Interactive comment on “Detection of HO$_2$ by laser-induced fluorescence: calibration and interferences from RO$_2$ radicals” by H. Fuchs et al.

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This is a short comment to note that the findings of Fuchs et al. are in good qualitative agreement with results obtained at the MPIC in Mainz, as set out in our poster presentation to the 21st International Symposium on Gas Kinetics (Leuven, Belgium, July 2010, see Fig.1). Briefly, MPIC experiments were conducted by exposing a slow flowing mixture of O$_3$, H$_2$O and RH in synthetic air to 254 nm photolysis to generate (via O$_3$ photolysis then O(1D) + H$_2$O) small $[\text{OH}] < 10^9$ molecule cm$^{-3}$. The MPIC HORUS instrument # was used to detect OH & HO2 produced:

$$\text{OH} + \text{RH} \rightarrow \text{R} + \text{H}_2\text{O} \quad (\text{R1})$$

$$\text{R} + \text{O}_2 \rightarrow \text{RO}_2 \quad (+ \text{ M}) \quad (\text{R2a})$$

$$\text{R} + \text{O}_2 \rightarrow \text{HO}_2 \quad (\text{R2b})$$

Reagent concentrations, radical densities and the timescale of the experiment (typi-
cally a few seconds) were such that reactions (R1-R2) were complete before sampling, whilst secondary RO2 + HO2 or RO2 + RO2 chemistry was insignificant. Results were obtained by comparing the HO2 signal observed from the organic of interest with that from a calibration molecule, usually CH3OH, for which 100 % conversion of OH to HO2 (R1-R2b) is well-known.

Results Summary:

1) In common with the results presented by Fuchs et al., and previous literature (Weber 1998, Holland 2003, Kanaya 2001, Ren 2004) we found no evidence for any interference from small alkanes when testing RH = C2H6, C3H8. 2) Molecules with well-defined HO2 production chemistry (R2b) behaved as anticipated, with near unity yields obtained for RH = H2 and n-C3H7OH. 3) We did observe a large HO2 signal / interference for RH = c-C6H12. Near unity yields were typically obtained, larger than the 0.48 and 0.03 reported in Table 2 of the paper under discussion. Confirmation of a significant interference for c-C6H12 is of particular importance since this molecule is frequently employed as an OH scavenger in chamber experiments. 4) Among the largest interferences observed in the MPIC experiments was for RH = n-C5H12 where values of around unity were obtained. In the light of the results for n-C5H12 and c-C6H12 it may be wise to amend line 13 of the abstract to note that interferences associated with "small alkanes" were negligible. 5) Large HO2 signals were observed for RH = C5H8 (isoprene), typically 1 - 1.5, again larger than the values reported in Table 2. This may be a further indication (with c-C6H12 results) that the MPIC instrument configuration # was more sensitive to RO2 interferences. However, since the MPIC experiments were conducted on a longer timescale than those detailed in the discussion paper, an alternative explanation presents itself. Some of the extra signal observed may be from real HO2 generated via the intramolecular H-shifts proposed by (Peeters et al. 2009). Clearly more experiments are needed to clarify this point.

# = MPIC HORUS is a LIF based field instrument similar to that described in Fuchs et al. Typical operating parameters for the MPIC experiments were as follows (compare
with Table 1 of paper under discussion):

inlet orifice 0.9 mm
flow rate $\sim 7$ slm
[NO] in most experiments $8 \times 10^{13}$ molecule cm$^{-3}$
distance nozzle – detection 58 cm
distance NO addition – detection 10 cm
conversion reaction time travel time before detection 6 ms
cell pressure $\sim 3$ mbar
laser rep.rate 3 kHz
laser power $\sim 0.5$ mW
laser dimensions White Cell (32 reflections, radiation area $\sim 10$ mm x 20 mm) 1 sigma
accuracy of calibration 16 %

Experimental evidence for HO₂ production from OH + isoprene in clean air.

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Introduction

First direct measurements of OH over the Amazon [1] demonstrate clean tropical air maintains high OH levels (2). Model – measurement discrepancy increases with isoprene [2].

Isoprene oxidation proceeds via a host of intramolecular H atom shifts leading to HO₂ production from OH + isoprene (R1). This mechanism is only operative in clean-air, e.g. over rainforests, so was not evident in chamber experiments.

QM calculations from Peeters et al. [3] identified intramolecular H atom shifts leading to HO₂ production from OH + isoprene (R1). This mechanism is only operative in clean-air, e.g. over rainforests, so was not evident in chamber experiments.

Experimental

Slow flow reactor for 254 nm photolysis of O₃ / H₂O / C₅H₆ / air.

Gas mixtures sampled into LIF chamber after a few seconds.

OH detected directly, HO₂ detected as OH via (R4), HO₂ + NO → OH + NO₂. (R4)
T = 293 K
P = 1 bar.
Total flow 15–45 slm (air) residence time ~1–10 s.
H₂O @ 17000 ppm
O₃ @ 700–7900 ppb
[OH] = 10⁻³ – 10⁻⁴ molecule cm⁻³.

Typical observations (all dark corrected):

• HO₂ yield from (R1) [β] ∼ 100–130 % (calibrate CH₃OH or H₂O).
• No trend with [O₃], reaction time etc.
• Small, significant dark signal (no C₅H₆) and with RH = CH₃OH (defines zero).

Summary and conclusions:

• HO₂ signals observed in all isoprene experiments.
• HO₂ yield [β] ∼ 100 %, even after dark correction.
• 95 % yields on this timescale.
• β values for C₅H₆, C₆H₅ and n-C₆H₁₄ may make sense.
• Larger C₅ or C₆ organics also yield β [≤ 100 %]. No rational explanation for this unless:

R₂O + NO → HO₂ + OH

⇒ verification using CIS detection of HO₂ as yet inconclusive.
⇒ improved experiments needed.

Literature