The authors describe an experimental apparatus to determine HO_2 yields and OH reaction kinetics in a pump-probe flow-tube experiment. The paper is suitable for publication in AMT after addressing the following points:

Comment 1:

P1 L19/20: As written now, the statement only verifies the OH kinetics.

"As an application of the new instrument, the reaction of OH with n-butanol has been studied at 293 and 616 K. The bimolecular rate coefficient at 293 K, $(9.24 \pm 0.21) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (18 , 19) is in good agreement with recent literature, verifying that this instrument can both measure HO_2 yields and accurate OH kinetics."

Response:

Agreed, the wording is unclear and is now worded as (removing mention of yields):

'The bimolecular rate coefficient at 293 K, $(9.24 \pm 0.21) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is in good agreement with recent literature, verifying that this instrument can measure accurate OH kinetics.'

Validation of the HO_2 yields is emphasised later in the abstract, where we now state:

'Direct observation of the HO_2 product in the presence of oxygen has allowed the assignment of the α-branching fractions (0.57 ± 0.06) at 293 K and (0.54 ± 0.04) at 616 K), again in good agreement with the literature;'

Comment 2:

P2 L41/42: It would be useful to show the explicit reactions.

"whereas abstraction at other sites leads to alkylperoxy radical (C4H9O2)formation with varying fractions of the RO2 forming alkoxy radicals, and subsequently HO2 (McGillen et al., 2013) on a longer timescale."

Response:

The decision has been made to use Scheme 2 to provide clarity on these reactions (listing all reactions takes up too much space) and this has been moved to the relevant part of the manuscript.

Comment 3:

P6 L148: What was the repetition rate of the laser?

"The photolysis of the OH precursor, H2O2, at 248 nm (Lambda Physik, Compex 200 operated using KrF) or 266 nm (frequency quadrupled Nd-YAG output, Quantel, Q-smart 850) initiated the chemistry."

Response:

Experiments were carried out with repetition rates varied between 0.5 and 10 Hz, varying the repetition rates within this range did not affect the observed OH kinetics and HO_2 yields. As a result of this repetition rate independence, in general experiments were carried out at 5 Hz for 248 nm and 10 Hz for 266 nm. However, for each reaction the assumption of repetition rate independence was verified by performing an experiment at 1 Hz in addition to the higher repetition rate experiments.

An explicit description of this is now included. In addition, this will be discussed clearly in the description of the work done to check for the effect of any radical radical processes that will be included at the behest of Reviewer 1.

Revised wording (**line 155**):

'The photolysis of the OH precursor, H_2O_2, at 248 nm (Lambda Physik, Compex 200 operated using KrF at 1 or 5 Hz) or 266 nm (frequency quadrupled Nd-YAG output, Quantel, Q-smart 850 at 1 or 10 Hz) initiated the chemistry. No significant difference was noted in the kinetics or yields as a function of laser repetition rate.'

Comment 4:

P8 L182: Which range and which resolution was used for the delay between photolysis and detection?

Response:

Typical experimental traces contained 200 – 300 data points sampling the experimental time frame which were in the range 50 – 190,000 microseconds at 5 Hz, and 50 – 95,000 microseconds at 10 Hz. Typical delays between the pump and probe lasers were on the microsecond timescale with control of these timings in the high nanoseconds.

This is now described more clearly in the provisional revised manuscript (**line 189**). 'A delay generator (BNC DG535) was used to vary the delay (time resolution ~10 ns) between the photolysis and probe laser, facilitating generation of time profiles of the OH concentration. The traces, typically 200 – 300 data points and ranging in time from ~50 µs – 20 ms, were scanned through multiple times (5 – 20) and the signal at each time point was averaged, giving high precision OH loss traces.'

Comment 5:

P8 L201: Could the authors show here or elsewhere that the chemistry stopped, when the air entered the low-pressure cells or what the influence on the measurement was, if not?

Response:

The pressure drop (1600 – 0.5 Torr) from the high pressure to the low pressure cell will reduce the rate of bimolecular reactions proportionally. It is acknowledged that the density in the jet itself is higher (10 – 60 Torr). However, rate constants can be measured within 1-2 % of the literature (Medieros et al. *J. Phys. Chem. A* 2018), and minimal quenching of the OH LIF signal over a wide range of added oxygen show that chemistry occurring within the jet is minimal. For unimolecular reactions, the temperature change from the expansion ensures that the rates of these processes are slowed significantly.

