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 H\(_2\)O\(_2\) = 5e14 (left) and [OH]\(_0\) = 1e13 and [H\(_2\)O\(_2\)] = 1e15 (right graph). The blue symbols show the simple model OH + H\(_2\)O\(_2\) \(\rightarrow\) HO\(_2\) + H\(_2\)O, while the green symbols include on top the reaction of OH + HO\(_2\) \(\rightarrow\) H\(_2\)O + O\(_2\) with 1e\(-10\) cm\(^3\) s\(^{-1}\). 

| t / s | [OH, HO\(_2\)] \(0.000 0.002 0.004 0.006 0.008 0.010 0.012, \ldots\) | Y\(_0\) Plateau K oh 1.001e+012 = 0.0 887.4 x 10.000e+011 = 0.0 848.7 HO\(_2\)_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, HO\(_2\)] 0.000 0.002 0.003 0.004 0.005 0.5\times10\(^1\) 2 1.0\times10\(^1\) 3 Y\(_0\) Plateau K oh 1.002e+013 = 0.0 2003 x 9.998e+012 = 0.0 1687 HO\(_2\)_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 HO\(_2\) yield is not 100% anymore, situation gets much worse with 1e13 OH: only 60% of the initial OH is converted to HO\(_2\). This has also an influence on the OH decay rate, as well as on the retrieved HO\(_2\) 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 HO\(_2\) 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 + CH\(_3\)OH experiments, secondary chemistry might play a role as well. Very recently, Assaf et al (PCCP, 20, 10660, 2018) have measured the rate constant of CH\(_3\)O + HO\(_2\) and CH\(_3\)O + CH\(_3\)OH/O\(_2\) (n.b. note that the same high [O\(_2\)] is used in both experiments). The result is that even under moderate high initial radical concentrations, some CH\(_3\)OH will react away before it is converted into HO\(_2\). 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 HO\(_2\) 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\(_2\)O\(_2\) and OH + CH\(_3\)OH/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] \(\approx\) 3E13 cm\(^{-3}\) and OH + H\(_2\)O\(_2\) is used as the OH \(\rightarrow\) HO\(_2\) conversion reaction. Also the observed OH removal kinetics of the OH + H\(_2\)O\(_2\) reaction should increase with [OH]; >20% faster when [OH] \(\approx\) 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\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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\(_3\)O and diffusion.](image)

The crucial reaction in attenuating the HO\(_2\) yield in the OH + H\(_2\)O\(_2\) 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\(_2\)O\(_2\) kinetics will be significantly faster than the literature. Based on these predictions we have done further experiments.

By comparing HO\(_2\) yield when CH\(_3\)OH(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\(_3\)OH(O\(_2\)) as100%. Comparing the HO\(_2\) yield from OH and methanol in the presence of high oxygen, to the yield in the absence of methanol allowed for the assignment of HO\(_2\) yields from the reaction of OH with hydrogen peroxide.
The literature predicts a large decrease in the HO\(_2\) yield from hydrogen peroxide as the [OH] is increased, see Fig 1. Below is our yield for HO\(_2\) from OH + \(\text{H}_2\text{O}_2\) and is compared to when a large amount of CH\(_3\)OH(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] was varied over a factor of ~300, and the HO\(_2\) yield from all the experiments was the same, within error, for OH + \(\text{H}_2\text{O}_2\) compared to when CH\(_3\)OH(O\(_2\)) is added. The [H\(_2\)O] and [CH\(_3\)OH] in the system is too small for significant complexation to HO\(_2\). Our experiments assign yields as 100\% (101 ± 7 at 1E11 [OH], 101 ± 2 at 3E12 [OH] and 102 ± 3 at 3E13 [OH]).

Also, the impact of the HO\(_2\) + OH on the observed OH + \(\text{H}_2\text{O}_2\) 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\% when initial OH radical concentrations are >1E12 cm\(^{-3}\). The results are summarised in the graph below.
Again, this kinetics test versus [OH] demonstrates that under our conditions HO$_2$ + OH is having little impact on the OH + H$_2$O$_2$ 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$_2$O$_2$ (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$_2$O$_2$ 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.
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. However, we will adjust this figure to highlight the different traces better.

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 will provide for clarity in this figure, 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. A legend will add clarity to this figure.