Response to the comments from the editor:

Dear Paul,

Thanks for the comments to our paper. They were very useful and helped us a lot to improve the manuscript.

Find below the point-by-point answers to your comments. We hope that we could address all the points you raised appropriately.

minor comments: p1 l10, p2 l38, p2 l44, p2 l50, p3 l64, p3 l84, p3 l87, p3 l89, p4 l115-117, p4 l119, p4 l122, p4 l125, p5 l129, p5 l132, p7 l206-207, p7 l210-214, p7 l217, p7 l219, p10 l292, p10 l296, p10 l298, p11 l319, p11 l323, p12 l364, p12 l369-372, p12 l372, p12 l374, p12 l376, p12 l378, p12 l380, p12 l381, p12 l383-384, p12 l386, p12 l397, legends of figures

Response: We will change the text according to the suggestions of the editor.

Comment: p1 l12: Given Crounse et al., I don't understand this claim. In my reading, you have essentially confirmed the findings of that study.

Response: We will change the sentence that this again refers to the MCM.

Comment: p3 l61: While it is true that OH concentrations were not measured, OH recycling (>50%) was confirmed by isotopic measurements reported in this work.

Response: We will modify this sentence: "The new reaction path is attributed to a 1,4-H-shift isomerization reaction with concurrent reformation of OH as co-product confirmed by isotopic measurements reported in the work by Crounse et al."

Comment: p4 l106: Not sure I understand this claim. Are you suggesting that the RO2 do not include HO2? A more accurate sentence is that for the excess CO experiments, the OH is converted to HO2.

Response: In a zero air experiment with high CO concentrations, no production of RO2 is expected in the chamber, but is observed in the experiment. We will change the sentence: "This is evident from reference experiments with CO, in which the RO2 radical concentrations persisted even though OH was completely scavenged by excess CO, so that no RO2 production is expected from the reaction of OH with organic compounds."

Comment: p4 l24: It seems odd to follow this sentence by one that shows a (relatively) large bias between the methods.

Response: This sentence refers to the statement in the sentence before and is in our opinion still true, although measurements differed during a specific experiment. We will start a new paragraph at this point.

Comment: p5 l133: This assumes that the OH regeneration described in this study occurs on a time scale longer than the decay is measured in the flash system. If the RO2 isomerization chemistry is occurring at 0.5s-1 as suggested by Crounse is that the case ? Has this been studied (i.e. measuring the OH reactivity of standard mixtures of MACR)? Please add a comment.

Response: OH generation from subsequent chemistry can play a role in this technique. This would be evident by a bi-exponential decay curve as explained in Lou et al. 2010. We carefully looked into the data, but such a behavior was not found. The reason is that the time scale of the OH decay during the MACR oxidation was much shorter (around 0.1s) than the time scale of OH regeneration from the isomerization (2s). We will add the statement: "OH regeneration from subsequent chemistry can disturb measurements (Lou et al. 2010), but was not observed during these experiments, because OH was regenerated from RO2 radicals on a much longer time scale (see below) compared to the time scale of the OH decay in the instrument."

Comment: p5 l140: I disagree. MCM is a compilation where choices are made either by the editors or by machine learning. I don't believe that the MCM editors would agree with the comment that it represents "the current knowledge of atmospheric chemistry". For example, 3.2 doesn't include any of the isomerization chemistry! The standard GEOS-CHEM isoprene chemistry is more up-to-date.

Response: We will change this sentence: "The MCM provides near-explicit mechanisms of the atmospheric degradation of organic compounds."

Comment: p5 l153: How do you know that it is an RO2 source and not an OH source?

Response: In fact we do not know the exact mechanisms, we only try to parameterize the observations during zero air experiments. The important point is, however, that these mechanisms do not play any role when we investigated the MACR mechanism, because the influence on trace gas concentrations are small.

Comment: p5 l155: please explain further. I'm not sure why this scaling "confirms the applicability of this procedure".

Response: We did zero air experiments, which were used to determine the production of RO2. Again, the effect on the MACR oxidation experiments is small. We will change the sentence to "Test experiments with only humidified zero air in the chamber showed that RO2 time series can be well described by this procedure. Effects on measurements during VOC oxidation experiments are small."

