First comment 1:

"However, I have, besides some minor remarks, a major concern: you do not take into account any secondary radical-radical reaction with the argument, that your radical concentrations are low enough. I do not agree with this point, even though it is not always easy to get enough details from the manuscript to judge. So my comment is based on your statement page 6, that the typical initial OH concentration is between 2e11 and 5e13 cm-3. In the below graph are shown two simulations with [OH]0 = 1e12 and H2O2 = 5e14 (left) and [OH]0 = 1e13 and [H2O2] = 1e15 (right graph). The blue symbols show the simple model OH + H2O2 ◊ HO2 + H2O, while the green symbols include on top the reaction of OH + HO2 ◊ H2O + O2 with 1e-10 cm3 s -1 . t / s [OH, HO2] 0.000 0.002 0.004 0.006 0.008 0.010 0 5.0×101 1 1.0×101 2 HO2 OH with secondary reactions OH w/o secondary reactions Y0 Plateau K oh 1.001e+012 = 0.0 887.4 x 10.000e+011 = 0.0 848.7 HO2_ini k_slow HO2_sec k_fast ho2 = 0.0 3.015 8.923e+011 949.9 xy = 0.0 -0.03680 9.998e+011 849.2 HO2 t / s [OH, HO2] 0.000 0.001 0.002 0.003 0.004 0.005 0 5.0×101 2 1.0×101 3 Y0 Plateau K oh 1.002e+013 = 0.0 2003 x 9.998e+012 = 0.0 1687 HO2_ini k_slow HO2_sec k_fast ho2 = 0.0 20.16 6.379e+012 2596 xy = 0.0 -0.09674 9.993e+012 1691 ho2 oh x It can very clearly be seen that even under the relatively low initial radical concentration of 1e12 (which is at your lower end) already the HO2 yield is not 100% anymore, situation gets much worse with 1e13 OH: only 60% of the initial OH is converted to HO2. This has also an influence on the OH decay rate, as well as on the retrieved HO2 rise time (both get faster). This "problem" has been discussed in detail by Assaf et al, JPCA 2016, when using this system to retrieve the OH absorption cross section. In your case not taking into account secondary chemistry will lead to an overestimation of the HO2 yield.

Of course taking into account this chemistry is possibly only if you know the absolute initial OH concentration. Maybe you did some experiments were you varied the photolysis energy? Because this would give you an idea if secondary reactions are important or not under your conditions. In the case of the OH + CH3OH experiments, secondary chemistry might play a role as well. Very recently, Assaf et al (PCCP, 20, 10660, 2018) have measured the rate constant of CH3O + HO2 and CH3O + CH3O, both have found to be very fast (1.1e-10 and 7e-11 cm3 s -1). The result is that even under moderate high initial radical concentrations, some CH3O will react away before it is converted into HO2. You find a yield in good agreement with literature, either your initial radical concentration are at the lower end of the indicated range, or maybe the internal calibration, tending to overestimate the yield, makes up for this underestimation. Please give more information on the estimated initial radical concentration for the different experiments and check, if your systems are really free from secondary chemistry. In any case, before I can agree to the sentence that your instrument can accurately measure HO2 yields, I would like to see a more detailed discussion on possible secondary chemistry."

Response

Thank you for this very pertinent question. Prior to submission many checks for radical-radical effects were made by varying the repetition rate and photolysis laser power, and no observed differences were seen in the HO_2 yields. We had based our statement on the empirical observations rather than a review of the possible secondary chemistry, however, your careful review and analysis, does suggest that we ought to see a significant difference. The literature does imply we should see a change in HO_2 yield between OH + H_2O_2 and OH + CH_3OH/O_2 (n.b. note that the same high [O_2] is used in both experiments. As the [OH] is increased we should get an ~50 % yield when [OH] ~= 3E13 cm^{-3} and OH + H_2O_2 is used as the OH → HO_2 conversion reaction. Also the observed OH removal kinetics of the OH + H_2O_2 reaction should increase with [OH]; >20% faster when [OH] ~=3E13 cm^{-3}. Because of this inconsistency of our result with the literature, we have carried a number of new experiments, where the [OH] is varied over a greater range, varying pump laser power from 0.5-60 mJ cm^{-2}. The take home message is that we cannot reproduce the literature, and our HO_2 yields / kinetics for the reaction OH + H_2O_2 are close to unchanged over all [OH] from 2E11 up to 5E13 molecule cm^{-3}.

We are in agreement with the reviewer as to the implications of the literature. From a model (as detailed by the reviewer), when [OH]0 = 1E13 cm^{3}, the HO_2 yield from OH + H_2O_2 is about 50% compared to when a large excess of methanol is added, see Fig 1.

