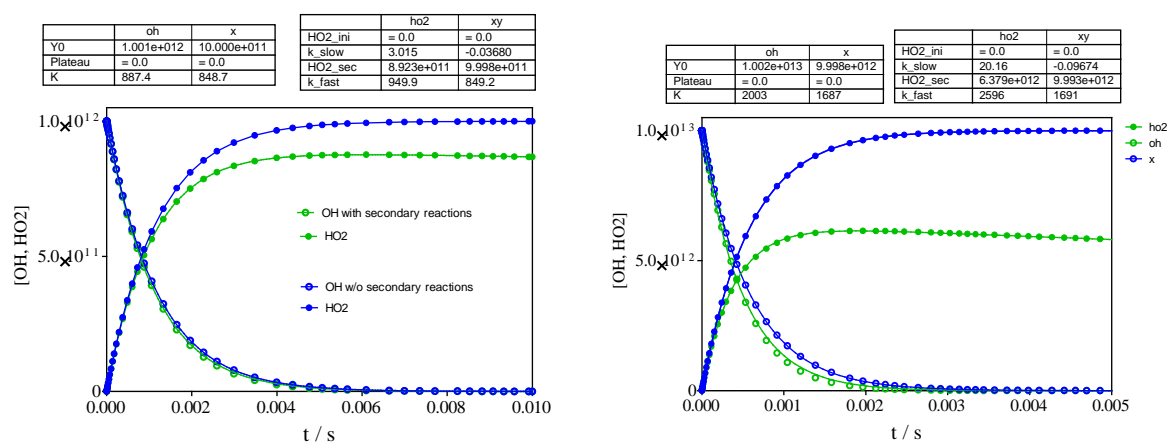


The paper describes a new experimental set-up allowing the measurement of time-resolved HO₂ traces. This is a very interesting approach, and the paper should be published. However, I have, besides some minor remarks, a major concern: you do not take into account any secondary radical-radical reaction 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 cm³s⁻¹.



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 where 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 cm³s⁻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.

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

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).

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