Comment: p6 l174: What if anything are you assuming about the lifetime of these RO2 radicals? Is the 5% the upper limit assuming no unimolecular chemistry?

Response: This estimate includes the overall effect of RO2 interferences from all RO2 species during the experiment, not only those from MACR. In fact, unimolecular RO2 reactions as suggested by Crounse et al. would shorten the lifetime of RO2 during the experiments such that only a small part of RO2 that can be detected by our instrument would be those from MACR. For the estimated RO2 interference we compare model calculations from HO2 and the sum of HO2 and RO2 that causes interferences weighted by their conversion efficiency as described by Lu et al. 2012. The magnitude of RO2 interferences from RO2-derived MACR have been determined experimentally. Isomerization reaction most likely do not play a role inside the RO2 detection system, because they occur on longer time scale than the lifetime of RO2 in the instrument.

Comment: p6 l185: Given that the model overpredicts the MACR concentration, wouldn't you expect that the measured reactivity also be lower than the model?

Response: The effect on the reactivity is less clearly seen, because the reactivity includes also other OH reactants. Only approximately a 10-15% change is expected from the difference in the reactivity values. Nevertheless, if you look at Fig. 1, you may see what you expect. We will add on p.7 l199: "The overprediction of MACR would change the OH reactivity by only 10-15 %. This change in the modelled reactivity is not significant."

Comment: p7 l199: Please provide a more quantitative analysis. Given the known amount of MACR added, you should be able to estimate the <[OH]> over the experiment and compare this to the model.

Response: We will add an paragraph providing an analysis of averaged OH concentration calculated from the decay of MACR: "The decay of measured MACR concentrations can be used to calculate average OH concentrations following the approach described by Poppe et al. 2007. In this approach, the difference of MACR concentrations between to injections is related to the average OH concentrations taking the degradation of MACR by OH and the dilution in the chamber into account. The average OH concentrations required to explain the observed MACR decay are $4 \times 10^6\,\mathrm{cm}^{-3}$, $2.5 \times 10^6\,\mathrm{cm}^{-3}$, and $1.4 \times 10^6\,\mathrm{cm}^{-3}$ between the first and second, second and third, and after the third MACR injection, respectively. This is again consistent with larger measured OH concentrations compared to the modelled OH concentrations."

Comment: p7 l216-217: References

Response: These reference experiments are regularly performed in the chamber, but have not been published in a separate paper. We will change the wording of the statements: "This can be seen in similar experiments, when CO or butene was the dominant OH reactant. A model-measurement agreement for radical species within 30% is achieved in these reference experiments, which are performed on a regular basis in the chamber."

Comment: p7 l218: again, you should explain what the relevant timescales are for the reactivity measurements and explain why the reactivity should agree even though the model has too much MACR.

Response: The point we want to make here is that it is likely that there is an OH source missing, in contrast to an over-prediction of the OH loss. An over-prediction of the OH loss in the model due to an over-prediction of the reactivity of either MACR or its oxidation products could suppress the OH concentration in the model. As explained in our response above the expected change in the kOH due to the over-prediction of MACR in the model is not that large. We will change the sentence: "The underprediction of the OH concentration in the model could be caused either by an overestimation of the OH loss or by an under-estimation of the OH production. The relatively good agreement of the measured OH reactivity with model calculations (Fig. 1) indicates that an OH source is missing in the model."

Comment: p8 l226: Should at least mention that you assume in Fig. 2 that there is no OH source from RO2+HO2.

Response: We will add: "As discussed below a potential production from the reaction of HO2 with RO2 would be small."

Comment: p8 l248: What is the sensitivity of [NO2]/[NO] and P(O3) to this chemistry?

Response: We would like to discuss this issue, when we discuss the model modifications. We will add on p11 l319: "For conditions of these experiments, the ozone production rate is only little less ($< 10\,\%$), when the model modification including the RO2 isomerization reactions is applied, compared to the base case MCM model run. This can be seen in the small changes of the NO mixing ratio and peroxy radical concentrations. The missing contribution of MACRO2 to the ozone production, when isomerization of MACRO2 is the dominant pathway, is partly balanced by the faster production of other RO2 radicals such as CH3O2, which contribute to the ozone production, due to enhanced OH level. For the same reason, also the ratio of NO2 to NO mixing ratios does not change much ($< 15\,\%$) between the two models."

