

Interactive comment on “ROOOH: the Missing Piece of the Puzzle for OH measurements in low NO Environments” by Christa Fittschen et al.

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(A formatted version of this comment is attached as a supplement PDF)

The results from this study are very interesting and could have wide reaching implications, not only for the understanding of atmospheric oxidation mechanisms, but also for the OH measurement community. The authors state that the possible interference from ROOOH decomposition in the FAGE apparatus could account for high OH concentration measurements around the globe from multiple groups. I am keen to understand more about the experiments and hence have some questions.

* Could the authors clarify their idea for the mechanism (chemical and/or physical) of

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the decomposition of the ROOOH in the FAGE inlet?

* No two FAGE instruments are alike. Instruments where interference signals have been categorized have a range of different inlet lengths and inlet pinhole constructions (e.g. Faloon et al. (2004), Martinez et al. (2010) and Rickly and Stevens (2018)). Could the authors comment on the possible effects of FAGE instrument design on this interference?

* Were there any experiments conducted with different inlet pinhole diameters and inlet lengths to try and elucidate the effect on the possible ROOOH decomposition?

* Could the authors comment of the losses of ROOOH in the system? Are there expected losses on surfaces (e.g. the FAGE inlet pinhole)? Also, Müller et al. (2016), hypothesised a loss pathway for the ROOOH species via the reaction with water dimer. Will this be important under the experimental conditions presented here?

* The manuscript mentions the importance of OH scavenger experiments to determine whether there is a production of OH in the FAGE inlet (Novelli et al., 2014; Rickly and Stevens, 2018). Were similar experiments conducted here?

The flow tube experiments were conducted at high relative humidity (12000 ppmv) and with low flow rates to promote the formation of ROOOH over subsequent photolysis laser shots. I have a few questions about the chemistry and apparatus used. I think it would be useful information for the SOM for those in the FAGE community that might be interested:

* It has been hypothesized that RO₂ radicals generated in the OH initiated oxidation of unsaturated hydrocarbons could form complexes with H₂O molecules (Clark et al., 2010; Clark et al., 2008; Khan et al., 2015). Could the authors comment on the use of high [H₂O] concentrations during these experiments and the possible effects this might have on the, already complicated, isoprene + OH oxidation mechanism?

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* Was the effect of varying the initial conditions of the experiment investigated (e.g. [H₂O]₀, [O₃]₀ and [OH]₀)? Was an alternative OH source used (without H₂O)? Did the authors try other unsaturated hydrocarbons/terpenes such as pinene, as in Rickly and Stevens (2018)?

* Were more than two OH probe laser powers used in the determination of the absence of laser induced photolysis?

* The flow experiments were conducted in a regime where the photolysis beam did not fill the entire diameter of the flow tube. Could the authors comment on the possible impact of diffusion in and out of the photolysis region during the 20 s residence time?

* It would be useful to see an OH decay trace with pre-photolysis signal to judge the increase in the background level signal. Is the observed rise in the ILIF plateau above the S/N (and limit of detection) of the background signal, for example? Does the ILIF plateau value extend to the subsequent OH probe pulse? Was a run without an organic completed, to show the ILIF plateau base case in the absence of RO₂ (and therefore ROOOH)?

Finally, I have a couple of comments about the conclusions:

* The contribution of ROOOH to [OH] measured with FAGE instruments depends highly on the production rate and loss processes for these molecules – both of which are highly uncertain at this stage.

* The interferences measured in the lab based ozonolysis experiments conducted by Novelli et al. (2014) and Rickly and Stevens (2018), have been shown to be removed upon addition of a reaction partner for Criegee intermediates (sulphur dioxide (Novelli et al., 2017) and acetic acid (Rickly and Stevens, 2018)). This suggests that stabilized Criegee intermediates decomposing in the FAGE inlet may be responsible in these cases.

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* The experiments conducted by Fuchs et al. (2012) did show a 30 – 40 % higher measurement of OH in a few cases, involving methyl vinyl ketone and toluene, which is indeed interesting. However, these runs were carried out under comparable NO conditions to other runs, for example containing isoprene, earlier in the campaign.

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Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-441/acp-2018-441-SC1-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-441>, 2018.