

Response to Editor

Thank you for reviewing this paper. We hope we have appropriately addressed all of your concerns below.

1) The method of determining the functional group compositions of various alkane SOA using FTIR data were not described adequately in the manuscript. For example, what reference compounds were used? What peaks were used to quantify the different functional groups? How were the functional group compositions converted into O:C values? This type of information is needed to determine if the analysis is appropriate and for others to be able to reproduce the current measurements.

Response: We have FTIR database from numerous chemical species which vary in functional groups and carbon lengths. FTIR data were collected from NIST database and some were measured from SOA related compounds (i.e., pinonaldehyde and pinic acid).

Table S4. Peak assignments of FTIR spectra

Functional group	Peak ranges cm^{-1}	O content	C content
OH stretching in alcohol	3650-3200	1	0
OH stretching in carboxylic acid	3550-2500	2	1
CH stretching	2861, 2927, 2972	0	1
C=O stretching in ketone and carboxylic acid	1725	1	1
C-O stretching (non-carboxylic acid and non-alcohols)	1080-1240	1	1

The area of each functional group is converted to the relative intensity of each functional group. The intensities are normalized by the intensity of CH stretching and used, alongside the values for Oxygen content and Carbon content, to calculate O:C values. This information has been added to Section S8.

2) Response to Reviewer 2, Question 2. The response is good, but the authors should include some or all this text in the revised manuscript to address the Reviewers comment.

Response: "Additionally, compounds used in this study, which were picked from a limited set of commercially available branched alkanes, are generally larger and less branched compared to those identified in the atmosphere and in fuel exhausts. However, even in the case that the atmosphere contains significant amounts of small, highly branched compounds, those would be less relevant for SOA formation potential than compounds used in this study due to negligible SOA yields."

3) Response to Reviewer 2, Question 4. The authors have improved clarity partially, but the description of the lumping array method still remains unclear. Please expand the discussion and consider using examples to improve the clarity.

Response: Discussion has been added to improve the clarity of the lumping array method description.

(Section 3.3) "For example, consider the compound 3-dodecanol, a product of n-dodecane photooxidation. 3-dodecanol has a calculated vapor pressure of 5.1E-3 mmHg (Myrdal and

Yalkowsky, 1997; Zhao et al., 1999; Stein and Brown, 1994). Because the vapor pressure is smaller than that of group 7 (1E-2 mmHg) and larger than that of group 6 (1E-3 mmHg), 3-dodecanol is lumped into volatility group 6. Due to a lack of functional groups which promote particle phase reactions (i.e. ketone and aldehyde), 3-dodecanol is lumped into reactivity group P and will only participate in partitioning. This process is performed to lump each non-radical gas oxidation product, with a sufficiently low vapor pressure, into one of the 48 lumped groups. If group 6P contains only 3-dodecanol, then the α value of that group represents the units (i.e. $\mu\text{g}/\text{m}^3$) of 3-dodecanol produced per unit of precursor HC consumed. If group 6P has multiple compounds, then then the α value of that group represents that the sum of the units produced of all products classified under 6P per unit of precursor consumed. After the initial lumping process, the amounts of each gas oxidation species produced per unit of HC consumed is extracted via a standardized gas simulation. This gas simulation predicts gas oxidation product concentrations for a given initial precursor concentration at various NO_x levels under a sunlight file near the middle of summer (06/23/18). These simulation results produce lumped arrays for 4 different conditions: high NO_x fresh, high NO_x aged, low NO_x fresh, and high NO_x aged. The α value of each group is represented as a polynomial equation which is a function of the HC ppbC/ NO_x ppb level (Table S3). After α values are calculated for a specific HC ppbC/ NO_x ppb level, they can be scaled between fresh and aged compositions as described below.”

Response to Reviewer 1

Thank you for the additional comments. We hope we have appropriately addressed all of your concerns below.

1) Figures S2 Ozone: While the authors have corrected the ozone data for C19B, they have not addressed the concerns regarding C16B. Given that C16B exhibits higher NO_x and HC levels compared to C16C, it is expected that C16B would show higher ozone levels than C16C according to the ozone isopleth. This is consistent with chamber data. However, the simulation significantly underestimates ozone for C16B, leading to much lower ozone levels than those of C16C. This discrepancy raises questions about the possibility of using incorrect data again or potential errors in the simulation.

