Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-17-RC1, 2021

Referee comment on acp-2021-17

Anonymous Referee #1

Referee comment on "Estimation of secondary organic aerosol viscosity from explicit modeling of gas-phase oxidation of isoprene and *α*-pinene" by Tommaso Galeazzo et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-17-RC1, 2021

Summary + General Comments

In "Estimation of Secondary Organic Aerosol Viscosity from Explicit Modeling of Gas-Phase Oxidation of Isoprene and α-pinene," Galeazzo et al. present the use of GECKO-A modeling on isoprene and α-pinene SOA to model the chemical composition and calculate the viscosity at various relative humidities. Though experimental samples, either from real-world conditions or from controlled conditions in a chamber, can lead to measurements of viscosity, global climate models will not be accurate solely using viscosity data from a small number of locations or test chambers. Numerous factors, including environmental (e.g. T, RH), chemical (e.g. compound structure, functional group contribution, atomic ratios), and physical (e.g. partitioning) processes, can contribute to large variance in aerosol behavior, e.g. glass transition temperature and viscosity. Recent progress made in parameterizing the prediction of viscosity has reduced the necessary inputs to elemental composition, stopping short of functional group analysis, thus providing a different pathway for viscosity prediction through high-resolution mass spectrometry.

Experimentally, viscosity of aerosol has been determined using a few different methods/instruments, e.g. poke flow mobility, a differential mobility analyzer, a particle impactor coupled with scanning electron microscopy, or a rebound impactor. By taking the priors from those experiments (precursor concentration, ozone concentration, T, RH, reaction time) and running those through GECKO-A, the researchers were able to predict glass transition temperatures and viscosities, which they could then compare to the experimental values.

When comparing modeled to experimental isoprene SOA viscosity with respect to relative humidity, the modeled values were found to be within error to experimental values assuming a hygroscopicity of 0.10. The modeled viscosity values for α-pinene were underestimated by 1 to 4 orders of magnitude, though wide experimental uncertainties led to some experimental values possibly lining up with the model. Better agreement was found between modeled and experimental values when mass loading was varied. A few interesting breakdowns of chemical composition were displayed as well.

Finally, the authors tried varying the mass accommodation coefficient, a property that measures how likely a gas molecule approaching an aerosol will be taken up. They selected two starting experimental conditions from a couple of different papers and observed a stark contrast between the expected viscosity vs. RH curves when predicting using a mass accommodation coefficient from unity to an effective value dependent on

penetration depth.

Scientific Comments

This article is generally well-written, has a logical flow and is well-organized, has a clear description of results, and presents clear and concise graphs. The authors properly point out where future research remains and do well in pointing out subtleties in the models and the data. The section on varying the mass accommodation coefficient is novel, considering the same lab recently published the work on effective mass accommodation coefficients (Shiraiwa and Pöschl, 2020). Some sentences have interesting phrasing, which I will point out in the subsequent "technical corrections" section. I would tentatively recommend this article for publication, provided the authors address the following points.

My biggest concern is a notable similarity of the first few figures in this paper and their corresponding results/discussion paragraphs to the paper Gervasi et al. published in early 2020, also in ACP (Gervasi et al., 2020). Comparing Figures 1 and 2 in Galeazzo et al. (this paper) to Figure 7a and 7c in Gervasi et al., we can note that Gervasi et al. incorporate data from more studies in their figure, specifically from the Bateman et al. study for the isoprene SOA and the Abramson et al. and Pajunoja et al. studies for the α-pinene SOA. Perhaps for the pinene experiments, this is because each of these papers only have one data point each and they use different experimental techniques than the ones mentioned here?

These two papers remain different because the Gervasi et al. study uses MCM instead of GECKO-A with box modeling; however, this paper by Galeazzo et al. is missing any reference to Gervasi et al. Additionally, Galeazzo et al.'s paper, by means of chronology, would benefit from a comparison of the effectiveness of their model to the one found in Gervasi et al. While their isoprene SOA models yield fairly similar results in the viscosity vs. RH space, the α-pinene SOA data in Gervasi et al. appear to outperform the Galeazzo et al. model, bringing into question whether this paper represents an improvement on previously published methods. In theory, GECKO-A's model is more detailed and provides many more minor reactions pathways that the MCM does not. However, it is unclear whether this extra information makes the model more accurate or if these results point to some shortcoming in GECKO-A's processing.

One other concern I have with this paper is the current lack of supplementary information. The experimental inputs and/or the model outputs would be useful information to provide for other scientists who wish to investigate such work. Having this more simple data be publicly available, either in the SI or in a repository, would be preferred. The data in Figures 4 and 5 would be helpful in table format for other scientists, while Figure 3 itself may be more efficiently placed in the SI, if it existed.

Gervasi et al. paper also builds up validation of the model using various solutions, including pure water, pure single component solutions, and then SOA. This manuscript would benefit from such an analysis, though this is not absolutely necessary for publication.

