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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 #2

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This paper presents measurements of OH, HO2, and RO2 radical concentrations in addition to measurements of total OH reactivity in Beijing during the AIRPRO campaign in summer 2017. A radical budget analysis using the measured sources and sinks of these radicals revealed a potential missing source of OH during most of the campaign, although rates of OH production and destruction were in better balance under the higher NOx periods. The measured rates of HO2 production were found to be significantly greater than the rates of destruction, while the measured rates of destruction of RO2 radicals was found to be greater than the rates of production, especially under the higher NOx periods. These results suggest that the rate of conversion of RO2 to HO2 may be significantly slower than currently assumed.

The authors also present the results of several 0-D box models using the MCM 3.3.1 chemical mechanism. The model was able to reproduce the measured OH concentrations, but underestimated the measured total OH reactivity, suggesting that the agreement may be fortuitous. The model also overestimated the measured HO2 concentrations and underestimated the measured RO2 concentrations, consistent with the experimental radical budget suggesting that the model may be overestimating the rate of conversion of RO2 to HO2 under high NO conditions. The model was found to be in better agreement with the measurements if the missing reactivity was assumed to be composed of VOCs that produced a-pinene derived RO2 radicals that upon reaction with NO results in isomerization reactions that reform other RO2 species before eventually producing HO2 effectively reducing the rate of conversion of RO2 radicals to HO2. While this model scenario improved the model agreement with the measurements of HO2 and RO2, it significantly underestimates the measured OH concentrations, consistent with a missing OH source. However, the proposed RO2 isomerization reactions may lead to the production of OH radicals and contribute to the missing OH source. The significant underestimation of the observed RO2 concentrations implies that the model is significantly underestimating the observed rate of ozone production under high NOx conditions.

The measurements appear to be of high quality and include measurements of unknown interferences, which except for a few instances were found to be negligible. The measured radical concentrations are consistent with previous ROx measurements in several urban areas and is of interest to the atmospheric chemistry community. I recommend publication after the authors have addressed the following comments.

1) The analysis generally focuses on the campaign average and the measurements under higher NOx conditions, but there is little discussion regarding the measurements under lower NO conditions, and in particular the extended period at the end of the campaign where the measured RO2 concentrations were the highest. The scale used in Figure 2 makes it difficult to see, but the discrepancy between the measurements

and the model appears to be as significant as the discrepancies at higher NOx for this period. Unfortunately, this is not apparent from the information provided in Figure 6. It is not clear whether the additional VOC reactivity producing RO2 radicals that isomerize after reaction with NO to form additional RO2 would improve the model agreement for this period, as it is not clear whether reaction with NO still dominates the fate of peroxy radicals during this portion of the campaign. While the manuscript is already long, it would still benefit from a discussion of this aspect of their measurements.

2) Related to this, Berndt et al. (2018) report that RO2 + RO2 accretion reactions for a-pinene may be significant under low NOx conditions, and this type of accretion reaction may also be important for the peroxy radicals of other large VOCs. It's not clear whether these reactions could impact the modeled RO2 concentrations overall, but could be important during the low NOx period at the end of the campaign when the RO2 concentrations are high. Given that the authors are hypothesizing that isomerization of peroxy radicals of large VOCs produce additional peroxy radicals, the authors should comment on the potential impact of these reactions on the model results.

3) The authors should provide plots of some of the diurnal averaged constraints for their model (NO, NO2, O3, CO, isoprene, etc.) to allow comparisons with other urban measurements and to put the results shown in Figure 5 into context. Adding the diurnal average of the low NOx period at the end of the campaign would also assist in interpreting the radical measurements during this period. This information could go into a supplement.

4) The definition of alpha on page 17 line 513 appears to be an error as it is not consistent with the value and the definition described on page 8 line 246. This should be clarified.

Reference Berndt, T.; Mender, B.; Scholz, W.; Fischer, L.; Herrmann, H.; Kulmala, M.; Hansel, A., Accretion Product Formation from Ozonolysis and OH Radical Reaction of alpha-Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene.

Environ. Sci. Technol. 2018, 52 (19), 11069-11077.

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Discussion paper