

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

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This study investigates the recycling of OH encountered in the oxidation of methacrolein. The study was conducted in a large simulation chamber (SAPHIR) located in Julich. The study used an array of instrumentation designed to characterize the free radical concentrations and budgets in the chamber. It shows convincingly that the OH concentration is larger (by almost a factor of two) than expected, and that the observations are most consistent with OH production from isomerization reactions previously proposed.

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The manuscript describes three experiments on methacrolein oxidation. The instrumentation used provided measurements of OH, HO₂ and RO₂ radical concentrations, along with the OH reactivity. The major primary radical source in the chamber, HONO photolysis, is unfortunately not well constrained, but measurements of HONO were made semi-continuously, so it can be quantified. As I mentioned in my pre-review, it is unfortunate that the carbon budget of the experiments could not be better constrained, since that would complement the excellent radical measurements. As it is, the only organic compounds that are reported are PAN and MPAN.

The flow of the paper is nice; the authors show first that the modeled OH does not match the measurements, then that the OH source scales with the RO₂ production rate, and finally explore various proposed isomerization mechanisms. The bottom line is that a 1,4 hydrogen shift, occurring with a rate coefficient in excess of 0.03 s⁻¹, accounts for the regeneration, a number that is consistent with earlier measurements made by Crouse et al. One subtlety that almost gets lost in the detail is that even in the presence of 90 ppt NO (or ~1 ppb NO_x), the isomerization reaction still dominates. Maybe this could be stated more forcibly.

Specific comments 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?

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

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

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.

5199-18. “products yields” should be “product yields”

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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”.

5205-16. “instable” should be “unstable”.

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

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

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.

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

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

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/NO_x 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.

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