Atmos. Chem. Phys. Discuss., 14, C1960–C1962, 2014
www.atmos-chem-phys-discuss.net/14/C1960/2014/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 30 April 2014

The manuscript presents a detailed study of methacrolein (MACR) oxidation by OH. The focus is on the recently published OH recycling of this reaction via fast H-shift reactions. The work shows that at 90 pptv, which is typically not low enough to be considered low-NOx from a generic RO2 perspective, (a) a missing OH source is clearly evident in the oxidation of MACR with OH and (b) that this source is consistent with previously published/proposed fast isomerization reactions. This isomerization as OH source is put in context with overall isoprene oxidation and field measurements, which shows that MACR derived peroxy radical isomerization alone can only explain a small part of OH missing from models compared to measurements. The experiments were

well designed, the work is very thorough, the topic is very timely and fits very well within the scope of ACP and the manuscript is very well written. I recommend publication after addressing the points below.

1. 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.

2. 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?

3. 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.

4. 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).

Minor/technical comments:

1. 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.

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

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

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

5. Figure 3: “has elapsed”

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