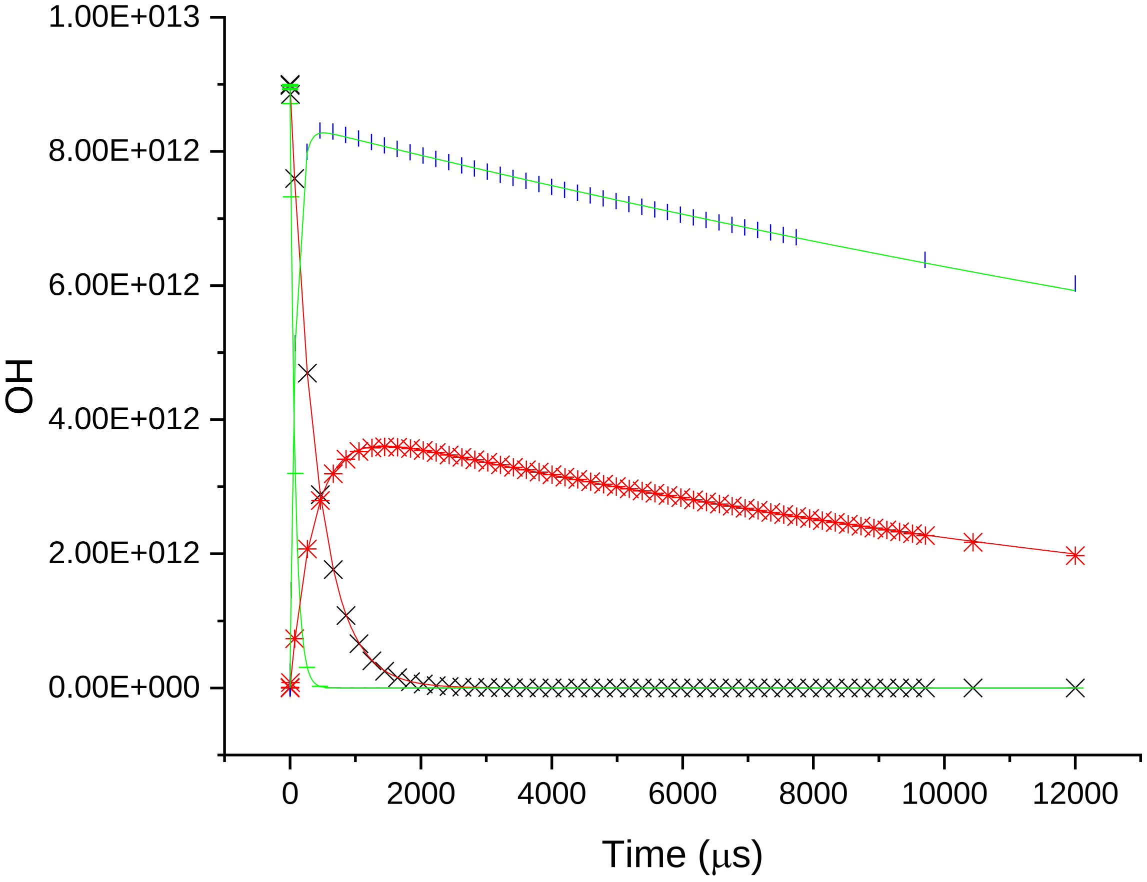

Figure 1 A simulation of the expected HO_2 yields for reaction of 9E12 OH with 1E15 H_2O_2 with 6E18 O_2, in the presence and absence of 1E16 methanol. Where the removal of OH by reaction with the HO_2, OH were included, and accounting for the loss of HO_2 via reaction with HO_2, OH, CH_3O and diffusion.

The crucial reaction in attenuating the HO_2 yield in the OH + H_2O_2 reaction is OH + HO_2. According to the literature the HO_2 yield will only be close to unity when [OH] < 1E12 cm^{-3}. Also, it is noted that when OH + HO_2 is significantly occurring the OH + H_2O_2 kinetics will be significantly faster than the literature. Based on these predictions we have done further experiments.

Also note that by comparing HO_2 yield when $CH_3OH(O_2)$ is present we can assign yields without knowing the absolute radical concentration; it is wholly reasonable to assign the HO_2 yield in the presence of sufficient $CH_3OH(O_2)$ as100%.

The literature predicts a large decrease in the HO_2 yield from hydrogen peroxide as the $[OH]_0$ is increased, see Fig 1. Below is our yield for HO_2 from OH + H_2O_2 and is compared to when a large amount of $CH_3OH(O_2)$ is added. It is clear that no attenuation of the HO_2 yield is observed in our system. Many other experiments were carried out as $[OH]_0$ was varied over a factor of ~300, and the HO_2 yield from all the experiments was the same, within error, for OH + H_2O_2 compared to when $CH_3OH(O_2)$ is added. The $[H_2O]$ and $[CH_3OH]$ in the system is too small for significant complexation to HO_2. Our experiments assign yields as 100% (99 ± 7 at 1E11 [OH], 99 ± 2 at 3E12 [OH] and 98 ± 3 at 3E13 [OH]).