P11 L246-252: Could the authors give some numbers for the correction?

" For reactions carried out where a reagent was added in addition to the H2O2, the resulting ratios can be compared with those from the calibration reaction to allow assignment of an observed HO2 yield. To assign the HO2 yield from the test reaction required accounting for secondary HO2 production in the high-pressure reactor, from OH + H2O2 and photolysis processes. From the known rate coefficients, it was possible to calculate the fraction of OH reacting with the H2O2 and hence the expected contribution to the HO2 signal. Photolytic production of HO2 was accounted for by measuring the observed HO2 signal in the absence of any H2O2."

Response:

OH and RH was typically kept 10 to 20 times faster than OH and hydrogen peroxide and from this using the kinetics of the respective reactions the fraction of OH that reacted with the precursor could simply be accounted for. In general, this accounted for 5 to 10 % of the observed HO_2 signal and this is accounted for explicitly within our analysis.

Where photolysis of the reagents leads to HCO or H in the presence of oxygen this provides an additional source of HO_2. The observed signal in the absence of the OH precursor was subtracted from signal in the presence of the OH precursor. For the reactions included in this paper there was no observed photolysis of the reagents.

$RO_2 + RO_2$ can be a source of HO_2 however under our experimental conditions this forms too slowly (2-80 s^{-1}) to provide a significant increased HO_2 yield.

Revised text (**line 257**)

'From the known rate coefficients, it was possible to calculate the fraction of OH reacting with the H_2O_2 (typically 5 – 10%) and hence the expected contribution to the HO_2 signal.'

P11 L253-268: The description could be extended by giving more details what exactly is calculated and how calibration numbers are derived. Is an absolute OH calibration of the cells needed for this approach? If so, how was this achieved?

Response:

No, absolute concentrations are not required. A reference reaction with a known HO_2 yield is used and then compared to the reaction under study, as stated in Lines 240 to 252 of the original manuscript.

This has been validated by comparing two reference reactions OH and H_2O_2 and OH and CH_3OH with high oxygen, 100 % HO_2. By proving that H_2O_2 and CH_3OH give the same HO_2 yields we can simply use OH and H_2O_2 on its own.

"For test reagents which can generate radicals similar to hydroxyethylperoxy, our instrument will detect both HO2 and RO2 with some selectivity to HO2."

Response:

As with all FAGE HO_2 detectors this instrument will not fully discriminate between RO_2 and HO_2. As highlighted in this section the instrument cannot be described as exclusively an HO2 detector.

Discriminating RO_2 from HO_2 relies on the requirement for multiple NO reactions for OH formation in the case of RO_2 radicals. By varying the [NO] and knowing the $RO_2 \to$ OH kinetics can identify where RO_2 is being detected, under these conditions defining HO_2 yields becomes complex as is described in (Nehr et al. PCCP 2011).

(**Line 355**)

'For test reagents which can generate radicals similar to hydroxyethylperoxy, our instrument will detect both HO_2 and RO_2 with some selectivity to HO_2. Potential RO_2 interference can be tested by examining the 'HO_2' yield as a function of added [NO].'

Comment 9:

"the α abstraction still leads to prompt formation of HO2 via R9, but R10, CH3O + O2, occurs on a much longer timescale"

Response:

R9 had a formation rate of over 50,000 s^{-1} compared with R10, which had a formation rate of approximately 10 s^{-1}. Even for the slowest OH and methanol reactions carried out the yield was assigned before 5 millisecond, under these conditions less than 10 percent of this channel, will have formed HO_2 under the measured timescale. With the HO_2 peak being retrieved from the biexponential fit, it is likely that this contribution would have been lower than at under 3 percent of this channel being titrated to HO_2 at the point at which the peak HO_2 signal was observed.

The relevant rate coefficients are presented in **line 366**.

Comment 10:

"It has additionally been demonstrated that the instrument had sufficient accuracy and precision to assign the branching ratios for differing abstraction channels when it was possible to separate the channels by the timescale for HO2 generation."

Response:

This statement was based purely on the result of simple statistical significance at the 95 % confidence level. When a Welch's t test (*Biometrika*, 1947) was performed on the low and high oxygen measurements ((0.87 $\pm$ 0.10), (0.97 $\pm$ 0.06), 2 sigma errors) a t value of 3.41 was derived with 5.10 degrees of freedom, for a 2 tailed test this gave a p value of 0.0184 which is statistically significant at the 98 % confidence level, this result was not significant at the 99 % level.

