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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: My main comment is that from the way the data in figure 4 is presented the measured OH, at least by LIF, seems noticeably higher than the one modelled using "RO2 isom. B", especially in the last segment of the experiments. I very strongly suggest showing the data in the top right of figure 4, specifically LIF-OH, DOAS-OH, MCM OH and RO2 isom. B OH as ratio of measured to model. It is likely that due to the way the data is shown the measured LIF values lie behind the other traces, which gives

rise to the impression I describe. I realize that Figure 5 shows something related for DOAS OH, but figure 4 does not look very similar and I think this needs to be clarified.

Response: The OH data in Figure 4 are from the experiment on 11 August 2011. On this particular day, the LIF data were indeed higher than the DOAS data by on average 0.5×10^6 cm^{-3} (determined from the intercept of a linear regression; Fuchs et al., 2012). Such a difference was not observed during other MACR oxidation experiments, leading to the conclusion that the OH measurements are not subject to a significant interference from MACR (Fuchs et al., 2012). In the present paper, we show data from the 11 August (Figs. 1, 2, 4, 5), because on this day the number of supporting measurements such as PAN, MPAN and HONO were available in contrast to the other two experiments. For the quantitative analysis in Figs. 2 and 5, we used the DOAS data because DOAS is regarded to be a reference technique. In Fig. 3, all data (LIF, DOAS) from all experiments were used to determine the OH yield of the missing OH source. The OH yield (slope of the regression line) has only a small sensitivity to the offset between DOAS and LIF. In fact, the offset has little impact on the results and conclusions of the present study. If we had used LIF data only, the result of the experiment would be still the same. All MACRO2 needs to produce OH from isomerization reactions, in order to explain the OH measurements. In order to address the referee's point, we will add the following explanations in the revised paper:

We will add a statement on p.5201 l.26: "On 11 August 2011 OH production rates from photolysis were highest and a large number of instruments was available. Therefore, time series and model calculations from this experiment are shown here. Experiments on the other two days give similar results and are included in the analysis of the OH budget."

We will add a statement on p.5202 l.28: "During the experiment on 11 August 2011, the correlation between OH measurements by DOAS and LIF shows a small intercept of 0.5×10^6 cm^{-3}, which was not observed in other experiments investigating MACR oxidation (Fuchs et al., 2012). For the analysis of data from 11 August 2011 in Fig. 2

and 5, we chose the DOAS data, which is regarded to be an absolute measurement reference."

We will add a statement on p.5211 l.22: "This result is independent of the choice of OH data from either the DOAS or the LIF instrument, because the lower limit is determined by the slightly smaller OH concentrations measured by DOAS compared to LIF (see above)."

Comment: Could the authors comment on the model under-prediction of HO2 observed in Figure 4 (it probably is not statistically significant?). Is the "unknown factor related to water vapor" (Fuchs et al. ACP 10, 12233-12250, 2010, doi:10.5194/acp-10-12233- 2010) of relevance for the work presented here?

Response: The reviewer is correct. The HO2 is described by all model modifications reasonably well within the accuracy of measurements considering the uncertainty of the calibration (except maybe the isomerization case A, which is not considered as a good description of the experiment). The reason for difference between measurements of three LIF instruments depending on water vapor observed during HOxCOMP is still not clear. We do not think that this is an issue for the work here, because differences between instruments during HOxCOMP were largest for small water concentrations, but reasonably well agreed for higher water concentrations like in this study.

Comment: It could be useful to have a figure that shows the fractional contribution to sources of OH, as well as the (source) and sink of HO2. The reason is that although this is a regime in which HO2 is likely well coupled to OH via NO, HO2+NO cannot explain the OH, as the RO2 isomerization is so fast. This is quite interesting as it highlights that isomerizations have to be considered even outside of what is often considered strictly low NOx conditions.

Response: We fully agree with the reviewer that the fast isomerization reaction makes this reaction important for regimes with relatively high NO concentrations. We already tried to highlight this point and will strengthen it in the revised version (see also response to reviewer 1). Fig. 2, which shows the source and sinks of OH on an absolute scale, demonstrates the importance of the additional OH source, which is required to balance the OH destruction. A similar figure with fractional contributions would be redundant without new information. The values of the fraction of RO2 radicals that would isomerize for conditions of these experiments are given in the text (p.5211 l.6-9, l.22-24).

In contrast to the OH budget, it is not possible to deduce the HO2 budget from measurements alone. The main source of HO2 is the reaction of RO2 with NO, so that specified RO2 measurements would be required, in order to determine the correct HO2 production rate. The measurement of the sum of RO2 alone as done here, however, is not sufficient to determine the fraction of RO2 that would isomerize instead of reacting with NO. Similarly, one contribution to the HO2 loss rate would be the reaction of HO2 with RO2, which again would require specified RO2 measurement. Therefore, we do no think that a plot of the HO2 budget from measurements performed during these experiments would help, but would require a lengthy explanation of the limitations of such a plot.

Comment: P. 5214: "therefore substantial MACR" only if the conditions are not low NO(x). The MCM v3.2 being used in this work should have low MACR production from isoprene under low NO(x) (only via RO2+RO2).

Response: This statement refers to the reference Kubistin et al. 2010, where measured isoprene and MVK+MACR are given. For the case with the largest difference between measured and modelled OH concentrations 1.6ppbv MVK+MACR was measured in the presence of 4.3ppbv isoprene. We will change the first two sentences to: "... isoprene was the dominant OH reactant. Measurements of the sum of MVK and MACR also indicate substantial amounts of MACR (Kubistin et al., 2010)."

Comment: P. 5201 Line 20: Milli-q water is defined via conductivity, but organic species could be present that are not conductive (e.g., carbonyls). Were total organic carbon measurements conducted for these or previous experiments?

Response: The total carbon content of the water is monitored during the purification process. It was always less than 10ppbv in the liquid water before evaporation. Only small traces of organic compounds are typically found in the chamber after humidification of the chamber air (measured by GC).

Comment: P. 5205 Line 16: “unstable” or “labile”

Response: Done.

Comment: P. 5206: Line 6: Perhaps “blank experiment” or something similar would be clearer than “initial phase”

Response: We will change the text to: “...during the part of the experiment before OH reactants are injected into the chamber...”

Comment: Figure 1: Please clarify whether the shown measured and modelled HO2 includes the RO2 contribution or not.

Response: We will add to the legend of Fig. 1: “HO2 measurements and calculations include a small interference from specific RO2 (see text for details).”

Comment: Figure 3: “has elapsed”

Response: Done.

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