

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-649

Anonymous Referee #2

Referee comment on "Prediction of secondary organic aerosol from the multiphase reaction of gasoline vapor by using volatility–reactivity base lumping" by Sanghee Han and Myoseon Jang, Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-649-RC2>, 2021

The study at hand by Han and Jang deals with environmental chamber experiments at the UF-APHOR facility in Gainesville, Florida, which are interpreted using a high-level modelling framework (UNIPAR-CB6r3). The experiments look at the formation of secondary organic aerosol (SOA) from gasoline, and its hydrocarbon constituents individually. A primary focus is the importance of particle-phase chemistry in SOA formation, while a secondary focus is the treatment of gas-wall partitioning (GWP) of volatile vapors. These topics fit well within the scope of Atmospheric Chemistry and Physics.

The authors find good correlation between the model and experiment. They find that a substantial amount of gasoline SOA is due to oligomers formed in the particle phase and GWP has a significant effect on model results. Both findings are very interesting and I believe lots can be learned from their model. However, from reading this paper alone (and not also a wide range of previous publications), it is very hard for me to deduce what the fundamental parameters were in this model simulation and which parameters were optimized / fitted for this study. This makes it very hard to gauge the significance of the conclusions. Thus, before I can recommend this paper for publication within ACP, the authors must present their approach more clearly, with an emphasis on when and how coefficients / polynomials / fits to the data are obtained (if at all) and what the model is calibrated against.

Major Comments

It did not become clear to me if fit parameters were used in this study to align the observed and modelled SOA mass concentrations. If I understand correctly, an important part of this modelling approach is the determination of the polynomial equation that lead to all α_i . Line 138 states "These equations are mathematically derived by using explicit products predicted from MCM v3.3.1." How is this done, as MCM does not specify

an aerosol phase reactivity scale (l. 126)? Line 139 describes the parameters α_i as “dynamically predicted”, what does this mean? Is there fitting to the data happening?

Figure S4 shows and it is stated throughout the manuscript that “OM_P”, the organic mass attributed to gas-particle partitioning, is very low or even close to zero for some SOA precursors. In turn, this means that SOA mass must be almost exclusively (> 90 %) due to particle-phase reactivity (OM_{AR}). It is not entirely clear to me how solid the result is because I do not understand how the authors come to this conclusion. Is this just a result from the MCM-trained model, or does this rely on previous chamber experiments to optimize α_i parameterizations?

Given this result, it is surprising to me that Figure 6 shows that vapor pressures are the most relevant model parameters. Is that because low vapor pressure is a prerequisite to molecules being present in the particle phase where they undergo particle-phase chemistry?

Does OM_{AR} mean that the product itself would not condense and only the particle-phase reactivity makes it stay in the particle phase? What types of reactions and products would this be that make up such a large share of SOA? I think my questions are inherently connected to point 1 above: have any of these parameters (α , or $k_{o,i}$) been fitted for this study or does the model just naturally fit the data? My skepticism comes from the simulations results of gasoline, where particle-phase reactivity suddenly is of less importance (especially Figs. 3a,b,c). Why is that so?

The reaction rate $k_{o,i}$ must be a very influential parameter, given the high fraction of OM_{AR}. Why is its sensitivity in Fig. 6 so small? It follows a semi-empirical description. Is there a $k_{o,i}$ for every one of the 51 lumping species for each of the 10 hydrocarbons, so 510 individual parameters? How about cross-reactions between lumping species, how are these treated?

To me, the abstract seems very technical and does not reflect the discussion in the manuscript well. For example, OM_P and OM_{AR} are not mentioned there.

It is not clear to me what role the inorganic particle phase reactions play for this study, can the authors comment on that in the manuscript?

Can it be calculated with the model which components of the gasoline HC mix form the most SOA?

Minor and Technical Comments

l. 88 – It is not clear what CCl₄ is used for in this work.

Figure 2 – Caption is missing what red and black markers are, respectively.

Eq. 7 and l. 183 – I cannot follow how with Eq. 7 the impact of viscosity on oligomerization rate is considered. Why would viscosity affect chemical reaction rate?

Fig. S4 and l. 232 – The model lines for benzene OM_p are not visible in the figure.

Fig. 3 and S4 – It was confusing to me at first that the dotted lines stand for OM_P in Fig. S4 and for OM_{AR} in Fig. 3. I might be good to align this.