Further experiments were carried out on this reaction with respect to the question posed by Reviewer 1, and through this work the upper yield has now been revised to 99 $\pm$ 4 % where the error is again given as 2 sigma.

When the new revised value for the high oxygen measurements is used the p value returned is 0.0156, again significant at the 98 % level but not the 99 % level.

In the low oxygen experiments the $[O_2] < 1E15$ cm^{-3} and therefore $CH_3O + O_2 < 20$ s^{-1}. When the HO_2 was assigned < 5% of CH_3O would have been titrated to HO_2.

(**Line 375**)

'The resulting observed yield (second row of Table 1) is consistent with 100% conversion of OH to HO_2 and is statistically different from the low oxygen measurements based on a Welch t-test at the 95% level.'

Comment 11:

P16 Section 3.3: The description would benefit from a discussion about the reproducibility of these effects and their impact on the accuracy of results for experiments.

"3.3 Assessment of transport effects on observed kinetics"

Response:

Kinetics measured in the jet require no corrections.

Any kinetics measured in a FAGE expansion outside of the jet itself are subject to transport. The kinetics measured on the second detector are always slower (10% under 250 s^{-1} 50 % at 2500 s^{-1}), this deviation can be corrected for via Figures 6 and 7. The effect of transport on kinetics has been discussed in detail by Stone et al. (R.S.I 2016) and by Taatjes (Int. J. Chem. Kinet. 2007) for transport in the jetting gas. The effects on transport when sampling from high to low pressures is also described in detail in Baeza-Romero et al. (Int. J. Chem. Kinet. 2011), references to these works are included in the provisional revised manuscript (line ***).

Comment 12:

Figure 6/7: The authors should make clear, which experiments are shown in these figures.

Response:

These experiments were measurements of OH and H₂O₂ over varied H₂O₂ concentrations. Legends have now been included, and the description has been updated to provide the experimental detail.

Comment 13:

Table 3: The table is not correctly displayed.

Response:

Thank you, the table will display fine in a final print, the issue is line numbers have displayed over the table as oppose to at the side of the page as would normally be expected. The table itself seems correct though.

Comment 14:

The authors might somewhere discuss the approach used in Nehr et al., PCCP, 2002 to determine HO2 yields.

Response:

Nehr et al PCCP 2011, Phys. Chem. Chem. Phys., 2011, 13, 10699–10708 on HO2 from OH and benzene using a modified OH reactivity instrument does include an interesting and thorough description of assigning HO_2 yields from OH initiated reactions. A discussion of the technique of Nehr et al. and a comparison to the method used in this work will be included.

Material has been added in **lines 126-8**

'The instrument has some similarities to that presented by Nehr et al. (2011) where a conventional OH lifetime instrument was altered to allow for chemical conversion of HO_2 to OH and hence the sequential determination of OH and HO_2.'

and **616-629.**

'As mentioned in the introduction, the instrument has similarities to that presented by Nehr et al. (2011), where a FAGE system for sequential OH and HO_2 is coupled to a lifetime instrument and yields of HO_2 from OH initiated reactions are reported. Although the principles of HOx detection used in both systems is similar, there are some significant differences between the two instruments. Some differences relate to the reaction cell in which the kinetics takes place: 1 atm of air and 298 K for Nehr et al. and 0.5 – 5 atm of any gas and 298 – 800 K for this work. However, in principle, the Nehr et al. FAGE cell could be coupled to a different reaction cell to probe a wider range of conditions. A more substantial difference is the timescale of the chemistry taking place. Typical temporal profiles from Nehr et al. are of the order of a second compared to <10 ms in this work. The enhanced sensitivity of the Nehr et al. instrument means that radical-radical reactions should not interfere, but the technique may be subject to interferences from first order (or pseudo-first order) reactions including heterogeneous

processes. Detection of radicals in kinetics or yield experiments is difficult and studying reactions under a range of conditions is important to identify systematic errors, hence both instruments have a role to play.'

General remark to the figures: It would be easier to work with legends instead of descriptions in the captions.

Response:

Use of appropriate legends supported by detailed figure captions will indeed improve the overall readability of this work. See above comment.