

Review of the manuscript "SOA formation from the photooxidation of α -pinene: systematic exploration of the simulation of chamber data"

General comments:

This manuscript presents results from simulations of Caltech smog chamber experiments on photooxidation of α -pinene with the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A). The manuscript is well written and present interesting and new experimental and theoretical results on the SOA formation from photooxidation of α -pinene at different OH concentrations. The authors perform an extensive set of sensitivity tests in order evaluate the relative role of VOC chamber wall losses, gas to particle mass transfer limitations, second and later generation oxidation products, condensed-phase photolysis and particle-phase dimerization for the SOA formation. However, according to my opinion no one of the suggested model setups is able to capture the observed evolution of the SOA formation in a convincing way for all experiments. Instead the model always tends to overestimate the SOA formation during the high OH concentration experiments and underestimate the SOA formation during the low OH concentration experiments. As the authors suggest this can possibly be because the model do not take into account the autoxidation of α -pinene and formation of first generation ELVOC oxidation products. Most of the sensitivity tests are well motivated and described but I have a few critical questions (comments) that I would like the authors to answer (consider). If this is done in an appropriate way I think the manuscript is well worth to be published in ACP.

Experiment 141125 has the highest SOA yield. Based on your modeled OH concentration of $2 \times 10^5 \text{ molec cm}^{-3}$ you get an overall OH reaction rate of 10^{-5} s^{-1} (P 33177, L 7). I compared this with how much O_3 that needs to be present in order to get the same overall O_3 reaction rate as the OH reaction rate. My calculation gave that at an O_3 concentration of 4.5 ppbv half of the α -pinene is oxidized with O_3 instead of OH ($k_{\text{O}_3} = 9.4 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1}$). According to Fig. S2 the measured O_3 concentration increases from 0 to 10 ppbv during this experiment while the modeled O_3 concentration only reaches 4 ppbv in the end of the experiment. Thus, according to the measurements I think that more than half of the consumed α -pinene reacts with O_3 and not OH. How does the model handle the O_3 oxidation of α -pinene and the chemistry beyond the formation of the Criegee biradicals? How much SOA is formed from ozonolysis of α -pinene? This is not mentioned at all in the manuscript but could potentially be a large source of error that need to be discussed. I think it is suitable to add figures to the supplementary material that shows how large fraction of the α -pinene that react with O_3 according to both the model and the measurements. Because the autoxidation mechanism that is suggested to generate ELVOCs is much more effective when α -pinene is oxidized by O_3 instead of OH I think this could at least partly explain why the model and measurements disagree. This needs to be estimated and discussed.

On page 33169, L10-12 you write that the particle number concentration remains unchanged in the model during the course of the experiments. Why do

you not include particle wall losses in the model? On page 33173, L1-2 you write that the measured particle volume distributions are corrected with the size-dependent wall loss rates. Thus, it should be straightforward to also consider these particle wall losses in the model.

I guess that the observed SOA growth curves displayed in e.g. Fig. 2 and 4 are not what actually were observed but the wall loss corrected SOA mass derived from the SMPS measurements. You need to explicitly write this in the manuscript. I also wonder how uncertain the corrected SOA mass is. How much did you need to correct the measured SMPS particle volume? I know from experience that chamber wall losses in Teflon smog chambers can vary from experiment to experiment because of e.g. variations in the electrical field strength of the chamber and how long time it takes between that the seed particles are added to the SOA formation starts. I think you should add the not wall loss corrected SOA or total particle mass to the panels in Fig S3.

How was the particle number size distribution described in the model? Did you only consider one particle size or did you include several size bins? This should be mentioned in the article. If you only use one effective particle size bin how was the initial particle radius of the seed aerosol estimated?

On page 33173 L24-25 you write that the background levels of NO_x in the chemical model was set to 0.1 ppb and split evenly between NO and NO₂. I thought that you explicitly modeled the NO and NO₂ concentration. How were the inorganic gas-phase chemistry treated by the model?

On page 33178 L5-7 you write “A reduction to 10% and a wall loss rate of 10^{-5} s^{-1} results in the best fit to both high and low UV experiments (Fig. 6), albeit with a slight overprediction for the high UV experiments and slight underprediction for the low UV experiments.” I would not say that the model underprediction for experiment 141125 is a “slight” underprediction but a rather substantial underprediction of about 40 %. I suggest that instead of using the terms “slight overprediction” and “slight underprediction” give values of how much in % that the model over- and underpredicts the SOA mass in the end of the experiments.

On page 33180, L4-10 you conclude that the underprediction of vapor pressure is likely not responsible for the enhanced contribution of later-generation species to SOA. I am not totally convinced about this. It might be correct but I don't think that you can base these conclusions only based on a comparison of different functional group contribution methods since they all have in common that they estimate the vapor pressures by summing up the contribution from different functional groups and in the best case take into account some interactions between the different functional groups. It might very well be that all these methods systematically underestimate (or overestimate) the vapor pressures of compounds with many functional groups.

The difference in seed aerosol (SA) surface area (a proxy for the condensation sink) is not that great between the experiments called low SA, medium and high SA. Maybe you could give the value of the initial seed surface area in the figure

legends instead of calling the experiments “Low SA”, “Medium SA” and “High SA”. For the nucleation experiment I think that one possible reason for the relatively high SOA yield is caused by substantially lower wall losses of these particles. This is because I suspect that the particles that are formed via new particle formation are under charged with respect to the Boltzmann charge distribution. I guess the SA was neutralized before it was introduced to the chamber. Thus I don’t think it is appropriate to do the same wall loss correction for the nucleation experiment as for the SA experiments. Did you use different size resolved wall loss corrections for the SA experiments and the nucleation experiment?

Technical correction:

The text is very small in Fig. 3 and hard to read. If Fig. 3 should be included in the final manuscript the font of the text needs to be larger. I personally think that Fig. 3 can be removed from the manuscript because it adds very little to the article and you only refer to it once in the text.