Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #2

Received and published: 8 August 2018

The paper is an interesting one, and suggests that ROOOH, present in the atmosphere from the reaction of RO2 with OH, can somehow generate OH within the inlets and fluorescence chambers of instruments that use laser-induced fluorescence to determine OH levels in the atmosphere. Results are shown for the Lille system, where a signal is seen from a mixture of isoprene and an OH precursor (O3/H2O/hv) when the RO2 + OH reaction is initiated within a flow-tube that is sampled by the FAGE instrument. The paper then discusses that ROOOH present in the atmosphere may act as a source of interference for OH measurements in order to explain some previous model/measurement discrepancies.

The results are interesting, and I agree that ROOOH decomposition within the inlet or cell of the instrument should certainly be considered as a possibility for generating

some artificial OH signal. Nowadays FAGE instruments by some groups are operated with a scavenger inlet, which would enable any OH from ROOOH to be allowed for, so this finding is more relevant to previous field measurements without a scavenger inlet where the signal may partly be from an interfering species.

The range of experiments performed certainly seems to show that there is OH signal at long times (which grows after exposure of the OH reactivity flow tube to multiple photolysis laser shots) which is only present for the longer chain RO2 (butane and also isoprene as the VOCs) where the ROOOH yield is expected to be larger. The RO2+OH reaction until recently was largely overlooked as important in the atmosphere, but work by the Lille group, and more recently from a US group, have measured the rate coefficient. For R=CH3 there is still a significant disagreement in the rate coefficient (the disagreement was initially worse, but a revised rate coefficient from Lille brought the values closer to each other). Lille have studied RO2+OH now for a number of R, and have measured the HO2 yield, which decreases for larger R (Assaf et al., IJCK 2018), providing evidence that the yield of ROOOH increases as R gets bigger. Recently the yield of CH3OH from CH3O2+OH was quantified experimentally to be small (there had been some theory on this reaction regarding the CH3OH yield).

Although there is clearly a signal in the Lille FAGE system at long times which grows further with the number of photolysis shots and which may derive from the ROOOH product of RO2+OH, it is surely a considerable stretch to say that this constitutes convincing evidence that the disagreement between model and measurements seen in previous field campaigns (under relevant conditions like low NOx forests where ROOOH is expected to have higher concentrations) is due to interference by the decomposition of ROOOH, and that ROOOH reflects the missing piece of the puzzle. There are several parameters which are unknown or poorly known, the most important of which is the concentration of ROOOH in the atmosphere, another is the fraction of ROOOH which may decompose within the fluorescence inlet/cell (which will be instrument dependent). In order for the atmospheric model in this paper to generate

something that would generate a relevant level of OH, a decomposition fraction is assumed (based on an estimate from the Lille lab. data) and the loss rate of ROOOH was varied over 3 orders of magnitude and a value chosen to give a level of OH similar to atmospheric levels.

Another major point is even if ROOOH in the atmosphere were to constitute an interference that needed consideration, different FAGE instruments behave differently when it comes to interference formed in the inlet / fluorescence cell. This depends on a variety of factors including the residence time inside the instrument, inlet length from sampling pinhole to fluorescence cell, cell geometry (size, distance from walls), fluorescence imaging volume (e.g. single pass or multi-pass as the case here) and others like the pumping rate. For the case of HO2 interference from RO2 for example, the residence time and the geometry of the sampling/cell system has been shown to control the level of interference shown. This needs to be stated in the paper.

Concerning the mechanism of the decomposition of ROOOH within the low-pressure FAGE cell, it is not clear what the mechanism is? It is colder (initially in the expansion) and the number density is low so what is the source of the energy? Is it a homogeneous or a heterogeneous process? For a gas phase process the energetics (Assaf et al., IJCK 2018) seem to suggest if decomposition occurs this would be via RO + HO2 rather than RO2 +OH? As the energetics are known can the ratio of RO2+OH to RO +HO2 be calculated? Is the ROOOH decomposing at all in the OH reactivity flow-tube (which is at atmospheric pressure – presumably any OH is then very quickly removed but could decomposition sustain a small steady-state level).

There will be mixing in of non-photolysed gas where 266 nm is not present – and so not all of the gas will have been illuminated by the same number of pulses? Also, would the 266 nm radiation generate any OH from hitting the metal pinhole at the end of the flow-tube?

The OH signal does not decay to zero at long times for the isoprene (and to a lesser

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extent butane) and the long time signal (plateau signal) increases for the number of 266 nm laser shots – and this is the main evidence that OH (signal in the FAGE cell) builds up with time as more ROOOH is made in the OH reactivity flowtube for longer exposure as the isoprene gets used up. Monitoring the OH reactivity with the number of photolysis shots is a clever idea, and it clearly decreases as the isoprene gets used up. It would be nice to see the t<0 baseline level to compare with the long time plateau signal. The t<0 signal is not shown for any of the plots. For Figure S8 for methane, there is no build up of the long time signal with the number of pulses (evidence for no ROOOH being formed for R=CH3), but the signal is not zero? Presumably the t<0 signal should be zero? Why is there a "constant" underlying signal at long times, even for just 1 photolysis pulse there seems to be a long time signal, i.e. for Figure 2, for 1 photolysis pulse the plateau value is around 0.05 or so (right axis) and it only increases to 0.055 or so after 40 pulses?

