Response to Referee comments (comments in black, response in blue)

Anonymous Referee #2

In this manuscript, Galeazzo et al. presented the organic aerosol viscosity estimated using a recently developed glass transition parameterization coupled to an explicit chemical mechanism, GECKO. This approach is used to predict the viscosity of secondary organic aerosol (SOA) produced from isoprene and α-pinene oxidation, and the results are evaluated using the chamber/flow tube measurements in the literature. It is found that the simulated viscosity of isoprene SOA is in reasonable agreement with the measurements, but major bias exists for α-pinene SOA. The authors explored the potential drivers of such discrepancy. This manuscript is fairly compact and generally well prepared, and is in line with the scope of the Journal. I do have several major and specific comments, and I recommend this manuscript for publication in Atmospheric Chemistry and Physics, provided the following major and specific comments are addressed.

We thank Referee #2 for the review and positive evaluation of our manuscript.

Major comments: The approach to estimate the organic aerosol viscosity presented in this work consists of two key components: (1) glass transition temperature parameterization based on elemental composition (DeRieux et al. 2018 and Li et al. 2020). (2) explicit chemical mechanism generator GECKO (Aumont et al. 2005, etc). The glass transition temperature parameterization appears to be robust for both isoprene SOA and α-pinene when combined with volatility basis set which is largely derived based on measurements (e.g., Li et al. 2020). What is missing in the current manuscript is how GECKO performs for isoprene and α-pinene. It will be valuable to show the GECKO predictions for the chamber and flow tube experiments, and compare to key measurements available (e.g., mass loading alone may explain some of the variations in viscosity). Evaluating GECKO against measurements might sound out of the scope. However, I would argue that, a recent study (Gervasi et al. 2020) showed that the viscosity of α-pinene SOA can be reasonably well captured using MCM, a near-explicit gas-phase mechanism that also does not have particle-phase chemistry and underestimates high molecular weight compounds.

Validation of the GECKO-A mechanisms has been conducted extensively for the purpose of SOA formation in previous studies (e.g., Valorso et al. 2011, Denjean et al., 2015, McVay et al., 2016, La et al., 2016). These evaluations have been performed by comparison with chamber experiments of SOA formation from the oxidation of a-pinene, and C7 to C17 alkane and alkenes. The isoprene mechanisms generated with GECKO-A have not been evaluated. The following sentences have been added in Sect 2.1 of the revised manuscript:

"α-pinene GECKO-A mechanisms were evaluated in previous studies by comparisons with chamber experiments of SOA formation from photo-oxidation (Valorso et al. 2011, McVay et al., 2016) and ozonolysis (Denjean et al., 2015). The model captures the qualitative features of SOA formation with the variation of NOx levels during photolysis experiments, and with temperature for ozonolysis experiments. The measured SOA mass was overestimated by the model in Valorso et al. (2011) and Denjean et al. (2015), which could be in part explained by the loss of low volatile organic compounds onto the chamber wall (McVay et al., 2016 ; La et al., 2016). In addition, McVay et al (2016) highlighted a possible overestimation of the simulated contribution of later-generation oxidation products to SOA mass at high OH levels, and an underestimation of the SOA growth at low OH levels that could be due to lack of autoxidation processes in the mechanisms generated with GECKO-A. The influence of these limitations on the results simulated here are discussed along the paper. … Isoprene mechanisms generated with GECKO-A is for the first time indirectly evaluated in this study."

In addition, we have reported the information needed to compare our model results to experimental O:C ratio in SOA for α-pinene and isoprene.

We cite and discuss Gervasi et al. (2020) in the revised manuscript (please see our response to first comment by Referee #1). We would like to point out that Gervasi et al. (2020) did not explicitly applied MCM for viscosity estimations but selected 14-21 representative compounds based on MCM for viscosity estimations. This study, on the other hand, explicitly couples detailed chemical mechanisms with viscosity estimation, allowing us to investigate the role and impacts of different experimental conditions and SOA composition (O:C ratio, functional group distributions) on resulting particle viscosity. We clarify this point in the revised manuscript.

Specific comments: Page 2, Line 24-25. "As gas-phase oxidation is often regarded as the rate-limiting step of SOA formation, there is a strong need for a computational tool enabling to generate exhaustive gas-phase chemical mechanisms." I'm not sure if I follow the logic here. There is a need for a tool that is capable of generating chemical mechanisms based on "first principles", but it has little to do with whether gas-phase oxidation is the rate-limiting step of SOA formation.

