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Interactive comment on "OH regeneration from methacrolein oxidation investigated in the atmosphere simulation chamber SAPHIR" *by* H. Fuchs et al.

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We thank the reviewer for the helpful comments.

Comment: One subtlety that almost gets lost in the detail is that even in the presence of 90 ppt NO (or ≈1 ppb NOx), the isomerization reaction still dominates. Maybe this could be stated more forcibly.

Response: We agree. We will add a sentence at the end of the abstract: "The isomerization reaction would be the dominant reaction pathway for this specific RO2 radical in forested regions, where NO mixing ratios are typically much smaller." We will change

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the text on p.5213 l.22-23 to: “Thus, the 1,4-H-shift reaction would be competitive to the reaction of MACRO2 with 150 pptv NO or even higher NO mixing ratios.

Comment: The measured loss of methacrolein is larger than that predicted by MCM. However, the MPAN concentration is modeled quite well. Why is this the case?

Response: The calculated MPAN mixing ratio depends on the yield of MACO3 in the reaction of methacrolein and OH, the calculated NO2 concentration, temperature and the thermal equilibrium constant. Only few studies exist investigating the MACO3 yield and the thermal equilibrium of MPAN. Therefore, calculated MPAN mixing ratios are considered to have a large uncertainty. The measurements of MPAN have a larger uncertainty (20%) than stated in the original manuscript. The value has been corrected in the revised version (Tab. 2), because the sensitivity of the GC for MPAN was deduced from the measured sensitivity for PAN with a correction taken from literature (Flocke et al., J. Atom. Chem., 2005). As seen in Fig. 4 calculated MPAN mixing ratios do not change more than 30% between the model runs. Adjustment of the MACO3 yield in the reaction between methacrolein and OH and/or the thermal equilibrium constant within their uncertainties can easily change calculated MPAN mixing ratios for a perfect match with observations. Therefore, we do not regard the apparently better agreement of calculated MPAN mixing ratios compared to the agreement of methacrolein in the MCM model run as a hint for an inconsistent description.

Comment: Could you comment on the MPAN profiles? Do they roll off because of loss by OH + MPAN, or because of decreased production efficiency?

Response: The shape of the MPAN profile is eventually determined by the production of MACO3 radicals. MACO3 production decreases after each methacrolein injection due to the consumption of MACR. Therefore, MPAN production decreases, but also the loss of MPAN due to its thermal equilibrium with MACO3 increases. The loss rate of MPAN due to its reaction with OH is at least four times smaller for conditions of this experiment. We will add on p.5206 l.3: “The shape of the temporal behavior of MPAN

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mixing ratios is determined by the thermal equilibrium between MPAN and MACO3, forcing the fast built up of MPAN after each methacrolein injection. At later times, the MPAN reservoir starts to deplete, when MACO3 concentrations are decreasing with the decreasing production from the reaction of MACR with OH."

Comment: Do the formaldehyde measurements provide any constraint on the chemistry, and in particular the extent of cycling?

Response: Formaldehyde is not thought to be a co-product of hydroxyacetone, the product species, whose concentrations is affected most by the additional OH cycling processes. It is mostly determined here by the processing of acetaldehyde, PAN, and MPAN. Because we have a small source of acetaldehyde and also formaldehyde in the chamber, the contribution of formaldehyde from MPAN is too small for a better constraint of MPAN (and therefore the production of MACO3 as a product of the MACR+OH reaction) for conditions of these experiments.

Comment: I presume that the RO2 instrument is mainly measuring “MACRO2” radicals. If so, a short, specific statement as to their detection efficiency, and their contribution to the HO2 measurement, would be useful.

Response: Only model calculations allow concentrations of specific RO2 to be estimated. Here, a larger part of the total RO2 was also methyl-peroxy radicals for conditions of these experiments. However, the fractional contribution changes over the course of the experiment and strongly depends on the model that is applied. For example, application of the model modification that includes the fast isomerization predicts that the majority of RO2 radicals is CH3O2 due to the short lifetime of MACRO2 in this case.

For these reasons, also the contribution to HO2 measurements can only be estimated using model calculations as stated on p.5204 l.20-22. We will add two more specific statements:

p.5204 l.20-22: "... the contribution of this interference to the entire HO2 detection was less than 5%, most of which is caused by RO2 from MACR."

p.5202 l.22: "The detection efficiency for MACR derived RO2 which are efficiently converted is similar to that of methyl-peroxy radicals."

Comment: 5199-18. "products yields" should be "product yields"

Response: Done.

Comment: 5201-25. It looks like 3 injections of about 7 ppb MACR were made. This might be a more useful statement, rather than "maximum mixing ratio up to 14 ppb".

Response: We will change the statement accordingly: "The initial phase ("ZA") with zero air, water vapour, and ozone had a total duration of 2 hours. Thereafter, MACR was injected several times increasing the mixing ratio by 7 ppbv each time. The maximum mixing ratio was 14 ppbv."

Comment: 5205-16. "instable" should be "unstable".

Response: Done.

Comment: 5208, (R8) and (R9): The products in Table 4 are different from those in the text.

Response: We will correct the typo in the table.

Comment: Figs 4 and 5. The red and pink colors are a little hard to distinguish.

Response: We will change colors.

Comment: 5210, bottom. MACROHO2 can actually undergo two 1,5 H-shifts, both leading to the same products. Please state explicitly that it is the shift of the aldehyde H you are talking about.

Response: We will change the text on p.5210 l.26 to: "The 1,5-H-shift of the aldehyde H-atom in MACROHO2 would produce hydroperoxyacetone..."

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Comment: 5211-3. “According to this study” Please specify which (Crounse or the present one).

Response: We will change the text on p.5211 l.3 to: “According to the study by Crounse et al. ...”

Comment: 5212-1. I still think it is a little glib to say that the yield 0.47 is consistent with 0.77 +/- 0.3.

Response: The error of 0.3 of the slope in our correlation analysis results from the 1-σ accuracy of several measurements. Moreover, also the yield of MACROHO2 (8 %) needs to be added, if the mechanism by Crounse is applicable, because also MACROHO2 would exclusively isomerize for conditions of this experiment. We will change the text on p.5212 l.1 to: “Our OH yield of 0.77 for each OH radical consumed by MACR (Fig. 3) is larger than the yield of 0.55 predicted by the model calculation, if MACRO2 and MACROHO2 is completely converted to OH in the isomerization reaction. This is, however, no contradiction considering the relative large uncertainty of $\pm$0.3 (1-σ) of our experimental value and the uncertainty of the model. Thus, our SAPHIR experiments presented in this work do not allow to determine an upper limit of the 1,4-H-shift isomerization rate constant.”

Comment: Overall, this is an excellent study. The analysis understandably focuses on the radical budget, but this means that some details, such as the MPAN and NO/NOx profiles, get overlooked. The authors should consider whether the inclusion of any of these other results could help to reduce the uncertainties in their measurements.

Response: The reviewer is correct that the focus of this study was on the radical budget. We certainly looked into the budget for nitrogen oxides. However, the longer lifetime of nitrogen oxide species compared to HOx radicals makes an analysis more complicated, because chamber sources (HONO) and reservoir species (see response above) have to be known with high accuracy. This was beyond the scope of this study. Regarding the OH cycling, nitrogen oxide species would not give a better con-

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straint than determined from the OH budget. Especially MPAN is formed from the RO2 species (MACO3), which is not thought to produce OH from an H-shift reaction. Therefore, MPAN would only be useful to better constrain the yield of the different RO2 species.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 5197, 2014.