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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of NO_x on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation" *by* Julia Hammes et al.

Anonymous Referee #1

Received and published: 6 June 2019

General comments:

This manuscript reports results of laboratory experiments on secondary organic aerosol (SOA) formation from the photooxidation of 1,3,5-trimethylbenzene (TMB). TMB is an SOA precursor emitted from anthropogenic sources. The authors employ an original flow reactor combined with a chemical ionization mass spectrometer to investigated effects of OH exposure and NOx level on the distribution of oxidation products including particles, highly oxygenated molecules (HOMs), dimeric HOMs, and nitrated HOMs. They concluded that anthropogenic VOCs such as TMB could lead new particle formation (NPF) but NPF is suppressed under high NO conditions. The research

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subject of this study is paid central attention in the field of atmospheric chemistry. The authors employ cutting edge instruments and provide new physical insight into the field of atmospheric chemistry. Because flow reactor experiments under high NOx conditions are very new, the authors should discuss difference between examined reaction conditions and ambient ones. This manuscript suits for the scope of this journal and will be publishable after revisions are made by taking into account reviewer's comments.

Major comments:

(1) Please describe ozone concentration data in the text to discuss the reaction of remaining ozone with NO. If ozone level is higher than 50 ppb, the reaction of ozone with NO (with the rate constant of 1.8x10ˆ-14 cm3 molecule-1 s-1) can significantly occur within a reaction time of 34 s, and NO is converted to NO2. The authors primary assume that nitrated HOMs are formed from the reactions of HOM-RO2 radicals with NO. However, formation of peroxy nitrates from the reactions of HOM-RO2 with NO2 or formation of nitrates from the reactions of HOM-RO with NO2 might be important if NO2 level is much higher than NO level. In experiments with NOx under high ozone levels, NPF was observed. These results may suggest that NO become very low levels due to the reaction with ozone within the reaction time of 34 s, and the reactions of HOM-RO2 with NO2 may become more important than the reactions of HOM-RO with NO.

(2) The authors use NOx levels of 35-82 ppbv, which are similar to NOx levels in urban air, whereas they use HOx (including OH and HO2) levels much higher than ambient levels to accelerate reactions in the laboratory. These conditions may result in overestimation of HOM-RO2 + HO2 reactions and underestimation of HOM-RO2 + NO, HOM-RO2 + NO2, and HOM-RO2 autoxidation, compared to ambient conditions. The authors should discuss difference in branching of HOM-RO2 reactions between present laboratory conditions and ambient conditions.

(3) The authors assume that nitrogen-containing products formed from the oxidation

of TMB in the presence of NOx are nitrates or peroxy nitrates; however this is not evident and further discussion will be necessary in the text. Basically the reviewer agrees with authors' assumption, but in general major nitrogen-containing products, formed from the oxidation of aromatic hydrocarbons, are nitro-aromatic compounds. 1,3,5-Trimethylbenzene is highly methyl-substituted aromatic hydrocarbon and multiple methyl groups inhibit formation of nitro-aromatic compounds (Sato et al., 2012). At this point of view, TMB employed in this study is not a typical aromatic hydrocarbon and a specific molecule, which barely lead to formation of nitro-aromatic compounds.

Specific comments:

(4) Page 3, line 14 and reference list in page 18. Sato et al., 2018 should be Sato et al., 2012

(5) Page 3, line 32. In the unit, "L mol-1", "-1" should be superscript.

(6) Page 4, lines 1-5. Please discuss the phase of products detected by APi-TOF-MS. If it detects products in the aerosol phase, how were these particulate products vaporized in the ion source? Brief explanations would be necessary in the text.

(7) Page 9, lines 14-15. The formation process of compounds with 12 H and 16 H should be explained more in detail. For example, the words, "(terminated from C9H13Ox radicals)", should be written as "(formed from the C9H13Ox + RO2 -> C9H12Ox-1 + ROH + O2 reaction)".

(8) Page 9, lines 32-34. C9H14Ox products include first-generation and second-generation products, i.e., these are formed from the C9H13Ox+1 + RO2 -> C9H14Ox + R'CHO + O2 reaction as well as C9H15Ox+1 + RO2 -> C9H14Ox + ROH + O2 reaction. Please explain why C9H14Ox products have mainly characteristics of second-generation products.

(9) Page 9, last sentence. The authors describe "the contribution of C9H15Ox is reduced at expense of C9H14Ox and C9H16Ox – HOM and dimers," but the meaning

of this sentence is unclear. Do the authors mean that the contribution of C9H15Ox is reduced at the expense of C9H14Ox and C9H16Ox?

(10) Page 12, line 20. The reviewer cannot find “Figure 7.”

(11) Page 13, line 4. The description, “hydroxyl”, should be “RO2”.

(12) Page 13, eq. (6). The chemical formula, R=O, would not be accurate. If the authors use “R=O”, please explain that R=O represents carbonyl products.

(13) Page 13, line 29. Please correct “reaction 56)”.

(14) Page 15, line 15. “Wang et al. (2018)” should be “Wang et al. (2017)”.

(15) The caption of FigureS1. In the caption it is explained “Bottom: Modelled product distribution for all 8 experiments”, but the reviewer cannot find this bottom figure.

(16) Table S2. The symbol, “=”, represents reversible reaction if it is used in reaction equations. The reviewer recommends for the authors to use arrow symbols instead.

Reference:

K Sato, A Takami, Y Kato, T Seta, Y Fujitani, T Hikida, A Shimono, T Imamura, AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1, 3, 5-trimethylbenzene in the presence of NO x: effects of chemical structure on SOA aging, Atmospheric Chemistry and Physics, 12, 4667-4682 (2012).

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