While GECKO-A provides a plethora of chemical detail, it would be good to know if the researchers, either of this paper or elsewhere, are actively working to overcome the shortcomings and inefficiencies of GECKO-A.

At the end of the introduction, the authors could provide more detail on the overarching objective. The pharse "to expand our understanding on the relationship and interplay among" is vague, and possibly deliberately so. It would be helpful to provide the reader a quick summary clause at the end of the sentence to tie it back into something concrete, such as incorporation into global models.

At line 206, the authors wrote "Simulation results for Renbaum-Wolff's and Grayson's experiments fall within uncertainties of experimental measurements for the 40-60 % RH range." This observation is clearly true from Figure 2, but the uncertainties for those data points are quite large, spanning 3-5 orders of magnitude, and the experimental data trend higher than the model data. Such a detail may be worth including.

At line 220, the authors assert that the variance of model simulations and experimental measurements is very similar and give a correlation coefficient, but provide no data to support this claim. An SI would be useful to give the reader the option to verify this information.

Finally, at line 283, the viscosity curves seemed to line up fairly well for the Renbaum-Wolff experiments, but not for the Kidd experiment. Do these results have any bearing on either Kidd et al.'s methodology or results or do they point exclusively toward a general need for more research into how the mass accommodation coefficient should behave over time and chemical composition?

Technical Corrections

This manuscript has a number of sentences that would benefit from a read-through or from reading them out loud. I have also omitted changes I assume will be caught by a copy editor.

Lines 3-6

"In this study, we conduct explicit modeling of isoprene photooxidation and α-pinene ozonolysis and subsequent SOA formation using the GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) model. Our recently-developed parameterizations to predict glass transition temperature of organic compounds are implemented into a box model with explicit gas-phase chemical mechanisms to simulate viscosity of SOA."

These sentences are a tad bit awkward, and the authors used "explicitly" twice in quick succession. A possible fix, though this sentence can be fixed in plenty of different ways, is provided below.

"In this study, we use GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) to conduct explicit chemical modeling of isoprene photooxidation and α-pinene ozonolysis and their subsequent SOA formation. Coupling this level of chemical detail with box modeling and our recently-developed glass transition temperature parameterizations allows us to predict SOA viscosity."

Lines 24-25

Change "enabling to generate" to either "capable of generating" or "that can generate."

Lines 31-34

It may make sense to combine these two sentences together.

Lines 30-43

Depending on preference, the flow of this paragraph may benefit from lining up the order of each variable as they are first listed with the order of the sentences. To clarify, line 32 states "depending on chemical composition, relative humidity (RH), and temperature." You could move the next two sentences, "Notably, water…" and "It has been observed that…" to after the Petters et al. citation to make sure that subsequent sentences detailing work done with varying chemical composition, then temperature and RH are in closer proximity. Alternatively, or simultaneously, you could make the previous change for lines 31-34, which may make this juxtaposition more compact.

Line 44

Change "fast" to "quickly."

Line 87

Inconsistent spelling of "autooxidation" with "autoxidation" elsewhere.

Table 1

RH in the heading should be RH (%)

Put T and RH next to each other

Either convert the Song isoprene study to ppb or convert the pinene experiments to ppm for consistency.

Might be more visually striking to have an extra column on the left with vertical text indicating which precursor is used. As it is, the pinene and isoprene distinction blend in with the table.

In footnote, SEM should be written out, since it was not mentioned previously in the manuscript.

A footnote to explain reaction time would be useful.

Line 183

Change "Results" to "Results and discussion"

Throughout document, line 187

Copy editor's job, likely, but the 60 and % are on different lines.

Figure 1

Could you make the markers slightly larger?

Line 203

In previous literature, a hygroscopicity κ of 0.1 for pinene has been shown to fit quite well (Petters and Kreidenweis, 2007; Prenni et al., 2007).

Figure 2

Could you add the line and dashed line to the small legend?

Lines 278-279

Change "low volatile" to "low volatility" or "lower volatility." Also, add a comma after "unity."

Lines 299-302

Swap "by a few orders of magnitude" and "lower than experimental measurements."

Line 308 paragraph

Would it make more sense to have some of this paragraph be a discussion section?

References

Gervasi, N. R., Topping, D. O. and Zuend, A.: A predictive group-contribution model for the viscosity of aqueous organic aerosol, Atmos. Chem. Phys., doi:10.5194/acp-20-2987-2020, 2020.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., doi:10.5194/acp-7-1961-2007, 2007.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J. and Ziemann, P. J.: Cloud droplet activation of secondary organic aerosol, J. Geophys. Res. Atmos., doi:10.1029/2006JD007963, 2007.

Shiraiwa, M. and Pöschl, U.: Mass Accommodation and Gas-Particle Partitioning in Secondary Organic Aerosolsâ□¯: Dependence on Diffusivity , Volatility , Particle- phase Reactions , and Penetration Depth, Atmos. Chem. Phys., (July), 1–30, 2020.