

## ***Interactive comment on “Effect of NO<sub>x</sub> on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation” by Julia Hammes et al.***

### **Anonymous Referee #1**

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#### 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 investigate effects of OH exposure and NO<sub>x</sub> 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 NO<sub>x</sub> 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  $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) can significantly occur within a reaction time of 34 s, and NO is converted to NO<sub>2</sub>. The authors primary assume that nitrated HOMs are formed from the reactions of HOM-RO<sub>2</sub> radicals with NO. However, formation of peroxy nitrates from the reactions of HOM-RO<sub>2</sub> with NO<sub>2</sub> or formation of nitrates from the reactions of HOM-RO with NO<sub>2</sub> might be important if NO<sub>2</sub> level is much higher than NO level. In experiments with NO<sub>x</sub> 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-RO<sub>2</sub> with NO<sub>2</sub> may become more important than the reactions of HOM-RO with NO.

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

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

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of TMB in the presence of NO<sub>x</sub> 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<sup>-1</sup>", "-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 C<sub>9</sub>H<sub>13</sub>O<sub>x</sub> radicals)", should be written as "(formed from the C<sub>9</sub>H<sub>13</sub>O<sub>x</sub> + RO<sub>2</sub> -> C<sub>9</sub>H<sub>12</sub>O<sub>x-1</sub> + ROH + O<sub>2</sub> reaction)".

(8) Page 9, lines 32-34. C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> products include first-generation and second-generation products, i.e., these are formed from the C<sub>9</sub>H<sub>13</sub>O<sub>x+1</sub> + RO<sub>2</sub> -> C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> + R'CHO + O<sub>2</sub> reaction as well as C<sub>9</sub>H<sub>15</sub>O<sub>x+1</sub> + RO<sub>2</sub> -> C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> + ROH + O<sub>2</sub> reaction. Please explain why C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> products have mainly characteristics of second-generation products.

(9) Page 9, last sentence. The authors describe "the contribution of C<sub>9</sub>H<sub>15</sub>O<sub>x</sub> is reduced at expense of C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> and C<sub>9</sub>H<sub>16</sub>O<sub>x</sub> – HOM and dimers," but the meaning

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of this sentence is unclear. Do the authors mean that the contribution of C<sub>9</sub>H<sub>15</sub>O<sub>x</sub> is reduced at the expense of C<sub>9</sub>H<sub>14</sub>O<sub>x</sub> and C<sub>9</sub>H<sub>16</sub>O<sub>x</sub>?

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

(11) Page 13, line 4. The description, "hydroxyl", should be "RO<sub>2</sub>".

(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<sub>x</sub>: effects of chemical structure on SOA aging, Atmospheric Chemistry and Physics, 12, 4667-4682 (2012).

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