

Interactive comment on “Investigation of potential interferences in the detection of atmospheric RO_x radicals by laser-induced fluorescence under dark conditions” by H. Fuchs et al.

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We thank the reviewer for the helpful comments.

Comment: In the ozonolysis experiments, the authors add enough propane to remove OH produced in the flow tube and claim that since the OH from the ozone interference is not removed then any internally generated OH is not scavenged. However, if the mechanism of the ozone interference is different than that for other artifacts, the reaction time with propane of the OH produced from the ozone interference may be different than that for other artifacts. Thus it is possible that the added propane may have removed internally generated OH artifacts that were not produced by the ozone inter-

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ference. However, if the ozone interference behaves similarly to the ozonolysis interference, then it is possible that the mechanisms are similar. Does the ozone interference increase with increasing inlet length, similar to the observed ozonolysis interference? Does it increase with increasing residence time in the cell? One way to ensure that no internally generated OH is titrated by the added propane is to produce OH internally and determine whether it is scavenged. Did the authors perform experiments where they produce OH internally near the inlet and with the longest reaction time (similar to that described in Mao et al., 2012) to insure that the added propane is not scavenging any OH produced inside their detection cell?

Response: A similar question is raised by reviewer 1 and we would like to refer to our answer there.

Comment: In the flow tube ozonolysis experiments described in Table 1, are the OH concentrations produced in the absence of propane consistent with the expected OH yield given the concentrations of ozone and the alkene? This would provide some additional evidence that the measured OH under these conditions is not influenced by instrument artifacts.

Response: We thank the reviewer for this useful comment.

As a simplified approach, we have calculated the OH from the reactions alkene + O₃, using rate coefficients and prompt OH yields from IUPAC recommendations. Assuming that OH reaches steady-state and has negligible wall loss in the flow tube, we find the calculated OH to be about equal or somewhat larger than measured. We do not observe higher than expected OH concentrations which supports our conclusion that the LIF instrument is not influenced by artificial internal OH production.

One explanation why the observed OH could be smaller than predicted is a delayed production of OH from stabilized Criegees on a time-scale of a second at atmospheric pressure, as was shown for TME ozonolysis (Kroll et al., 2001). Thus, OH may not have reached its steady-state concentration. For detailed modelling of our flow tube

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chemistry, we would need detailed kinetic data of the Criegee intermediates as well as wall loss data of these species, both of which are not available.

Comment: The authors suggest that the observation that the artifact from the ozonolysis of α -pinene does not change in the presence of SO₂ implies that sCIs from α -pinene ozonolysis are not the source of the artifact based on the observed rate of SO₂ oxidation by sCIs by Sipilä et al. (2014). However, the results of Sipilä et al. (2014) reflect the average reactivity of all sCIs produced in the ozonolysis of α -pinene. Thus it is possible that the artifact is due to a particular sCI that does not react efficiently with SO₂. This should be clarified in the manuscript, as it does not necessarily rule out sCIs as the cause of the interference. Did the authors try adding a different sCI scavenger, such as an organic acid that may react differently with the sCIs than SO₂ (Sipilä et al., 2014)?

Response: We will add on p12496 l11: “This result, however, does not rule out that decomposition of sCI species that do not react with SO₂ are the cause of the interference.” and on p12503 l11: “However, internal OH production from the decomposition of sCI species that do not react with SO₂ cannot be excluded.”. We did not test other potential Criegee scavenger, but certainly will continue working on this topic.

Comment: The authors suggest that the NO₃ interference could explain some of the discrepancies between HO₂ measurements in the dark during the HO_xComp campaign. Could this interference also explain the unknown interference with OH measurements in the dark found for one of the LIF instruments as described in Schlosser et al. (2009)?

Response: As we show in our study, the NO₃ interference appears in all of our measurement modes including the detection of OH. If this interference was the reason for differences observed in HO₂ measurements during the HO_xCOMP campaign, this may have also been present in the OH detection. However, we do not want to comment on un-published data.

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