Additional Comment on acp-2022-119

Anonymous Referee #1

The paper has been improved. The presentation quality is partly still not satisfying. I recommend that the authors go through the manuscript once more to reduce the number of abbreviations that are used, to format references of reactions as "Reaction RXX", to make sure that all font sizes in figures are appropriate and lab jargon such as "HALO flight", "HALO base", is avoided.

Answer:

As suggested by the referee, the references of reactions have been changed as "Reaction RXX". The figure sizes have been optimised for adequate font size, and the words such as "HALO flight" and “HALO base" are change to ‘measurement flight’ and ‘aircraft hangar’ respectively. The number of abbreviations is already at its minimum.

Anonymous Referee #2

1. In my original comments I pointed out that there is a considerable amount of text in the introduction regarding the NO-NO_2-O_3 photostationary state equation (Eq. 1), and yet it does not appear later in the text. In their response document they note “This ratio calculated from the NO (in-situ) and NO_2 (miniDOAS remote) measurements during the EMeRGe campaign is considered to have a sufficiently large error for not to be a valuable approach to calculate the [HO_2+RO_2]”, and in their revision have only added ““The PSS radical calculation made on the assumption of the NO_2 steady state is very sensitive to the accuracy of the NO_2 to NO ratio and the O_3 measurements.” Yet, the considerable amount of text and equation 1 remain in the revision. This is very confusing for the reader. If the authors insist on keeping it then they should be much more explicit that this approach is not used (e.g., at least they could add that same sentence from their response document into the manuscript). Furthermore it would be useful to the reader if they clarified that there are two HO_x radical calculation methods discussed here: 1. The NO-NO_2 interconversion photostationary state, described by equation 1, discussed from lines 96 – 120, and 2. The pseudo-steady state analysis presented in section 4.3 “PSS estimation of the RO_2^* mixing ratios” , including equation 4: $P(RO_2^*) = D(RO_2^*)$

Answer:

The authors prefer to keep Eq. 1 and the discussion about NO_2 steady sate approach from previous publications as this was the main approach used in filed measurements to calculate the sum of peroxy radicals. So, the text has been modified as suggested by the referee to help the reader understand there are two steady state approaches, i.e., considering NO_2 under study state and sum of HO_2 and RO_2 under steady state. For these lines 117 to 136 are modified as:

“The radical calculation made on the assumption of the NO_2 steady state is very sensitive to the accuracy of the NO_2 to NO ratio and the O_3 measurements. The comparison of $[\mathrm{HO_2} + \mathrm{RO_2}]_{\mathrm{PSS}}$ calculated using Eq.1 with ground-based (e.g., Ridley et al., 1992; Cantrell et al., 1997; Carpenter et al., 1998; Volz-Thomas et al., 2003), and airborne measurements, has shown in the past different degrees of agreement. The underestimations and overestimations found in air masses with different chemical compositions are not well understood. For the case of airborne measurements, the NO_2 steady state calculation generally overestimates the measured peroxy radicals (Cantrell et al., 2003a, 2003b). The differences observed could not be attributed to systematic changes in NO, altitude, water vapour and temperature, although these variables are often correlated. The NO to NO_2 ratio calculated from NO measured using in-situ technique and NO_2 measured using remote sensing (more detail about the measurement techniques is given in Table 1) used in this study is considered to have a sufficiently large error. So, the NO_2 steady state approach is not accurate enough to calculate $[HO_2+RO_2]$ for the measurements considered in this study.

Ground-based (Mihelcic et al., 2003; Kanaya et al., 2007, 2012; Elshorbany et al., 2012; Lu et al., 2012, 2013; Tan et al., 2017, 2018; Whalley et al., 2018, 2021; Lew et al., 2020) and airborne (Crawford et al., 1999; Tan et al., 2001; Cantrell et al., 2003b) measurements have also been compared with model simulations of HO_2 and RO_2. The discrepancies encountered depend upon the chemical composition of the air mass and the chemical mechanisms and constraints used in the model simulations. Recently, Tan et al., 2019 and Whalley et al., 2021 reported experimental radical budget calculations using PSS assumption for OH, HO_2 and RO_2 together with the published reaction rate coefficients of the reactions (R1 to R26), which control OH, HO_2 and RO_2 in the lower troposphere, and the ground-based measurements of all relevant reactants and photolysis frequencies. In this study, a similar approach has been used, i.e., the sum of HO_2 and RO_2 is assumed to be in PSS, to calculate the amount of peroxy radicals in the air masses measured on-board of the **H**igh **A**ltitude **Lo**ng range (HALO) research aircraft over Europe during the first campaign of the EMeRGe (**E**ffect of **Me**gacities on the transport and transformation of pollutants on the Regional to Global scal**e**s) project."