Comment: p8 l250: or from RO2 + HO2?

Response: At this point, we do not want to specify the reaction channel. We notice that a reaction partner that is highly correlated with the RO2 production could also explain the observations, potentially HO2. We will add a potential reaction partner in R7 and add the sentence: "R7 could be either a unimolecular reaction or could involve a reaction partner whose concentration is highly correlated with the RO2 production."

Comment: p10 l286: If I understand the calculation, MACO3 + HO2 would give 0.2 ppbv h-1 if OH yield is 0.8. This is 10% of the 'missing' OH production. How much OH is produced from CH3CO3 + HO2 in the model?

Response: The turnover rate of the reaction of CH3CO3+HO2 is rather small, if calculated CH3CO3 concentrations are correct. MCM predicts maximum CH3CO3 concentrations of 4x10^7 cm^{-3} for conditions of this experiment, resulting in maximum turnover rate of less than 0.05 ppbb h-1 for the reaction with HO2. Any change of the OH yield from this reaction suggested in literature does not contribute much to the OH production. We will change on p 10 l282-286: "Although the qualitative behaviour of the missing OH source would be consistent with a larger OH yield from the reaction of HO2 with MACO3 or other acyl peroxy radicals (Fig. 3), the turnover rates of these reactions are too small, in order to significantly increase the OH production rate. Doubling of the OH yield from the reaction MACO3 with HO2 would increase the OH production rate by less than 0.1 ppbv h-1 and from the reaction of CH3CO3 with HO2 less than 0.05 ppbv h-1, much smaller than the missing OH production rate."

Comment: p11 l335: Does the 0.55 yield in the model calculation include the RO2 + HO2 -> OH?

Response: This yield refers to the yield of MACRO2 and MACROHO2 in the reaction of MACR with OH. In this statement we assume that the isomerization is such fast that all MACRO2 and MACROHO2 undergoes isomerization and any other reaction including that with HO2 cannot compete with the isomerization. We will change the on p11 l333: "The yield of OH regenerated by isomerization becomes limited by the yields of MACRO2 and MACROHO2 from the reaction of MACR with OH. This implies that the isomerization reaction is much faster than all other reaction of MACRO2 and MACROH2 for conditions of the experiment."

Comment: p12 l367-386: suggestion by the editor: cancel statement

Response: We prefer keeping this statement, because in our opinion the determination of the missing OH source from only measurements is an important part of this work.

Comment: p12 l369-372: suggestion by the editor: "... can explain SAPHIR experiments."

Response: The mechanisms can increase modelled OH concentrations, but do not explain our experiments quantitatively. We will change: "... give the same products."

Comment: p13 l389: To the extent that all MACR reacts with OH (only) the absolute rate doesn't matter in terms of the net recycling. More importantly, only 1/2 the reactivity goes via addition (and then isomerization).

Response: This is correct In terms of the total number of OH produced from MACR. Our statement, however, refers to question, how a missing OH production in field experiments can be explained. In this case only the turnover rate of the reaction of MACR with OH matters. Only part of the RO2 species from MACR can undergo isomerization, but this reaction is much faster compared to the isomerization reaction of RO2 from isoprene. Much lower NO concentrations are required for a comparable yield in the case of isoprene. We will add: "(3) the total OH production from RO2 isomerization reactions is limited by the yield of MACRO2 and MACROHO2."

Comment: legend Fig. 2: OH production from acylperoxy radicals + HO2 are not included. [perhaps you should do so using the measured PAN/MPAN?]

Response: We will add: "OH production from the reaction of acyl peroxy radicals with HO2 is negligible here (see discussion)."

Comment: legend Fig. 3: why do you say immediately? What does this mean (within a ns, ms, s, 100s)?

Response: The editor is correct. This analysis alone does not allow to determine a specific time scale. We will cancel "immediately".

Comment: legend Fig. 5: Add reference

Response: see response to the same comment in the text.

Comment: Figure 6: I suggest you add the recycling from the MACO3 and CH3C(O)O2 + HO2 reactions to this figure.

Response: We will change this figure accordingly.