Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-785-RC1, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NO_x in Beijing" *by* Lisa K. Whalley et al.

Anonymous Referee #1

Received and published: 28 October 2020

This paper presents the measurements of OH, HO2, and RO2 radicals and OH reactivity in central Beijing in the summer of 2017 as part of the APHH campaign. It reportes the highest ever observed OH concentration of 2.8×107 cm-3 in urban area, even slightly higher than that reported in PRD in China by Lu et al. (2012).

Experimental budget analysis of OH, HO2, RO2, and ROx 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 HO2 budget and RO2 budget. The HO2 production rate exceeded the destruction rate by the similar rate as the RO2

destruction rate exceed production rate. The authors explained the opposite difference as the substantially slower than assumed net propagation rate of RO2 to HO2. If only 10% of the RO2 radicals propagate to HO2 upon reaction with NO, the HO2 and RO2 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 NOx levels. To understand the model biases, the authors performed several sensitivity tests. The inclusion of heterogeneous loss of HO2 to aerosol surfaces and ClNO2 chemistry could not entirely explained the HO2 overestimation and RO2 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 CH3O2, OHCH2CHO2O2, CH3(O)O2, and C96O2. The authors proposed that missing OH reactivity converted OH to a larger RO2 that undergo several reaction with NO, before eventually generating HO2, could improve the agreement between observation and simulation, and they used an α-pinene-derived RO2 species (C96O2) as an example.

The results are of interest to the atmospheric chemistry community, enriching the ROx 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 + NO3.

2. According to the Fig.4, the RO2 neutral reaction rate (RO2+NO->RO2) has no dependence towards NO concentration since the P:D(HO2) showed no tendency towards lower NO. However, as the NO decreased, the competitive reaction of RO2 with HO2

or RO2 isomerization would become more and more important, and was even comparable to the rate between RO2 and NO. Thus, the multiple conversion of one RO2 to another should be reduced towards low NO.

3. The experimental configuration of RO2 convertor is missing.

4. In Line 573, the estimated NO concentration is the reactor is 4e13 cm-3. The reaction time scale of RO2+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 RO2 and ROx budget is missing the part of Cl oxidation.

6. How sensitive of the experimental budget of HO2 and ROx radical towards the organic nitrate yield in the reaction of RO2 and NO? The organic nitrate yield varies from 0.01 to 0.5 among different RO2 species and it might have notable influence on the ROx and HO2 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 RO2 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 RO2 would react with NO to produce another RO2, in which the majority of the RO2 was probably derived from long-chain alkanes, monoterpenes, and other like-VOCs, this part of RO2 should be detected in the RO2-complex. According to Fig 5, the RO2-complex only made up less than 50% of the total RO2. Besides, if the multiple bimolecular reaction of RO2 with NO made up such a proportion (90%), the ozone production would be inconceivably enhanced, but was not embodied in the observed O3 concentrations.

8. Line 563, Line 574-575, and Table 3, the author attributed the missing OH reactivity to additional reaction converting OH to C96O2, which is an α-pinene derived RO2,

but C96O2 is formed in the α-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, α = 0.87 seems to be wrong or the description of α was confusing.

5. Conclusion should be section 4.

References

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häseler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, Atmospheric Chemistry and Physics, 12, 1541-1569, 10.5194/acp-12-1541-2012, 2012.

Tan, Z., Lu, K., Hofzumahaus, A., Fuchs, H., Bohn, B., Holland, F., Liu, Y., Rohrer, F., Shao, M., Sun, K., Wu, Y., Zeng, L., Zhang, Y., Zou, Q., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Experimental budgets of OH, HO2, and RO2 radicals and implications for ozone formation in the Pearl River Delta in China 2014, Atmospheric Chemistry and Physics, 19, 7129-7150, 10.5194/acp-19-7129-2019, 2019.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-785, 2020.