The sentence has been revised to:

"As gas-phase oxidation is a driving step of SOA formation, there is a strong need for a computational tool that can generate exhaustive gas-phase chemical mechanisms."

Page 4, Line 107-108. Some key technical details are missing here. How is the number concentration determined for each experiment? How does the model handle particle size evolution (e.g., is it only condensation or does it include nucleation/coagulation)? Is the aerosol scheme modal or sectional?

GECKO-A does not treat nucleation (line 104-106). As particle number concentrations were not reported in most studies, the particle number concentration was assumed to be 10^4 particles cm^{-3} following McVay et al., (2016). The particle number concentration was assumed to remain constant during simulations, as coagulation was not treated. We did not resolve evolution of particle size distributions, which are also not reported in experiments. We added some more details in the revised manuscript to clarify this point:

"The particle number concentration is assumed to remain constant during simulations (coagulation is not treated), while the particle radius evolves following the partitioning of organics."

Page 4, Line 112. Please fix the citation throughout this manuscript per the Journal requirements.

The citation style has been corrected.

Page 4, Line 120-121: “SOA particles were formed under dry conditions and then SOA were exposed to water vapor at different RH for viscosity measurements.” This sentence is not well connected with the previous one. The previous sentence explains how the box model is configured for chamber experiments. Yet it is unclear if this sentence describes the same box model configuration, or if it actually describes how experiments were conducted.

We clarify this point in the revised manuscript:

“SOA particles were formed under dry conditions and then exposed to water vapor at different RH for viscosity measurements; the same procedure is applied in our simulations by forming SOA at RH = 0.5% and then viscosity estimations are conducted by considering hygroscopic growth at elevated RH.”

Page 5, Table 1: what is the unit of RH? It looks like fractional (for all α-pinene experiments) but then for isoprene RH goes beyond unity.

The unit is % and we make it consistent in the revised manuscript.

Page 9, Line 225-226: Could the authors please elaborate the experimental uncertainties, and how these are translated/propagated into the uncertainties of the viscosity? This also calls for a closer look at GECKO, e.g., how does GECKO predicted aerosol loadings in all experiments compare to measurements.

Experimental uncertainties were elaborated and discussed in Grayson et al. (2016) and resulting upper and lower bounds of viscosity measurements are shown in Fig. 3. Grayson et al. (2016) did not report the exact precursor concentrations for their flow tube experiments, while they provided a range of precursor concentrations varied to produce samples at 5 different mass concentrations between 100 - 14000 μg m^{-3}. Thus, it is not possible to make comparisons for mass loadings of specific experiments, while the GECKO-A box model successfully captured the observed ranges.

Page 10, Line 233: how does the GECKO modeled overall particle-phase O/C ratio compare to measurements? This may provide key insight, i.e., to what degree can GECKO explain the bias in the predicted viscosity.

Following your comment, we added the below paragraph in the revised manuscript:

“None of these experimental studies measured average O:C ratio of SOA particles, but some of them reported estimated O:C ratios based on previous experiments with similar experimental conditions. Song et al. (2015) estimated the O:C ratio of isoprene SOA to be 0.64 -1.1, which is consistent with our simulated O:C ratio of 1.0. Renbaum-Wolff et al. (2013) estimated O:C ratio of a-pinene SOA to be 0.3 – 0.4, which is slightly lower than our simulated value of 0.49. Valorso et al. (2011) reported that the GECKO-A box model tends to overestimate the O:C ratio of SOA generated by a-pinene photooxidation. Denjean et al. (2015) showed that the O:C ratio of SOA simulated with GECKO-A from α-pinene ozonolysis was coherent with the one simulated with the Master Chemical Mechanism, and within the uncertainty range of the experimental value. A recent study by Gervasi et al. (2020), which selected 14-21representative reaction products based on the Master Chemical Mechanism to simulate viscosity of the same measurement dataset, estimated the O:C ratio to be 1.1 for isoprene SOA and 0.51 for a-pinene SOA. Overall, the O:C ratios simulated by the GECKO-A box model are reasonable and in line with available measurements and modeling studies, while further studies are warranted for simultaneous measurements of O:C ratio and viscosity along with model applications."

