

# ***Interactive comment on “Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NO<sub>x</sub> in Beijing” by Lisa K. Whalley et al.***

**Anonymous Referee #1**

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This paper presents the measurements of OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals and OH reactivity in central Beijing in the summer of 2017 as part of the APHH campaign. It reports the highest ever observed OH concentration of  $2.8 \times 10^7$  cm<sup>-3</sup> in urban area, even slightly higher than that reported in PRD in China by Lu et al. (2012).

Experimental budget analysis of OH, HO<sub>2</sub>, RO<sub>2</sub>, and RO<sub>x</sub> was performed in the similar way as Tan et al. (2019) did in PRD in 2014. Consistent with other studies in China, the authors found a missing OH source under low NO (<0.5 ppb) and high VOC condition. Besides, the authors found the opposite trends in HO<sub>2</sub> budget and RO<sub>2</sub> budget. The HO<sub>2</sub> production rate exceeded the destruction rate by the similar rate as the RO<sub>2</sub>

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destruction rate exceed production rate. The authors explained the opposite difference as the substantially slower than assumed net propagation rate of RO<sub>2</sub> to HO<sub>2</sub>. If only 10% of the RO<sub>2</sub> radicals propagate to HO<sub>2</sub> upon reaction with NO, the HO<sub>2</sub> and RO<sub>2</sub> budget would be closed. The authors also performed a model simulation based on MCM 3.3.1, and found consistent results with the experimental budget analysis, except for the OH radical. The model simulated OH concentration very well due to a cancellation of missing OH source and sinks terms in its budget. The model underpredicted the kOH consistently across all NO<sub>x</sub> levels. To understand the model biases, the authors performed several sensitivity tests. The inclusion of heterogeneous loss of HO<sub>2</sub> to aerosol surfaces and CINO<sub>2</sub> chemistry could not entirely explained the HO<sub>2</sub> overestimation and RO<sub>2</sub> underestimation, respectively. Several sensitivity tests were done to see the impact of missing OH reactivity on the modelled radical concentrations by assuming reactants convert OH to CH<sub>3</sub>O<sub>2</sub>, OHCH<sub>2</sub>CHO<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>(O)O<sub>2</sub>, and C96O<sub>2</sub>. The authors proposed that missing OH reactivity converted OH to a larger RO<sub>2</sub> that undergo several reaction with NO, before eventually generating HO<sub>2</sub>, could improve the agreement between observation and simulation, and they used an  $\alpha$ -pinene-derived RO<sub>2</sub> species (C96O<sub>2</sub>) as an example.

The results are of interest to the atmospheric chemistry community, enriching the RO<sub>x</sub> measurement in megacity, and the paper is worthy of publication. However, there are some critical issues and mistakes have to be addressed and corrected in advance before publication. Also, the paper could be shortened quite a bit and the writing could be more concisely and logically.

#### Specific comments:

1. Line 337, Alkyl nitrates are not formed from aldehydes + NO<sub>3</sub>.
2. According to the Fig.4, the RO<sub>2</sub> neutral reaction rate (RO<sub>2</sub>+NO->RO<sub>2</sub>) has no dependence towards NO concentration since the P:D(HO<sub>2</sub>) showed no tendency towards lower NO. However, as the NO decreased, the competitive reaction of RO<sub>2</sub> with HO<sub>2</sub>

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or RO<sub>2</sub> isomerization would become more and more important, and was even comparable to the rate between RO<sub>2</sub> and NO. Thus, the multiple conversion of one RO<sub>2</sub> to another should be reduced towards low NO.

3. The experimental configuration of RO<sub>2</sub> convertor is missing.
4. In Line 573, the estimated NO concentration in the reactor is 4e13 cm<sup>-3</sup>. The reaction time scale of RO<sub>2</sub>+NO reaction is 0.003s. If such large flow was used in the reactor, the conversion to OH could be finished and the OH could further react with NO to form HONO. How do the author account for such conversion?
5. The RO<sub>2</sub> and RO<sub>x</sub> budget is missing the part of Cl oxidation.
6. How sensitive of the experimental budget of HO<sub>2</sub> and RO<sub>x</sub> radical towards the organic nitrate yield in the reaction of RO<sub>2</sub> and NO? The organic nitrate yield varies from 0.01 to 0.5 among different RO<sub>2</sub> species and it might have notable influence on the RO<sub>x</sub> and HO<sub>2</sub> budget. Tan et al. (2019) not only set the yield to 0.05 but also performed the sensitivity tests by varying the yield from 5% to 20%, and notable influence was observed for their study although the bias was still within the experimental errors. Considering the large measured RO<sub>2</sub> concentration, the yields might play significant role on this budget analysis in this study.
7. If it was the case as the author said, 90% of the measured RO<sub>2</sub> would react with NO to produce another RO<sub>2</sub>, in which the majority of the RO<sub>2</sub> was probably derived from long-chain alkanes, monoterpenes, and other like-VOCs, this part of RO<sub>2</sub> should be detected in the RO<sub>2</sub>-complex. According to Fig 5, the RO<sub>2</sub>-complex only made up less than 50% of the total RO<sub>2</sub>. Besides, if the multiple bimolecular reaction of RO<sub>2</sub> with NO made up such a proportion (90%), the ozone production would be inconceivably enhanced, but was not embodied in the observed O<sub>3</sub> concentrations.
8. Line 563, Line 574-575, and Table 3, the author attributed the missing OH reactivity to additional reaction converting OH to C<sub>96</sub>O<sub>2</sub>, which is an  $\alpha$ -pinene derived RO<sub>2</sub>,

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but C96O2 is formed in the  $\alpha$ -pinene reaction with O3 but NOT with OH. How do the authors justify this assumption? Some discussion to make such assumption is needed.

Technical comments:

1. Line 234, the last [RO2] should be out of the right bracket in Eq (6).
2. Line 360, 'production and destruction'.
3. There is no need for 2.4.1.
4. Line 513,  $\alpha = 0.87$  seems to be wrong or the description of  $\alpha$  was confusing.
5. Conclusion should be section 4.

Interactive comment

References

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