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Reply on RC1

Jacky Yat Sing Pang et al.

Author 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-AC1>, 2022

We thank the reviewer for the useful comments improving our manuscript.

Line 58: no comma needed here

Authors response:

Thanks for the correction, the comma in line 59 is now removed.

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

Authors response:

To avoid confusion, we rephrase the sentences without using 'drawing' in Line 76 – 79: "H-shift reactions are very slow ($k < 10^{-3} \text{ s}^{-1}$ at 298 K) in an aliphatic peroxy radical without an oxygenated function group (e.g., carbonyl, hydroxyl, alkoxy) attached to the carbon atom, from which the hydrogen is abstracted (Otkjær et al., 2018; Praske et al., 2019). Therefore, H-shift reactions typically cannot compete with bimolecular reactions under atmospheric conditions ($k_{\text{bi}} \sim 10^{-2} \text{ s}^{-1}$, for 50 pptv of NO and $5 \times 10^8 \text{ cm}^{-3}$ of HO₂)."

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

Authors response:

Yes, HONO and VOCs are presumably formed from the reactions on the chamber wall surface. We added in Line 217: "...presumably from chamber wall reactions."

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?

Authors response:

Statements that mentioned the experimental conditions of the previous experiments are added in the introduction (line 92 – 95): “Radiation and relative humidity during the experiments were also relevant to the conditions that are typically found in the atmosphere, which was an improvement compared to previous experiments that typically used artificial light sources or were conducted under very dry conditions (e.g., Larsen et al. (2001) and Librando and Tringali (2005)).”

As far as we know, stabilised Criegee Intermediates (sCI) that are produced from the ozonolysis of limonene can react with water molecules. However, the sCI yield of limonene ozonolysis is about 32% (Cox et al., 2020) and it is estimated that less than 50% of the sCI reacts with water under atmospheric conditions (Vereecken et al. 2017). Therefore, we think that the variation of humidity does not affect the major oxidation pathways of limonene ozonolysis.

In addition, hydroperoxyl radical (HO_2) can form an $\text{HO}_2\text{-H}_2\text{O}$ complex with a water molecule. The complexation reaction can speed up the self-reaction of HO_2 to form hydrogen peroxide. Water vapour can also affect the size distribution of aerosol particles which could change the rate of the uptake reactions. However, the heterogeneous reactions are assumed to be not important in this study.

Humidity can affect the measurement of OH and NO_x concentrations. For example, water vapour can interfere with the measurements of OH using laser-induced fluorescence (LIF) by quenching the OH radical (Holland et al., 1995). However, these instruments are calibrated to minimize the interference in the measurements. Therefore, we do not think that the presence of humidity has a large impact on the experimental results.

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.

Authors response:

Radicals concentrations and OH reactivities are analysed only in part of the experiment with high NO concentrations. Values in Table 2 give concentrations for that period. The NO concentration in Table 3 is from the period after the first limonene injection, when the HCHO yield is calculated. In order to explain this we added in Line 232-238: “When most of the limonene was consumed within two hours after the first injection, an additional injection of 10 ppbv of limonene was done. In this work, the HCHO yield is only analysed based on the measurement before the second limonene injection (Section 3.1.1), because of the potential secondary production of HCHO from the oxidation of secondary products. The radical concentrations and OH reactivities are only analysed after the second limonene injection (Section 3.2.3), because radical measurements failed during the first part of the experiment. A large fraction of NO was already titrated by ozone after the second limonene injection.” The caption for Table 2 is also changed accordingly: “Experimental conditions during the time period when the radical budget of limonene oxidation experiments is analysed ...”

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.

Author response:

We assume that the reviewer means HCHO yield. We added in Line 376 – 380: “The HCHO

yield derived from the ozonolysis without the presence of the OH scavenger is similar to the HCHO yield in the experiments with low NO concentrations. This is expected because of the very low NO concentrations and the similar fraction of limonene that reacted with OH or O₃ in both experiments.”

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?