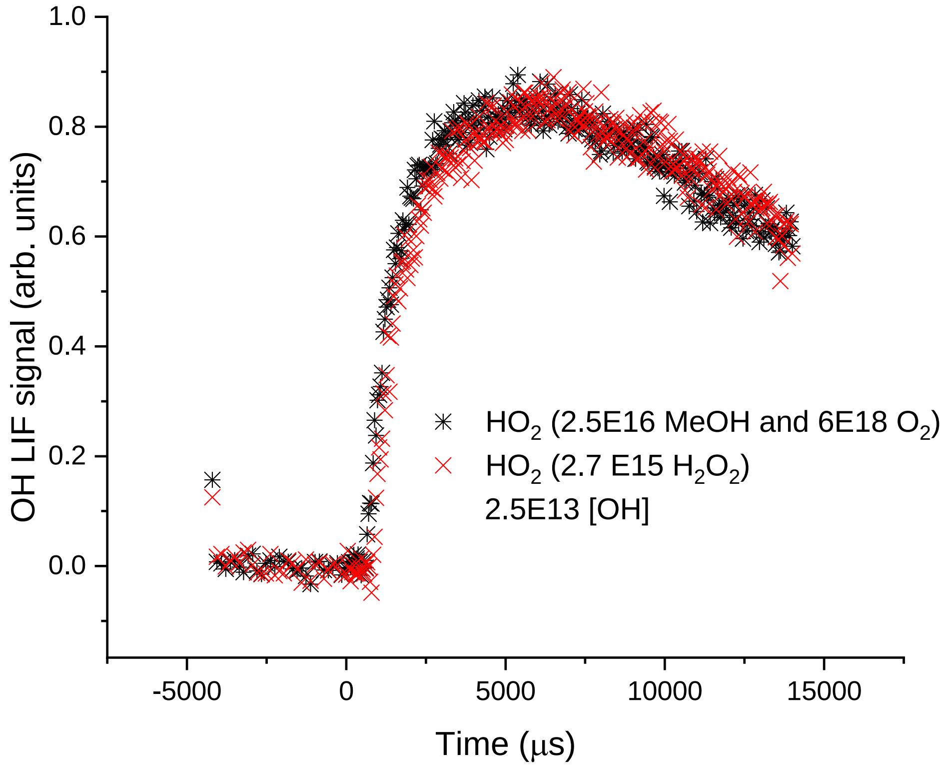

Figure 2 HO_2 growth profiles collected with 2.5E13 cm^{-3} [OH], 6E18 cm^{-3} O_2, 2.7E15 H_2O_2 in the presence and absence of 2.5E16 CH_3OH.

Also, the impact of the HO_2 + OH on the observed OH + H_2O_2 rate constant is to make it significantly faster as the initial [OH] is increased. From our literature model, measurable changes in the rate constant should be observed as [OH] is increased >20 % for 1 Hz experiments; in experiments carried out at 10 Hz where there is HO_2 present from the previous laser flash at time zero, this should lead to the observation of an increase in the OH removal rate by up to 50 %. The precision of the system means that we can readily see changes in the rate constant to ~ 1%. The results are summarised is the graph below.

