

## Interactive comment on "Role of methyl group number on SOA formation from aromatic hydrocarbons photooxidation under low $NO_x$ conditions" by L. Li et al.

## Anonymous Referee #1

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General comments:

The authors conducted a series of laboratory chamber experiments on secondary organic aerosol (SOA) formation from the photooxidation of benzene and five mthylbenzenes to study the effects of methyl group number on SOA yield, SOA chemical composition, SOA density, and SOA volatility. Benzene and methylbenzenes will play important roles as SOA precursors in urban air. The SOA precursors they used for experiments were benzene, toluene, m-xylene, 1,2,4-trimethylbenzene, 1,2,4,5tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene. The authors reported that SOA yield decreased, SOA O/C ratio decreased, SOA density decreased,

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and SOA volatility increased with increasing the number of methyl substitution. This manuscript provides new experimental results on SOA formation from the photooxidation of 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene; and it also provides a comprehensive data set of SOA formation from the photooxidation of six aromatic hydrocarbons. This manuscript will be publishable after the following comments are addressed.

Specific comments:

(1) Lines 24-26, page 31154. Information on the total concentration of aromatic hydrocarbons with more than three methyl groups would be necessary.

(2) Lines 12-14, page 31155. What is the definition of "methyl group branching ratio"? The terminology, "branching ratio", is often used for product branching ratio and would make readers confused.

(3) Lines 17-18, page 31155. The expression, "aliphatic hydrocarbons", should be substituted with "alkane and alkene hydrocarbons" because Sato et al. (2011) reported that the SOA yield from aliphatic dinene compounds are found to decrease with increasing the number of methyl side chains.

(4) Line 27, page 31158 – line 1, page 31159. The authors discuss on the results of product volatility parameter based on gas-particle partitioning model; however the authors conclude in the latter part of manuscript that particle-phase oligomerization plays important roles during SOA formation. Particle-phase oligomerization is not taken into account for the gas-partitioning model. Trump and Donahue (2014) reported that formation of oligomer-containing SOA particles can be interpreted by gas-particle partitioning model only if oligomer formation is reversible; however, present experimental results do not contain any evidences showing that oligomer formation is reversible. The product volatility parameters obtained by present fitting would not have physical meaning which is defined by the gas-particle partitioning model.

(5) Line 21, page 31159. Does "the methyl group number effect" mentioned here indicate the effect of methyl group number on SOA yield?

(6) Line 6, page 31161. The readers who do not belong to AMS community might not be familiar to "the AMS frag Table of Unit Resolution Analysis."

(7) Lines 17-21, page 31170. As described in comment (6), product volatility parameters should carefully be interpreted when particle-phase oligomerizations play important roles during SOA formation.

(8) Lines 2-7, page 31171. The authors describe that methyl groups inhibit oligomerization; however, ketones could proceed to aldol condensation and hemiacetal formation (Jang et al., 2002). For readers' understanding, further explanations would be necessary.

(9) Page 31189, Fig. 1. The curves of tetramethylbenzene and C10+ are extrapolated beyond the region of experimental data points. Extrapolated curves should be deleted.

(10) The caption of Table S1. What kind of approximation method was used for the prediction of the pentamethylbenzene vapor pressure?

(11) Table S2. HC/NO ratio data would be incorrect. For example, HC concentration in experiment 104A is 2,800 ppbC (= 350 (ppb) x 8 (C atmos)) and NO concentration is 64.4 ppb; therefore HC/NO ratio should be 43.5 ppbC/ppb (=2,800/64.4).

Technical comments:

(12) Line 7, page 31158. "Table 2" should be "Table 2S".

(13) Line 27, page 31158. The expression, "the more volatile parameters (Kom, 2)", should be substituted with "higher-volatility partitioning parameter (Kom,2)" for readers' understanding.

(14) Line 24, page 31166. "H2O" should be "H2O+".

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(15) Line 19, page 31170. "Oligomerization products (S2)" should be "oligomerization products (S3)".

References:

Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298, 814-817, doi: 10.1126/science.1075798, 2002.

Sato, K., Nakao, S., Clark, C.H., Qi, L., Cocker, D.R. III: Secondary organic aerosol formation from the photooxidation of isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene under high NOx conditions, Atmos. Chem. Phys., 11, 7301-7317, doi:10.5194/ac-11-7301-2011, 2011.

Trump, E.R., Donahue, M.N.: Oligomer formation within secondary organic aerosols: equilibrium and dynamic considerations, Atmos. Chem. Phys., 14, 3691-3701, doi:10.5194/acp-14-3691-2014, 2014.

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