Page 10-12, Line 241-265: It is interesting to see the GECKO simulated functional group distribution and all. However, it is unclear what the take-away message is and what the community can really learn from it. The authors did attempt to make a connection between the function group information (-RCHO) and the particle-phase reactivity affecting particle viscosity. This is promising and may point to potential future research. However, I find this paragraph (Line 256-266) not well supported and scratches only the very surface of the issue. MCM does not treat particle-phase chemistry either, yet Gervasi et al. (2020) showed better agreement for α-pinene with measured viscosity using MCM. This paragraph starts with Zhang et al. experiments yielding the highest –RCHO fraction but no further information is provided– does Zhang et al. also yield highest oligomer or HOM fraction? Whether a particular aldehyde (or a –RCHO group) actually facilitates oligomerization can vary a lot. The GECKO results presented here (Figure 5) do not provide any in-depth information on such potential of forming oligomers. Lastly, it'll be great if Figure 5 can be evaluated with measurements but I understand this may be difficult at this moment. Please comment on what techniques may provide such information, perhaps HRMS or FTIR?

We have added discussions of Gervasi et al. (2020) in the revised manuscript (see also our response to your comment 1 and also response 1 to Referee 1). Zhang et al. (2015) did not report HOM or particle-phase composition. Thus, we can only speculate that potential reasons for the high viscosity reported in their study. As pointed out, future studies are strongly desired for simultaneous measurements of viscosity and chemical composition by HR-MS or functional groups by FT-IR.

Page 11, Line 252-253: but isoprene oxidation also produces products with high O/C ratios. Can the authors please provide functional group distribution (similar to Figure 5) for isoprene?

In Fig. 5 we have added the functional group distribution for isoprene SOA simulated for the experimental conditions of Song et al. (2015). We have also added a few sentences comparing our simulation results to experimental measurements:

"Isoprene SOA is characterized by high concentrations of alcohols (–ROH) and hydroperoxides (–ROOH), followed by lower concentrations of ketones (–RC(O)R), and aldehydes (–RCHO). Our results are consistent with experimental measurements showing that polyols and organic peroxides are the primary species formed upon isoprene photooxidation under low NOx conditions (Surratt et al., 2006)."

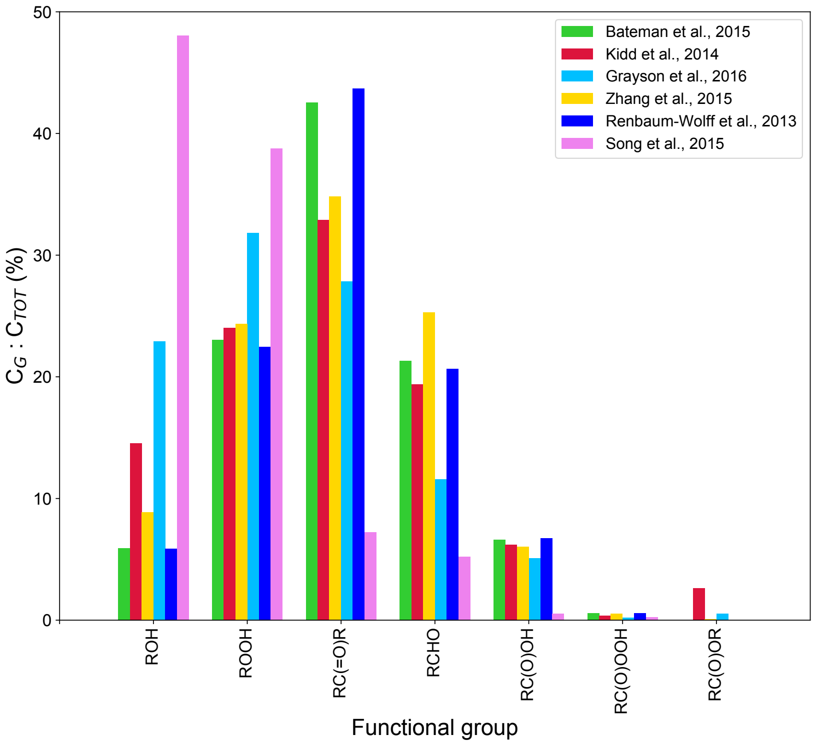

Figure 5: Simulated functional group distributions in particle-phase compounds derived from isoprene photooxidation and α-pinene ozonolysis.

