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Interactive comment on "Atmospheric photochemistry of aromatic hydrocarbons: OH budgets during SAPHIR chamber experiments" *by* S. Nehr et al.

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We thank Referee 1 for the positive evaluation and give detailed answers to specific questions and recommendations below:

(1) In equation (2) c(OH) is used to denote the fraction of O(^{1}D) which reacts to form OH rather than being quenched to form O(^{3}P). I suggest that f(OH) is used instead, which is more conventional. c(HO$_2$) and c(RO) are used later in Table A1 and so avoiding c(OH) could also avoid confusion there.

Reply: We replaced c(OH) by f(OH) as recommended.

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(2) Page 5546, line 22, replace “no likely” by “not likely a”.

Reply: Done.

(3) Please state the zero of the OH reactivity instrument. This is not clear at present, other than that the OH reactivity rose to 2 s^{-1} in the absence of any added reagents.

Reply: From the measured OH decay rate coefficients typically 1.5 s^{-1} were subtracted to account for OH losses measured in pure air containing virtually no OH reactants. These losses were regularly verified and are mostly caused by diffusional and wall loss but nevertheless result in exponential decays. This assumption is supported by the fact that HO_2 behaves similarly as was observed in other work (Nehr et al., 2012). We added the following sentence at the end of section 2.1:

"The reported k_{OH} were corrected for wall losses within the instrument that account for loss rate coefficients of typically 1.5 s^{-1} (Nehr et al., 2012).“

(4) Although within experimental uncertainties the budgets of the aromatic compounds are closed, as stated, the ratio D(OH)/P(OH) is systematically greater than 1 for low NO_x experiments, and higher than the ratio for high NO_x experiments which span unity. There is a comment on page 5546 about that. Can some further comment be made on why this is likely to be the case? It seems that RO_2+HO_2 giving OH being missing cannot be proven to be the cause of the D(OH)/P(OH) being greater at low NO_x, but that it may contribute towards this?

Reply: The discussion of the differences is difficult because they are within the experimental accuracy. Nevertheless, we extended the discussion section and included some thoughts about possible reasons:

“The agreement between P_{OH} and D_{OH} was slightly better at high NO concentrations. However, this difference should be treated with caution considering the experimental uncertainties and the fact that OH destruction and production rates were greater by a factor of about four under high-NO conditions, mainly caused by greater OH and

NO concentrations. Possible reasons for these discrepancies are measurement artefacts and additional OH recycling processes. Regarding the NO measurements, no problems are expected during low and high NO conditions because both concentration ranges were covered by regular calibrations using test gases. HO_2 concentrations were comparable during high and low NO conditions because HO_2 formation and destruction rates were both increased at increased NO. The same applies to RO_2 concentrations and associated potential difficulties regarding RO_2-HO_2 interferences (see Appendix). k_{OH} was also similar at high and low NO conditions and recycling of OH from HO_2 was too slow at high NO to influence the k_{OH} measurements. An unaccounted primary OH source that is specific for SAPHIR is also unlikely because that would have its greatest effect during the zero air periods when the OH budget was closed (red points in Figs. 3 and 4). However, after addition of an OH reactant under low NO conditions, OH drops strongly making these measurements more challenging. An unaccounted offset in the OH measurements could produce the observed mismatch between OH production and destruction rates, independent of the nature of the added reactant. That could explain why the ratios for CO and aromatics were mostly greater than unity under low NO conditions. In previous LIF-DOAS comparisons no such offset in the OH LIF measurements was found as mentioned above. But it has to be taken into account that also DOAS measurements are more difficult at low OH concentrations. The differences of the ratios could also be caused by additional OH recycling via HO_2 + RO_2 reactions that gain importance under low-NO conditions. Such radical-radical reactions... “

(5) Page 5544, line 29. I assume then that a single rate coefficient was used for reaction R9 as only the sum of RO_2 was measured. Perhaps make clearer.

Reply: We added "... and the same rate constant k_9 were used for the calculations“.

(6) Page 5548, most of page. A correction is made to the measured RO_2, which is under-measured owing to some RO_2 being measured as HO_2 (contributing towards HO_2* which is corrected according to equation (A1)). The model is used to facilitate the correction outlined in (A2), and although a brief description is given below that equation

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(and more is to be covered in Nehr et al., 2014, in preparation) just a few more details here would aid the comprehension of this section dealing with the corrections (which are small owing to technical changes in the operation of the instrument).

Reply: At the beginning of the Appendix we included an introduction into the problem of RO_2 interferences that will hopefully make the remainder more comprehensible:

“The LIF technique can only detect OH radicals. Measurements of HO_2 and RO_2 radicals by LIF work via conversion to OH upon addition of NO. The HO_2-to-OH conversion is direct and can be made shortly before the excitation of OH within the expansion of the sample gas (Holland et al., 2003). In contrast, RO_2 has to be converted to HO_2 first which requires at least one additional O_2 reaction following the RO_2 + NO reaction. This RO_2-to-HO_2 conversion is accomplished in a pre-reactor (Fuchs et al., 2008). The different reaction times thus allow a distinction between OH from HO_2 and RO_2. However, dependent on the nature of the RO_2 radicals this distinction is not complete because some RO_2 produce HO_2 too rapidly. Therefore, LIF HO_2 measurements, [HO_2*], have to be corrected for the concentration of a number of interfering RO_2 radicals ....”

Moreover, we deleted the first sentence after Equation A2 because it was misleading and rephrased the following two sentences:

“For peroxy radicals formed secondarily following the OH + benzene reaction, relative detection sensitivities compared to that for HO_2 of $\alpha_{\mathrm{RO_2}}^{\mathrm{benzene}}$= 0.86 were determined experimentally in 2010.”

(7) Page 5558, Table A1. In the caption it is stated that these RO_2 are detectable by LIF. This I think is a general comment, rather than implying that for each RO_2 listed in the Table the sensitivity of the LIF instrument for detection of that species has been determined.

Reply: In the caption of Table A1 we now clarify that the RO_2 are "detectable but not discriminable by LIF“.

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(8) Figure 1 and 2. The panels are very small. For figure 1, can the figure have two panels wide, two panels deep in order to increase the size? For Figure 2, can the 8 panels that are currently 2 (deep) and 4 (wide) be split instead into two wide, but four deep, again to make the panel sizes bigger?

Reply: The figures were prepared to fit to the final two-column upright format of ACP. Unfortunately, the landscape format of ACPD is not well suited to reproduce tall upright figures like Fig. 1 that is supposed to finally fill one column and will be enhanced by a factor of two for that. Fig. 2 was split into two parts that can be increased to fill a full page width each (four deep was tested but then needs strong downscaling to fit the page height).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 5535, 2014.