

Response to Referee 1 (comments in black, response in blue)

In the manuscript " Secondary Organic Aerosols Derived from Intermediate Volatility n-Alkanes Adopt Low Viscous Phase State, " the authors reported that n-alkane SOA with higher carbon number mainly consists of less functionalized first-generation products with lower viscosity, while the lower carbon number SOA contains more functionalized multigeneration products with higher viscosity based on the GECKO-A box model simulation and chamber experiments. In general, I am very supportive of the hypothesis that the increase of the alkyl group may reduce the viscosity of SOA from n-alkanes, and the topic of this work is interesting to readers of this subject.

We thank Referee 1 for the review and positive evaluation of our manuscript.

Only the functional group information was provided in this study, which can indeed help understand SOA's total properties. However, since there is no specific molecular information in the chamber data, it is very difficult to evaluate the mechanisms generated by the GECKO-A. Using the GECKO-A box model isn't helpful unless you know which products are really forming in the gas phase and subsequent particle-phase chemistry in the aerosol. Additionally, the mechanism's performance should be carefully characterized by chamber experiments before it is used to evaluate the molecular properties of SOA. Thus, for the publication of this manuscript, the following points should be addressed.

In this study, the modeled results were compared against all measured data available for the selected experiments on n-alkane oxidation at high-NO_x, including SOA yield, O:C ratio, and functional group distributions. A very recent study by Ranney et al. (2023) measured specific molecular information of n-hexadecane oxidation products, detecting alkyl nitrates, hydroxyl nitrates, hydroxyl carbonyls, cyclic hemiacetals, and cyclic hemiacetal nitrates as major products. These compounds are among top 15 SOA contributors as shown in Fig. 3a. This agreement is strong indications that GECKO-A simulates molecular products well. We add this point in the revised manuscript. We would like to point out that most previous SOA modeling studies simulate and compare just SOA yield and O:C ratio, and the model comparison with functional group distributions and N:C ratio in this study is highly unique, as they are often not measured nor modeled. The GECKO-A model is very powerful, as it is one of the only SOA models which resolves gas-phase chemistry explicitly to enable comparison with the measured functional group distributions. We also note that measurements of particle-phase concentrations of specific molecular products are very challenging. Mass spectrometry measurements provide elemental composition without resolving functional groups nor isomers, and one requires standard compounds to robustly quantify concentrations, which are often unavailable for SOA oxidation products.

Line 19, in the abstract section, the authors stated that SOA derived from n-alkanes is the dominant component of anthropogenic particulate matter; however, it is generally believed that aromatics and alkenes are the main precursors of anthropogenic aerosols.

Following your comment, we change the word dominant to major. As cited in the manuscript, there are plenty of studies showing that alkane SOA are major components of anthropogenic SOA: anthropogenic precursors are mostly composed of alkanes (40%), followed by aromatics (20%)

and alkenes (10%) with the rest being oxygenated and unidentified compounds (Ziemann and Atkinson, 2012; Shrivastava et al., 2022). We have added these references in the revised manuscript.

In the methods section, the authors showed that GECKO-A generated the chemical mechanisms of n-alkanes; however, the details about the mechanisms were not provided.

The detailed protocol for mechanism generation for n-alkane oxidation mechanism is available in previous studies (Aumont et al., 2013; Aumont et al., 2005; Aumont et al., 2012; La et al., 2016). We have added more information in the revised manuscript as below:

“The GECKO-A generator used for oxidation of linear n-alkanes treats chemistry of peroxy (RO₂) and alkoxy (RO) radicals. Under high NO_x conditions, RO₂ radicals mainly react with NO and NO₂, to form closed-shell compounds or RO radicals, which undergo reaction with O₂, unimolecular decomposition (i.e. C-C bond breaking) or isomerization, which generate stable compounds and/or to new RO₂ radicals. The detailed protocol for such mechanism generation is available in previous studies (Aumont et al., 2013; Aumont et al., 2005; Aumont et al., 2012; La et al., 2016).”

