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

Anonymous Referee #1

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In this paper measurements of OH, HO2, total RO2 and OH reactivity (k(OH)) are used to study the photoxidation of a number of aromatic VOCs in experiments performed over a number of years at the SAPHIR chamber in Julich. Supporting measurements of O3, NO, HONO, J(HONO) and J(O3) further enable the rate of production of OH to be calculated. These measurements allows an experimental determination of both the production rate of OH P(OH)), through the sum of the major production mechanisms at play in the SAPHIR chamber, and also the rate of destruction of OH (D(OH)) which is experimentally determined from the product of [OH] x k(OH). Thus it is possible to test the closure of the budget of OH, which according to the steady-state approxima-

tion would yield P(OH) = D(OH). Any deviation of D(OH)/P(OH) from one would signify some lack of understanding of the photochemical oxidation mechanism of the aromatic species studied. This test of our understanding is independent of any model or chemical mechanism, as measured quantities are used. This contrasts most other tests of our understanding of chemical mechanisms via OH or HO2 measurements which relies on the deviation between the measured values and a model calculation, often as k(OH) is not available (and hence inevitably some sinks are not included in the model description). The study is not quite independent of a model, as the interference from RO2 towards HO2* measurements, and accounting for RO2 that is not measured (detected as HO2 instead) is assessed using the modelled mix of peroxy radicals, RO2. However, as the conditions chosen for HO2 measurements now discriminate against significant interference in the HO2 measurement from RO2, the correction of HO2* into HO2 is small, and the use of the model is in fact not critical and no major result depends on an accurate description of the chemistry in the model. A follow-up paper is planned in which a box model using the detailed MCM v3.2 is utilised to compare with radical measurements.

The range of species and their quality of measurements are real strengths of the paper. Through HO2 measurements, the rate of HO2+NO can be used to calculate the rate of OH production from this route, and measurement of total RO2 also enabled a test of the hypothesis that RO2+HO2 is an important source of OH for aromatic species as recently suggested in the literature. In fact the HO2+RO2 reaction generating OH is not an important source of OH for aromatic RO2 here. Experiments were performed under low NOx (typical of the afternoon conditions of a campaign in China where OH was significantly underestimated by a detailed model) and high NOx conditions in the mornings of the same campaign (where agreement with the model was better). Experiments with just CO present verified that the approach was sound, with D(OH)/P(OH) ratios close to one being found as expected. The concentration of the starting aromatic was varied so that the OH reactivity of the aromatic was fairly constant between experiments (lower initial concentrations used for faster OH reacting aromatics).

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The results indicated that the deviation of the ratio D(OH)/P(OH) from unity was within the combined uncertainties of the measurements, and that the rate of the important processes controlling the OH budget were understood. The ratios tended to be higher under low NOx conditions, but still within the uncertainties. This contrasts with the field measurement/model comparison in China under low NOx conditions when the production and destruction budget was unbalanced by a factor of ~ 3. The fact that for the experiments conducted here the budgets are approximately balanced suggest that it is not aromatic chemistry which is driving the factor of 3 discrepancy seen in China.

This is a very high quality paper and is suitable for publication in ACP. There are a number of small points which the authors may wish to consider in a revised MS.

Specific points

(1) In equation (2) c(OH) is used to denote the fraction of (O1D) which reacts to form OH rather than being quenched to form O(3P). I suggest that f(OH) is used instead, which is more conventional. c(HO2) and c(RO) are used later in Table A1 and so avoiding c(OH) could also avoid confusion there.

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

(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.

(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 NOx experiments, and higher than the ratio for high NOx 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 RO2+HO2 giving OH being missing cannot be proven to be the cause of the D(OH)/P(OH) being greater at low NOx, but that it may contribute towards this?

(5) Page 5544, line 29. I assume then that a single rate coefficient was used for reaction

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R9 as only the sum of RO2 was measured. Perhaps make clearer.

(6) Page 5548, most of page. A correction is made to the measured RO2, which is under-measured owing to some RO2 being measured as HO2 (contributing towards HO2* 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 (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).

(7) Page 5558, Table A1. In the caption it is stated that these RO2 are detectable by LIF. This I think is a general comment, rather than implying that for each RO2 listed in the Table the sensitivity of the LIF instrument for detection of that species has been determined.

(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?

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