Page 12, Line 261: recent studies suggest that autoxidation may also play a role in isoprene chemistry under certain circumstances (e.g., low NOx). Does GECKO include autoxidation for isoprene?

The autoxidation of RO_2 has indeed been recently shown to be an important process under low NO and HO_2 concentrations. Autoxidation processes are currently not included in the GECKO-A tool. The addition of autoxidation processes in GECKO-A is currently under development (see response to Referee #1). We agree that the absence of autoxidation processes could have an impact on the simulated results presented in this study, and the potential influence of autoxidation processes on the model/measure viscosity comparison is discussed along the manuscript.

Page 13, Figure 6: Please also show the calculated alpha_eff, and discuss in the context of recent studies (e.g., Liu et al. 2019)

Following this comment, we have expanded the section of effective mass accommodation by exploring the difference of simulations for Kidd et al. and Renbaum-Wolff et al. (Fig. S1-S4). The simulated α_{eff} is now shown in Fig. S5 in comparison with Liu et al. (2019). Note that it is difficult to make a direct comparison between simulated and measured α_{eff} due to the lack of detailed information on SOA formation conditions in Liu et al. (2019).

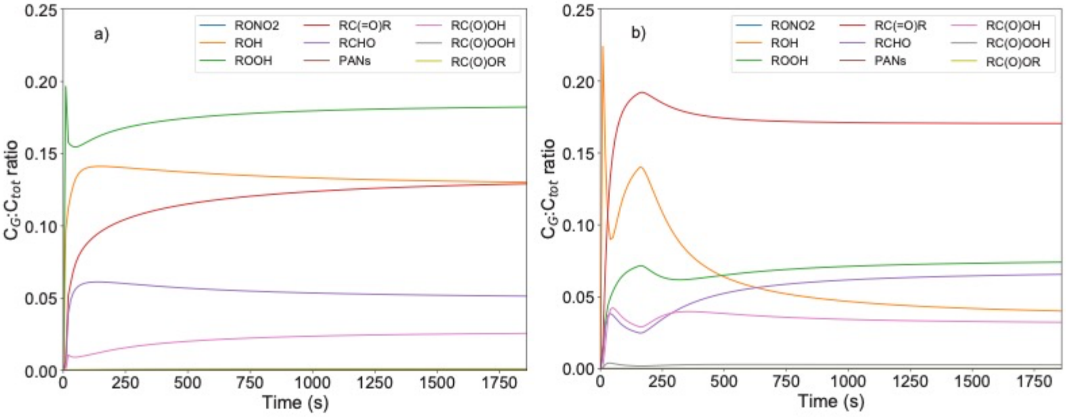

Figure S1: Time evolution of SOA compounds with different functional groups for simulations of experiments by (a) Kidd et al. (2014) and (b) Renbaum-Wolff et al. (2013) by considering effective mass accommodation coefficient α_{eff}. The simulations were conducted at RH = 0.5%.