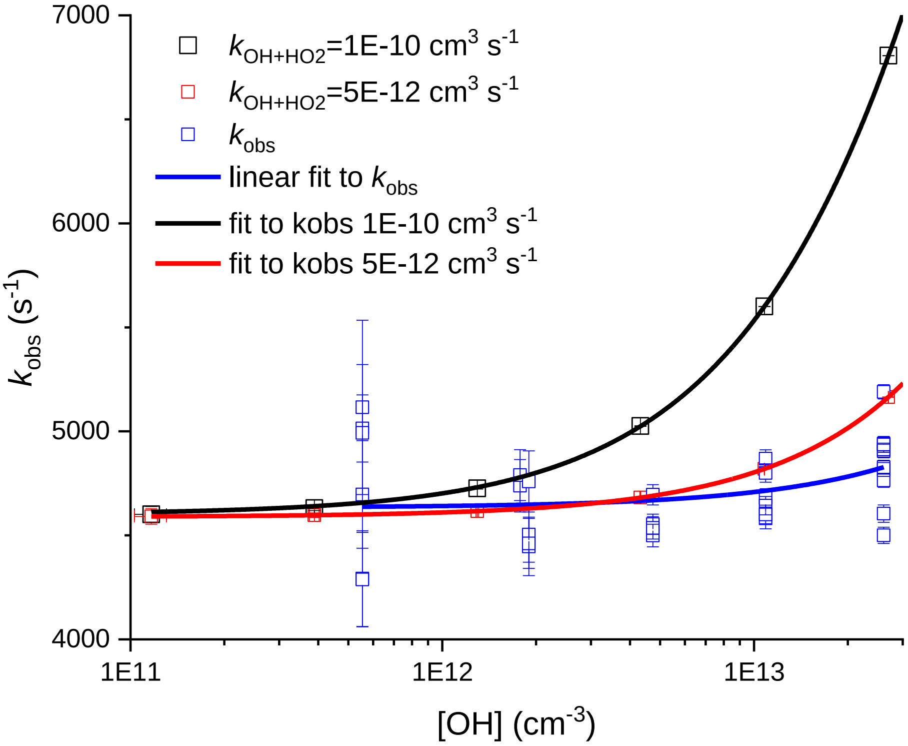

Figure 3 Expected and observed OH removal rates with 2.7E15 cm^{-3} H_2O_2 and 1-60 mJ cm^{-2} photolysis energy at 248 nm and 10Hz.

Again, this kinetics test versus [OH] demonstrates that under our conditions HO_2 + OH is having little impact on the OH + H_2O_2 reaction. The measurable increase in the figure 3 (6.8%) can be assigned to OH + OH (=1E-11 cm^3 s^{-1}, at 1600 Torr).

We recognise that our results are in contradiction with the literature rate coefficient for HO_2 + OH. The IUPAC literature value is 1.1E-10 cm^3 s^{-1}. In order to reconcile our experiments we require this rate coefficient to be < 1E-11 cm^3 s^{-1}. However, our result is wholly consistent with the previous paper on the reaction of OH with H_2O_2 (Wine et al. 1981 J. Chem. Phys). In Wine et al. the removal kinetics were not perturbed by additional HO_2 added to the system. In this work, with additional [HO_2] ~ 1E13 added, no measurable change in the OH + H_2O_2 was observed. This result is in agreement with our present study. We note that Wine et al study used flash photolysis study, as used in our present study. Most literature assignments on HO + HO_2 were carried out in low pressure, flow tubes; very different conditions. The flash photolysis is less prone to interference.

We have added new material in the provisional revised manuscript, **lines 382 – 396**.

‘A possible interference that could distort the yield of HO_2 is the role of the radical-radical reaction OH + HO_2 (Assaf and Fittschen, 2016):

$OH + HO_2 \rightarrow H_2O + O_2$ $k_{15} = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} Atkinson et al. (2006) (R15)

At the low radical concentrations used in many experiments in this work, this reaction could contribute 5 – 10% of the OH loss in an OH + H_2O_2 calibration experiment. However, we have looked at the dependence of the HO_2 yield from both OH/H_2O_2 and from OH/CH_3OH, but see no significant effects of secondary radical-radical reaction (<5%) as the calculated $[OH]_0$ is changed from 5×10^{11} to 5×10^{12} molecule cm^{-3}. For the OH/CH_3OH the much larger concentrations of substrate used lead to faster pseudo-first order decays, so radical-radical contribution is significantly reduced. The work of Assaf and Fittschen suggests that a more significant deviation in the OH loss rates, and one that we ought to be to detect given the precision of our data, should be observed. It is possible that our calculations of $[OH]_0$ are over-estimated, but we note that a study of the OH + H_2O_2 reaction by Wine et al. (1981), where they specifically looked for the interference on OH decays from R15, could find no evidence for an increase in the loss of OH, when $[HO_2]$ was artificially increased.'

Comment 2:

"Figure 3 : the black squares are difficult to distinguish from the blue triangle. Better chose other symbols or other colours."

Response:

In part, that these are hard to distinguish is due to these traces showing no evidence of back diffusion of NO into the region where the OH is probed in the first detection axis. We have tried to improve figures by using open symbols in cases.

Comment 3:

"Figure 7: Who is who? I guess red is HO2 and black is OH? What was the reaction system in Figure 7 and what was the estimated initial radical concentration? Because from the above model, one would expect a faster HO2 decay compared to OH decay if secondary reactions are taken into account (2003 s -1 for OH against 2596 s-1 for HO2 in the example of the right graph above)."

A legend has been provided in the revised manuscript and the OH concentrations were 1-3 E12 cm^{-3}. The experimental detail has now been included in the description.

Please see the response above for comment on observations of secondary reactions.

Comment 4:

Figure 10: what are the different colored symbols? Different experiments? Or is the blue line a fit to different data points?

Response:

The red fit is an exponential fit to the data, the blue fit is a multi-exponential fit that allows for assignment of the returned OH. The three colours of symbols are merely three different time scans of the same experimental conditions to allow for correct assignment of both the fast and slow loss processes. **Additional material in the caption has added clarity** to this figure.