

Atmos. Chem. Phys. Discuss., referee comment RC1
<https://doi.org/10.5194/acp-2022-239-RC1>, 2022
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Comment on acp-2022-239

Anonymous Referee #1

Referee comment on "Investigation of the limonene photooxidation by OH at different NO concentrations in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber)" by Jacky Yat Sing Pang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-239-RC1>, 2022

Review of:

Investigation of the limonene photooxidation by OH at different NO concentrations in the atmospheric simulation chamber SAPHIR

Pang et al. 2022

This manuscript presents an experimental study of the OH initiated oxidation of limonene under different NO_x concentrations, and the O₃ initiated oxidation of limonene at 'zero' NO_x. The experiments are performed in the atmospheric simulation chamber SAPHIR. The first generation stable product formaldehyde is measured, as well as the radicals OH, HO₂, RO₂, NO and NO₂. These measurements are used in conjunction with a box model and the MCM mechanism to interpret the results. Discrepancies between the modelled chemistry and the measurements highlight gaps in our understanding of the oxidation mechanisms. The largest discrepancy between measurements and model is with measured total RO₂, particularly at low NO_x concentrations, where the model greatly over-predicts measured RO₂. This is interpreted as there being a missing RO₂ sink(s) in the model, either bimolecular, e.g. RO₂+RO₂, RO₂+HO₂, or unimolecular. A number of model scenarios are run to try to further elucidate the nature of the missing reaction(s).

The paper is generally well written, particularly the detailed but concise introduction. There are in fact a rather limited number of experiments, though each has a large amount of data, and few conclusions can be drawn beyond that there are missing RO₂ loss processes. This conclusion is of course a useful conclusion to draw, and I presume that the experiments were not performed with the express goal of investigating specific RO₂ processes since they were not a coherent campaign but drawn together from various times. The work serves to further highlight that the behaviour of RO₂, particularly complex

RO₂, at low NO_x is one of the largest uncertainties in our current understanding of gas phase chemistry. It also highlights that there are a number of possible fates of these RO₂ and details the recent body of theoretical work which is attempting to elucidate the most important unimolecular pathways, which are particularly challenging to investigate experimentally. It seems to me that two processes that could be explored more easily experimentally are the possibility of cyclic OH-RO₂ self/cross reactions being particularly fast, through experiments with cyclohexene/pentene etc. And the reaction of these RO₂ and/or large acyl peroxy radicals with HO₂. A better understanding of these processes, gained through systematic experimental work would greatly aid the interpretation of the oxidation mechanisms of the more complex monoterpenes.

Specific comments

Line 58: no comma needed here

Line 75: should 'drawing' be 'withdrawing' ?

Line 207/8: Could the authors specify that these are (I presume) assumed to be from processes occurring on the chamber film surface?

Line 205: This could do with a little more discussion highlighting that the majority of previous experiments will have been done at low humidity. The conditions employed here are clearly more relevant to the atmosphere, but do you have thoughts on whether this may affect the major oxidation pathways. Also, does the high humidity have any negative effect on the instrumentation?

Table 2: Is this the correct NO concentration for the high NO experiment? Is it lower than expected because it's an average? It then doesn't agree with the value used for NO in Table 3.

Line 361: Highlight that this is as would be expected based on your OH+limonene experiments at low NO, which have a similar OH yield to the ozonolysis experiment.

Line 368: I'm not sure that this is worth noting without some further explanation of what you mean. Which experiments of Gong et al. does this refer to? All of them? This fact could mean different things based on the experiment. Is it because O₃ is so high that the

O₃+ limonene reaction is still dominant over the OH reaction? Or because, as in your experiments, OH is reacting with limonene, but, at low NO, the HCHO yield is similar to the ozonolysis?

SECTION 3.1.2: This seems like a rather convoluted process to calculate the organic nitrate yield and I would suggest that, based on this, the stated uncertainty is rather low!

Line 679: This seems like the more likely explanation. You will be forming very different RO₂.

Figure 9 and 10: Which experiment is which? Can these be labelled a and b.

Line 794: 'optimised'