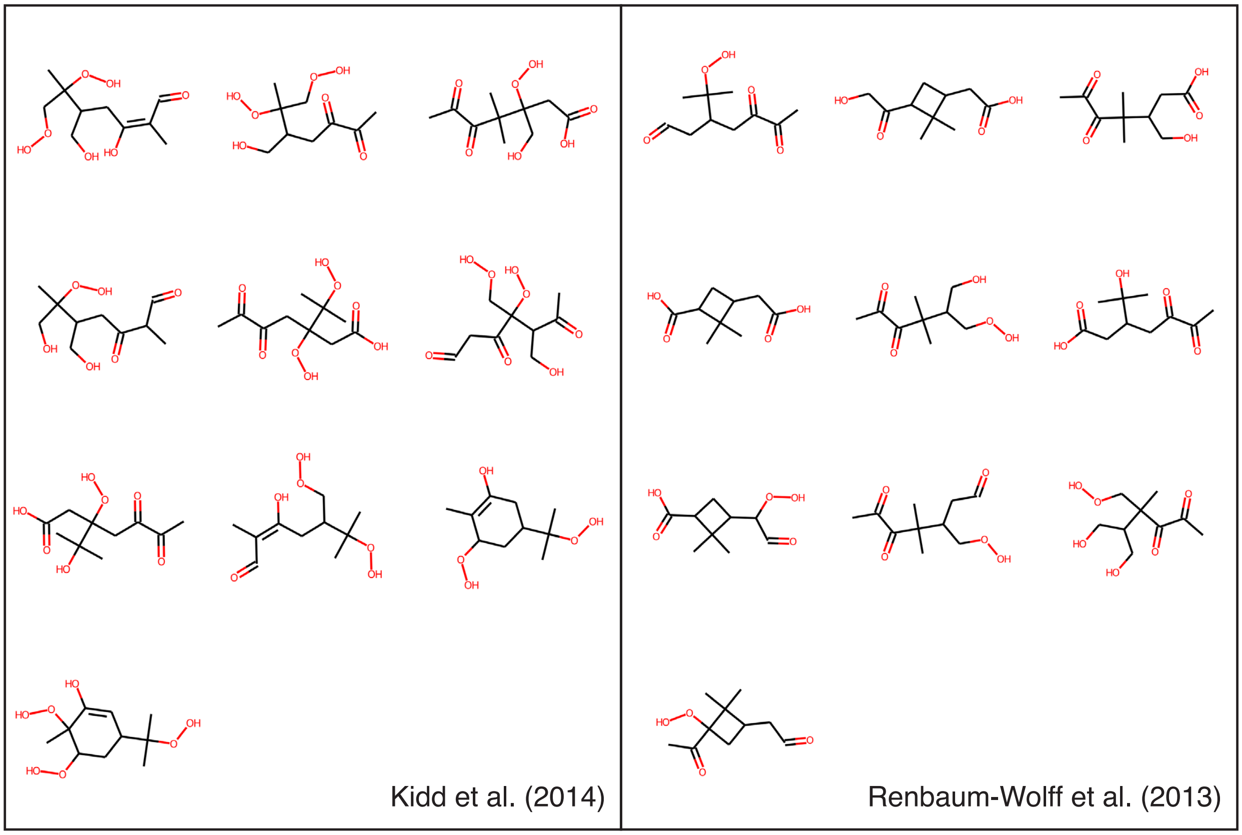

Figure S2: Ten major compounds found in the particle phase at the end of the simulations of Kidd et al. (2014) and Renbaum-Wolff et al. (2013). In both panels species concentrations decreases from the top row to the bottom row and from left to right. The simulations employed the effective mass accommodation coefficient α_{eff}. The simulations were conducted at RH = 0.5%.

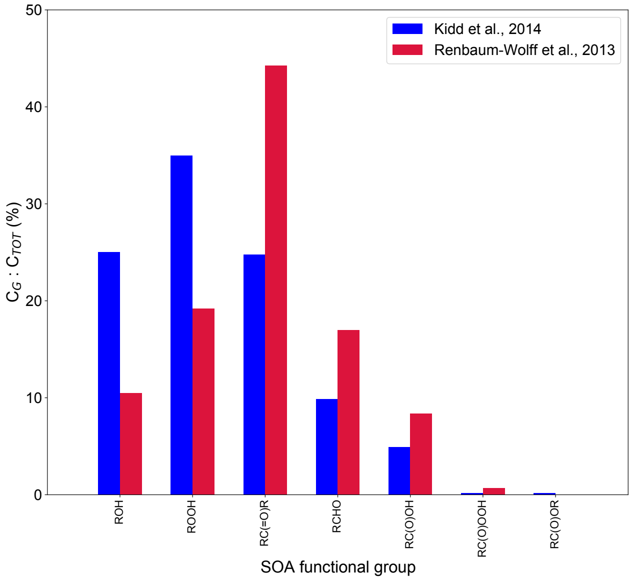

Figure S3: Functional group distributions in particle-phase SOA compounds in simulations of Kidd et al. (2014) (blue bars) and Renbaum-Wolff et al. (2013) (red bars). The simulations employed effective mass accommodation coefficient α_{eff}. The simulations were conducted at RH = 0.5%.

