

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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In further support of the findings presented in the paper and the results discussed in the short comment posted by Dillon, recent experiments conducted in Leeds have also shown high HO₂ yields from a range of RO₂ species reacting with NO. The tests were conducted using the University of Leeds OH reactivity instrument. A small fluorescence cell (held at ~1 Torr) sampled from a reduced pressure (~400 Torr) stainless steel flow-tube. A mixture of ozone, humidified nitrogen, oxygen and hydrocarbon were introduced into the flow tube. The ozone was photolysed by a 266 nm laser pulse to generate O(1D) which subsequently reacted with H₂O vapour to generate OH. The OH then reacted with the hydrocarbon present to form an RO₂ radical. Upon addition of NO to the fluorescence cell, close to 100% yield of HO₂ was observed from ethene-

C350

derived RO₂ radicals and ~90% yield from isoprene-derived RO₂. Significant HO₂ yields were also observed for the longer chain (>C₃) alkane-derived RO₂ radicals: A ~17% yield of HO₂ from n-butane and ~44% yield from n-pentane. In the most part these yields are consistent with the Master Chemical Mechanism predictions (although the MCM predicts a HO₂ yield closer to 70% for n-pentane). In the fluorescence cell used for these experiments the NO was injected into the centre of the ambient air-stream via 1/8" stainless steel tubing, this led to almost complete conversion of HO₂ to OH upon addition of ~5 sccm NO. Significantly reducing the amount of NO added did not provide distinction between RO₂ radicals and HO₂. Varying the pinhole size from 1 mm to 0.2 mm also had little effect, suggesting that the conversion reaction time within this particular fluorescence cell (estimated to be ~ 6 ms from these tests) was not significantly reduced by this change.

Tests have also been conducted on the University of Leeds ground-based FAGE instrument which uses much larger fluorescence cells. Under the operating conditions employed during the 2008 OP3 campaign that took place in the Borneo rainforest we have found that this instrument was relatively insensitive to detection of these RO₂ species. During the campaign only one fluorescence cell was used to make alternate measurements of OH and HO₂ and conditions were optimised to maximise its sensitivity to OH. Under this configuration incomplete mixing of NO into the ambient air-stream for the HO₂ titration was evident and resulted in low conversion of HO₂ to OH. Coupled with the high pumping capacity and therefore fast gas throughput of the fluorescence cell this configuration effectively minimised the potential interference.

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