Authors response:

The experiment that we are referring to is the experiment with high limonene: ozone concentration ratio (1:2). This is because HCHO could be produced quickly from the ozonolysis reaction of the secondary products if the ozone concentration is very high. In our analysis, we try to exclude the potential HCHO production from the ozonolysis of secondary products by only considering the measurements when less than 40% of the injected limonene was reacted. In this case, using the reported HCHO yield from Gong et al. with high limonene: ozone concentration ratio to compare with our reported yield is more appropriate. Gong et al. also investigated the effects of humidity and OH scavenger on the HCHO yield. We compared our HCHO yield with the yield reported from the experiments that were conducted under similar relative humidity (30 – 50%) in Gong et al. to see whether the effects of OH scavenger on HCHO yield are consistent in the two studies. The result from Gong et al suggests that OH scavenger does not affect HCHO yield when limonene: ozone concentration is high, which is consistent with our findings. Additional description is now included in Line 388 – 393: “The effects of humidity and presence of an OH scavenger on the HCHO yield were also investigated in Gong et al. (2018). In their experiments, the HCHO yield increases strongly with increasing humidity and in the absence of an OH scavenger when the limonene: O₃ ratio was very low (1:100). On the other hand, the positive dependence of the HCHO yield on humidity and the absence of OH scavenger is much less significant when the limonene: O₃ concentration ratio was high (1:2). There is no significant impact of OH scavenger on the HCHO yield found in this study consistent with findings in the experiments in Gong et al. (2018).”

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!

Authors response:

The organic nitrate yield is calculated by performing a regression analysis between two cumulative quantities: the total amount of RO₂ that reacts with NO, and the total amount of organic nitrate present in the chamber which is calculated by the cumulative nitrogen production subtracting the concentrations of inorganic nitrogen species. The stated organic nitrate yield (34±5%) here has a precision of about 15%, which is determined by the data points and their error bars of the two experiments. The size of the error bar is calculated based on the precision of the instruments with linear error propagation. The final precision (15%) is smaller than the precision of some of the measurements. This is because the precision of a cumulative quantity gradually increases when there are more data point available. On the other hand, the 1-σ accuracy of the nitrate yield is estimated to be about 30% at maximum, which is mostly attributed to the accuracy of the reaction rate constant $k_{\text{RO}_2+\text{NO}}$ (~30%) and the 1-σ accuracies of the HONO (10%) and j_{HONO} (18%) measurements.

Statements are added to Line 444 – 447: “The precision ($\sim 15\%$) of is determined by the precision of the measurements with linear error propagation. The error of is estimated to be about 30%, which is mainly attributed to the accuracies of the reaction rate constants $k_{\text{RO}_2+\text{NO}}$ ($\sim 30\%$) and the measurements of HONO (10%) and j_{HONO} (18%).”

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

Authors response:

We do not know the exact reason that causes the large difference in k_{add} . Although RO₂-limOH and RO₂-limO₃ are very different and have different chemistry, the difference in the fraction of RO₂-limOH and RO₂-limO₃ in the low-NO experiment and the ozonolysis experiment was too small to explain the large difference in k_{add} , as both experiments have about (40 – 60)% of RO₂-limOH and RO₂-limO₃. Therefore, temperature difference may be an important factor that causes the lower k_{add} in the ozonolysis experiment. However, we do not want to make a solid conclusion on which factor is more likely. The sentence (Line 708 – 712) is rephrased to mention that temperature and the structure of the RO₂ could both contribute to the large difference in k_{add} : “The large difference in k_{add} could be attributed to the different RO₂ species that are formed from the photooxidation reaction and the ozonolysis reaction. RO₂ formed from the photo-oxidation reaction have retain their 6-member ring moiety, whereas the majority of RO₂ formed from the ozonolysis reaction are acyclic. In addition, the low temperature during the ozonolysis experiment could slow down the additional loss pathway.”

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

Authors response:

Thanks for the suggestion. Each subplot in Figure 9 and 10 is now labelled.

Line 794: 'optimised'

Authors response:

Thanks for the correction, it is corrected (Line 829).