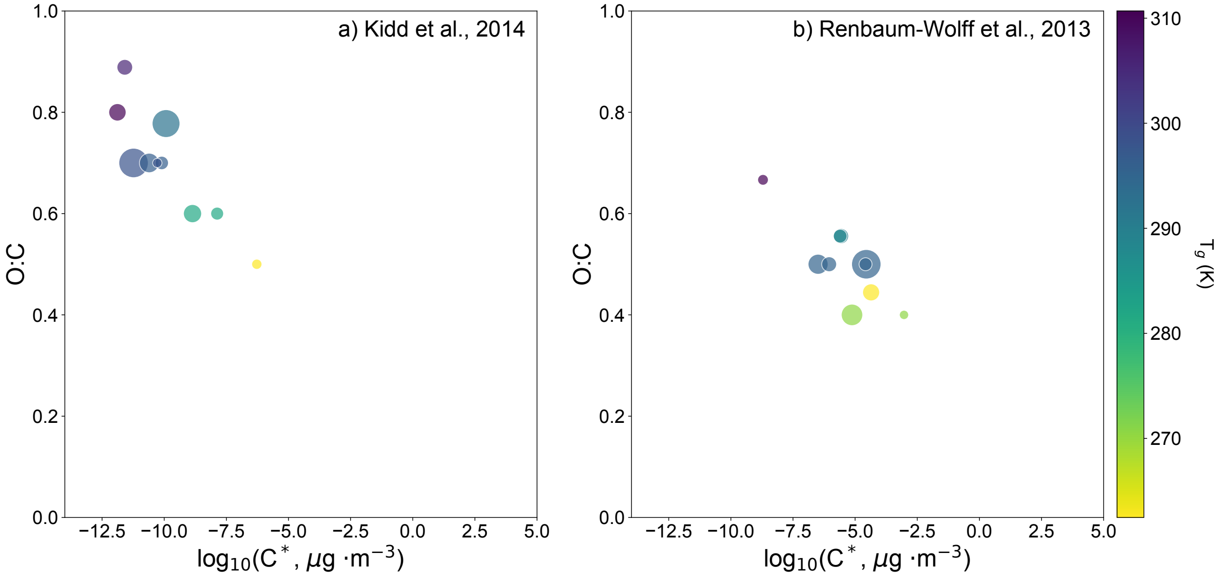

Figure S4: Chemical composition of SOA derived from oxidation of α-pinene from simulations of (a) Renbaum-Wolff et al. (2013) and (b) Kidd et al. (2014) experimental conditions plotted in the 2D-VBS framework of volatility and O:C ratio. The simulations employed effective mass accommodation coefficient α_{eff}. Markers represent the 10 most abundant particle-phase compounds from each simulation. The markers are color-coded with T_g. The marker size is scaled with particle-phase concentration in each simulation. The simulations were conducted at RH = 0.5%.

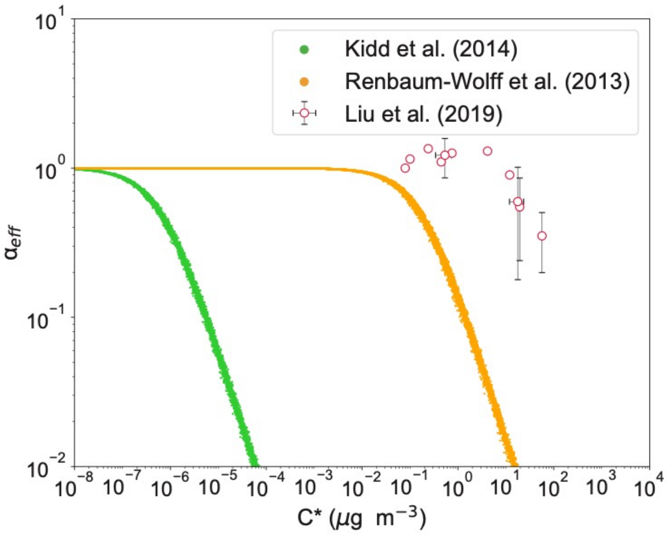

Figure S5: Simulated effective mass accommodation coefficients (α_{eff}) of α-pinene SOA compounds plotted against their effective saturation mass concentration (C^*) for simulations of Renbaum-Wolff et al. (2013) (orange) and Kidd et al. (2014) (green). C^* is assumed to be equal to C^0 with ideal mixing conditions. The markers represent measured mass accommodation coefficients for SOA generated by α-pinene ozonolysis by Liu et al. (2019). The simulations were conducted at RH = 0.5%.

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