Response: After closer review, we found that the sunlight intensity data was delayed by an hour due to daylight savings time. Additionally, initial HC concentration in the simulation was increased slightly to better represent the GC-FID measurements. The prediction of Ozone has been improved significantly but overconsumption of HC in the simulation has been increased.

2) L531: I recommend removing this sentence since the discussion on temperature dependency, in relation to Figure 8, has been removed.

Response: The discussion on temperature dependency has been removed in regard to its impact on the contribution of autoxidation products to SOA. However, Figure 8 still shows a significant temperature dependency for branched alkane SOA as a whole and this discussion is included within the text:

(Preceding Fig. 8) “As expected, due to the relatively high importance of partitioning, the SOA yields of all the 3-branched alkanes are significantly impacted by changes in temperature under both NO_x conditions.”

3) I recommend that the authors incorporate the comparison between the studies of Kwok and Atkinson (1995) and Jenkin et al. (2018), already detailed in their response, into the paper (supplement). Including this analysis would provide readers with an updated perspective on the recent developments on this subject.

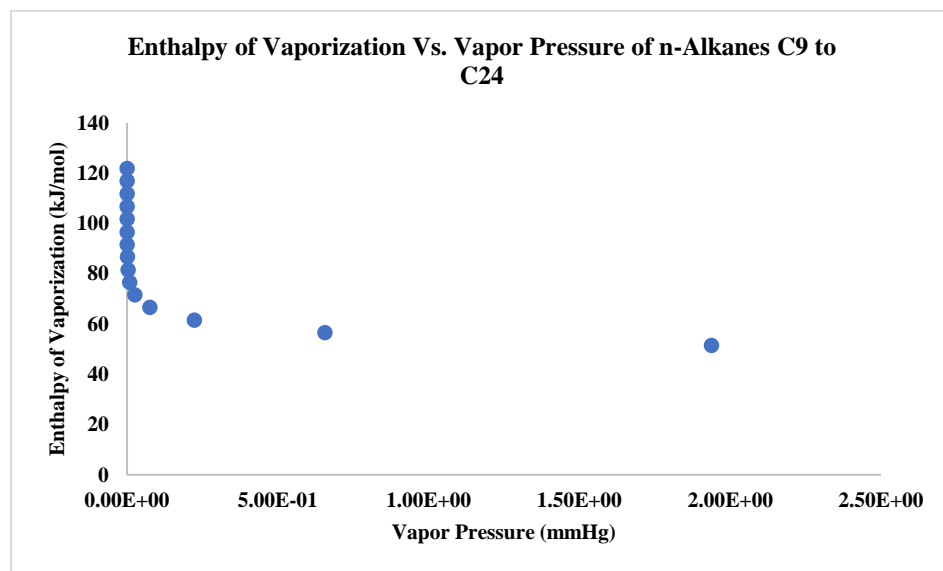
Response: Rate constants calculated using the Jenkin et al. (2018) framework have been added to table S1 under section S3.

Some discussion has also been added in section S3:

“Rate constants calculated using the framework by Kwok and Atkinson (1995) were used for gas simulations in this study. For comparison, rate constants calculated by a more recent framework (Jenkin et al., 2018) are included and do not show significant differences.”

4) What is the source of the enthalpy of vaporization values used in this study? The authors need to cite references or explain the basis for these values. While I agree that these values should increase as volatility decreases, it's not clear why the last three bins have the same enthalpy of vaporization values.

Response: The enthalpy of vaporization and vapor pressure of homologous series of alkanes were used to produce a regression equation to predict the enthalpy of vaporization at given vapor pressures in the SOA model. The three highest volatility bins have the same values because, after a certain vapor pressure, further increases do not result in a significant change in enthalpy of vaporization values. This is demonstrated in the figure below. Enthalpy of vaporization values were taken from the study by Chickos and Hanshaw (2004). A description has been included in section S8.



References

Myrdal, P. B. and Yalkowsky, S. H.: Estimating Pure Component Vapor Pressures of Complex Organic Molecules, *Industrial & Engineering Chemistry Research*, 36, 2494-2499, 10.1021/ie950242l, 1997.

Stein, S. E. and Brown, R. L.: Estimation of normal boiling points from group contributions, *Journal of Chemical Information and Computer Sciences*, 34, 581-587, 1994.

Zhao, L., Li, P., and Yalkowsky, S. H.: Predicting the Entropy of Boiling for Organic Compounds, *Journal of Chemical Information and Computer Sciences*, 39, 1112-1116, 10.1021/ci990054w, 1999.