Line 123: How many species were involved during the SOA formation process? Detailed information about the box model should be provided.

We run the mechanism up to four generations. The breakdown of species per chemical mechanism is: C8 = 12686, C9 = 23041, C10 = 36109, C11 = 52460, C12 = 73565, C13 = 92909, C14 = 118668, C15 = 136569, C16 = 141519, C17 = 159640. We think that such exact number of species is not essential, so we included the following sentence in the revised manuscript.

“Species with vapor pressure below 10⁻¹³ atm are assumed to be of low enough volatility to completely partition to the condensed phase and their gas phase chemistry is then not generated in the mechanism to reduce the mechanism (La et al., 2016). The number of species treated in the model was ~10⁴ species for dodecane (C₁₂H₂₆) that increases to ~10⁵ species for heptadecane (C₁₇H₃₆).”

In line 233, the authors only compared the yields of SOA between chamber data and model simulations; without further comparisons of chemical compositions, it is hard to conclude that particle-phase oligomerization contributes minor. Additional information or references are needed to support this statement.

First, we point out that, in addition to SOA yields, we also compared O:C and N:C ratios as well as functional group distributions (Fig. 1). In addition, the modeled viscosity was validated against thermal desorption measurements (Fig. 2b). Recently, Ranney et al. (2023) suggested that cyclic hemiacetals form acetal dimers in the particle phase for SOA formed from the reaction of n-hexadecane SOA and OH/NO_x. While they could not directly detect dimers, their derivatization measurements indicate the presence of acetal dimers. In the revised manuscript, we have toned down our statement to mention that oligomerization chemistry is not a dominant process and then mention these latest results by Ranney et al. (2023). We also note that the impact of such particle-

phase chemistry may warrant further investigations by future model development and experimental studies.

Line 261, why does the $T_{g,org}$ decrease for C_{8-12} in Figure 2a? Some explanation should be provided.

This decrease for C_{8-12} is likely due to steep decrease of O:C ratio upon an increase of n as shown in Fig. 1d, as lower O:C ratio can lead to a decrease of T_g (Shiraiwa et al., 2017; DeRieux et al., 2018). We clarify this point in the revised manuscript.

Figure 2b, some semi-volatile compounds may escape from particles into the gas phase in the aerodynamic lens due to the high vacuum; hence, T_g may be overestimated, and the effect of vacuum on SOA compositions should be discussed.

There seems to be misunderstanding. We did not use information in Fig. 2b to estimate T_g , but Fig. 2 was used to validate the predicted phase state based on GECKO-A modeling. Please note that Fig. 2b represents thermal desorption temperatures of dioctyl sebacate (DOS, vapor pressure is $\sim 2.4 \times 10^{-10}$ atm) that was present as seed particles in n-alkane SOA and it does not show thermal desorption temperatures of SOA itself. Compounds with vapor pressure $< 10^{-5}$ Torr (1.3×10^{-8} atm) is estimated to undergo negligible evaporation as the residence time in the aerodynamic lens is only ~ 0.2 s (Tobias et al., 2000). Thus, DOS and most of SOA products should not be affected, while some volatile oxidation products may undergo evaporation. We revised and clarified this point in the revised method and caption of Fig. 2.

In Line 397, It shows that the model performs well on SOA yields by comparing the chamber and the GECKO-A box model; still, the time profiles of SOA mass concentrations should be provided to evaluate the performance of the box model.

Actually, Fig. 4a represents time profiles, as SOA mass concentrations (x-axis) evolves as a function of time and SOA yields (y-axis) are time-dependent: the data points in this figure were measured at different reaction time in experiments and the modeled lines represent temporal evolution of SOA yield (please see also description in Presto et al., 2010). Good agreement between measurements and simulations confirms good performance by the model. We clarify this point in the revised manuscript.