There are some processes not considered in the model, namely RO2, isoprene (products) and ROOOH photolysis at 266 nm, which will generate products that may undergo secondary chemistry (e.g. second order isoprene oxidation products?) and build up something which makes OH in the FAGE cell?

If the photolysis is stopped after say 20 shots, could the loss of ROOOH from the flowtube be monitored in some way?

For the determination of the OH reactivity, was the same fitting window used for all of the decays, i.e. was it the same for the Pulse 1 decay as for the Pulse 40 decay? Or was a different start and end time used?

There is no doubt that the work is interesting, and the idea that ROOOH decomposing to OH and hence constituting a potential interference for OH instruments is worthwhile, and needs further exploration. However, it is unknown what the mechanism of decomposition might be, and it is a complex chemical system and the model used to explain the laboratory results has many assumptions/simplifications – and there may be other

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species generated in the system which could release OH once inside the FAGE cell. There is likely to be a cascade of chemistry over the 40 photolysis shots generating many species (some of the products and intermediates formed will be different to the real atmosphere owing to the conditions and wavelength of light present).

The language in the paper needs moderating considerably regarding extrapolating the laboratory observations to the conclusion that the work presents convincing evidence that previous model-measurement uncertainties in low NOx environments containing isoprene is due to ROOOH (R from isoprene or similar) decomposition. Our knowledge of ROOOH abundance and removal processes is virtually non-existent, and the model has been optimised using adjustable parameters so as to give a level of OH in the instrument which becomes important compared with atmospheric levels. The wording over the implications of the work, and also the title of the paper, needs changing.

Other points:

Title, abstract and conclusions – these need to be toned down to report the observations made, that ROOOH needs to be considered as a potential source of OH inside instruments. Any implication that the puzzle is solved is going too far and is rather premature. The title cannot remain as is. The abstract and conclusion also need to make it clear that any OH from ROOOH would be highly dependent upon the instrument design, and make implicit any assumptions made in the model.

Words such as "convincing" are of course subjective – and should be toned down or removed completely.

The balance of the main paper and the supplementary information seems skewed. There is information in the SI which really ought to be in the main paper (there is no compelling reason this has to be done for space reasons). e.g. Figures S1 and S4, S6 (this seems central to show) and probably one panel for butane and methane.

Page 4, line 18, it should be 200 microseconds (not ms).

Figure 1. It is not clear how the t=0 maximum in OH signal varies with the number of shots? Does this change with pulse 1 to 40 in any systematic way? Also what does "data analysis is carried out with raw data" mean?

Figure 2. The red line shows the plateau OH signal from the fit, gradually increasing with the number of photolysis pulses. Given the very small magnitude of the plateau OH compared with the initial OH signal the accuracy of the fit at long time is very important. Could Figure 1 at long times be plotted on a very expanded vertical scale (perhaps from y=0 to y=0.15) and the fits be shown with it? The results are very dependent on how well things fit at long times. Related to this point I would like to see Figure 2 plotted when the plateau is averaged using the data at later times. As the OH reactivity becomes smaller with the number of photolysis pulses, it takes longer for the signal to reach the plateau, so does this slower decay promote the increasing baseline signal in any way? There are certainly some decays in the SI that do not seem to have reached the baseline before the averaging window to obtain the plateau signal begins.

Page 6, lines 5-15. Excitation laser energy and photolysis energy are both used here – be clearer about which pulse energy was changed. Clearly Fig S2 and S3 are for probe (excitation) laser energies, but unclear if photolysis (266 nm) energy was changed also?

The error in [ROOOH] from the model after 40 shots (figure S6 model) needs to be stated.

Why was 10^{-4} s-1 chosen as the loss rate for ROOOH in the atmosphere? Presumably as this gave an OH concentration of around 1×10^{6}? There is a very large uncertainty in [ROOOH], and so the statement on page 9, line 8 that [ROOOH] is predicted to be of the order of 50-200 pptv seems very optimistic in terms of the range of concentrations? For Figure 4, were there RO2 measurements made in the field to constrain the model, or was modelled RO2 used?

Discussion

Page 10, line 6.

It is stated that the product of the RO2+OH reaction leads to an OH interference. The signal may originate from that, but there may be other origins of the signal also, and so the wording needs to be more flexible. This is also where a statement about the different FAGE designs is needed.

Supplementary material.

I think much of section 1 on the FAGE and probe system needs to go in the main paper.

What is the residence time of the FAGE detection cell (inlet from the pinhole and fluorescence cell)? There is no discussion of this and it is an important point. Was the pumping rate of the cell changed to change the residence time?

Figure S2 – in the caption add a line saying what the black line is.

Line 187 of SI – "is consistent with" is better than "is indeed due to"

For all of the OH signal versus time plots the y axis ends at zero. Are there any negative points, or is the "baseline" some value a bit above zero?

Figure S6. The concentrations versus no of photolysis pulses. This seems central and should be in the main paper.

Line 220, reword "very basically"