned that certain species (e.g., furan in SAPRC) that are assigned to an aromatic surrogate (in the case of furan and SAPRC, to xylene) for computational reasons skew the model findings presented in this work? (It should not be a concern for the box modeling, correct?) Second, recent combustion emissions work has pointed out that gasoline exhaust contains a wide variety of single-ring aromatic hydrocarbons separate from BTX species (e.g, Zhao et al., ES&T, 2016; Drozd et al., ES&T, 2019; Lu et al., ACP, 2018). This seems to be less true for diesel exhaust. These non-BTX species have been shown to be very important for SOA formation and, in some models, have been accounted for as intermediate volatility organic compounds (IVOC). Third, biomass burning has been shown to be an important source of oxygenated aromatics including phenols and methoxyphenols (e.g., Koss et al, ACP, 2018; Hatch et al., ACP, 2018). Since some of these biomass burning aromatics feature in the chemical mechanism presented in this work as intermediate oxidation products (e.g., phenol, catechol), I believe that they are likely to have similar effects as the explored BTX species. It's likely that the emissions of these oxygenated aromatics are considered in the GEOS-Chem inventories but it has not been made clear. All 3 factors described above will tend to generally increase (?) the effect size for aromatics.

- *Vapor wall losses: Page 10, line 4: Really? Recent work has argued that the timescales for vapor losses to the chamber walls are on the order of 5 to 15 minutes for a chamber volume of ~ 10 m^3. Since these losses have been shown to be important for SOA formation (Zhang et al., PNAS, 2014; Cappa et al., ACP, 2016; Akherati et al., ACP, 2019), I would expect them to have a similar effect on gas-phase chemistry and radical and oxidant concentrations. Further, Zhang et al. (2014) show that the vapor wall loss effect on SOA formation is different under different NOx conditions. Perhaps this mechanism can shed light on why that might be? Vapor wall losses can be modeled relatively easily following the work of Zhang et al. (PNAS, 2014) and Krechmer et al. (ES&T, 2016).

- *Chamber simulation results and comparisons (Figures 4-6): While I understand the rationale behind the study design to simulate a representative chamber experiment, this work should also explore sensitivity in model predictions (limited to GC13 perhaps) to a broader range of input conditions observed across the chamber experiments used to evaluate the mechanism. For instance, are the model predictions sensitive to whether one assumes a constant OH profile chamber experiment (relevant for OH produced from photolysis of H2O2) or an OH profile that decays with time (relevant for OH produced from photolysis of HONO)? Are the model predictions sensitive to the chamber lights (e.g., intensity, spectrum) that should control the time-varying concentrations of NO and NO2? How do the model predictions change if the results were presented for a different time point (instead of 20 minutes after lights on)? How about the influence of chamber size (5 m3 vs. 30 m3) and mode of operation (batch mode vs. steady state mode)? This mechanism sensitivity will be useful in interpreting the comparison with observations.

- *Boundary layer and 3D model evaluation: The authors should discuss if and how the mechanism changes presented in this work have the potential to improve predictions of oxidants and gas-phase species that are likely to be biased based on past literature.

- Page 10, line 30: I have always wondered what the NOx concentrations are in 'low NOx' chamber experiments. Literature from the Caltech group led by Prof. John Seinfeld has reported low NOx experiments to have NOx concentrations under 2 ppbv, reflecting the limits of quantification for their NOx analyzer. Assuming other chamber groups have encountered the same quantification problem with NOx, I wonder if a '10 pptv' assumption is justified here.

- Page 11, line 6: Here and elsewhere, I would encourage the authors to be quantitative on what 'low-to-moderate' NO/NOx and 'high' NO/NOx means.