

Interactive comment on “Detection of HO₂ by laser-induced fluorescence: calibration and interferences from RO₂ radicals” by H. Fuchs et al.

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Received and published: 28 March 2011

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 O₃, H₂O and RH in synthetic air to 254 nm photolysis to generate (via O₃ photolysis then O(1D) + H₂O) small [OH] < 10⁹ molecule cm⁻³. The MPIC HORUS instrument # was used to detect OH & HO₂ produced:

OH + RH → R + H₂O (R1) R + O₂ (+ M) → RO₂ (+ M) (R2a) R + O₂ → HO₂ (R2b)

Reagent concentrations, radical densities and the timescale of the experiment (typi-

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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

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with Table 1 of paper under discussion):

inlet orifice 0.9 mm

flow rate ~ 7 slm

[NO] in most experiments 8×10^{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 ~ 3 mbar

laser rep.rate 3 kHz

laser power ~ 0.5 mW

laser dimensions White Cell (32 reflections, radiation area ~ 10 mm x 20 mm) 1 sigma

accuracy of calibration 16 %

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1255, 2011.

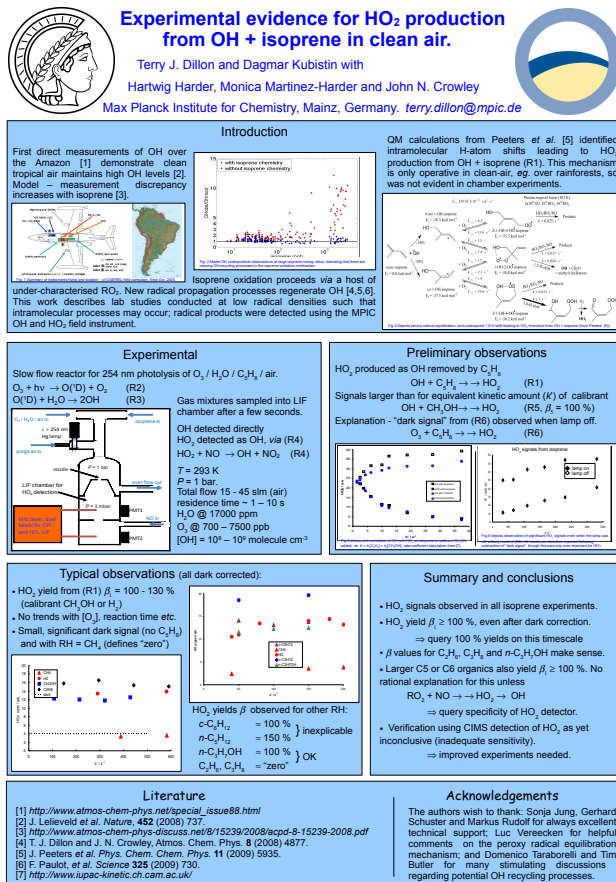
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Fig. 1.