2. Another comment of mine that was not adequately addressed:

The original manuscript contains ""The dominant removal processes of RO_2* in the airmasses measured up to 2000 m are the loss of OH and RO through the reaction with NO_x during the radical". In my original review I noted "reactions of RO with NO_x are rare and not discussed at all later in the manuscript". The revision now includes this text: "The dominant terminating processes for RO_2* in the pollution plumes measured up to 2000 m are the formation of nitrites and nitrates from radical reactions with NOx."

They have not understood my main point: formation of nitrites is not thought to be a major RO_2^* removal process. I am unaware of supporting data from their study or from the literature that indicates that formation of nitrites can be a major RO_2* sink. In their instrument a large amount of CH_3O_2 is lost by the reaction $CH_3O + NO + M \rightarrow CH_3ONO + M$, i.e. formation of methyl nitrite, but these types of reactions are thought to be quite minor in the atmosphere. If the statement that formation of nitrites is a major RO_2* sink is to be kept in the manuscript it needs to be supported (which would be difficult). Moreover, it is not clear if they are including HNO_3 as a nitrate. I suspect the correct course of action is to simply change the sentence to "The dominant terminating processes for RO_2* in the pollution plumes measured up to 2000 m are the formation of nitric acid and organic nitrates"

Answer:

The sentence has been changed on line 32 as the referee suggested:

"The dominant terminating processes for RO_2^* in the pollution plumes measured up to 2000 m are the formation of nitrous acid, nitric acid and organic nitrates."

3. Section 4.4.1. In my initial review I objected to the formulation of eq 11 (now eq 9 in revised manuscript). While I understand that the authors are referring to the analysis by Cantrell et al. (2003b), it is still very confusing:

$P_{RO_2^*}$ = k_{RR} $[HO_2 + RO_2]^2$ + k_{RN} $[HO_2 + RO_2]$ $[NO_x]$ (Eq. 9)

“The first term on the right hand refers to radical radical reactions and the second term to RO_2*-NO_x reactions where RO_2* is considered to be the sum of HO_2+ RO_2 and K_{RR} and K_{RN} are effective rate coefficients”

The authors (and Cantrell) are calculating P(RO_2*) by equating it to L(RO_2*) (very safe assumption), and then calculating the L(RO_2*) terms. For the last term, the relevant RO_2* loss reactions that need to be summed in that term are the following:

$OH + NO_2 \rightarrow HNO_3$

$RO_2 + NO_2 \rightarrow RO_2NO_2$

$HO_2 + NO_2 \rightarrow HO_2NO_2$

$RO_2 + NO \rightarrow RONO_2$

While the 2nd and third reactions can be combined with an effective rate constant, I simply do not see how all four terms can be combined into the single term k_{RN} $[HO_2 + RO_2]$ $[NO_x]$. The OH concentration does not necessarily scale with the $[HO_2 + RO_2]$ concentration.

Wouldn’t it be simpler to calculate P(RO_2*) more directly based on RO_2* formation reactions rather than the loss processes? ie, from photolysis of HCHO, O_3/H_2O, etc.

Figure 16 is a nice figure btw: I am not trying to suggest this entire section is bad, but its formulation is still problematic.

Answer:

In this study and in that of Cantrell et al. 2003b, the P(RO_2*) is calculated form the measured values radical precursors like O_3, HCHO etc. and their photolysis frequencies. The Eq. 9 uses this calculated P(RO_2*) and RO_2* (both calculated and measured) to fit Eq.9 and find k_{RR} and k_{RN}. Cantrell eta al. 2003b showed this relatively simple expression can reproduce the RO_2* to NO_x relation fairly well for both measured and model RO_2* from TRACE-P campaign. So, a similar approach was also made in this study were, the RO_2*_m and RO_2*_c binned by P(RO_2*) values calculated using Eq. 3 and the corresponding P(RO_2*) values are substituted in Eq. 9 to find the k_{RR} and k_{RN} as fit parameters. The weak agreement between RO_2*m and the fit profile (Figure 16 b) shows the k_{RR} and k_{RN} terms are not adequate to express the RO_2* reaction rate as suggested by the referee. This is already written in line 554.

In addition, figure 16 a) shows that neglecting the $RO_2 + NO \rightarrow RONO_2$ in Eq. 7 resultes in very weak NO_x dependency for RO_2*_c with $P_{RO_2^*}$ ≥ 0.7 pptv s^{-1} as pointed by referee #4.

Text has been modified in section 4.4.1 for better clarity and to address the point raised by referee #4.

4. Equation 2, last term is $\Sigma kO_3+alkenes_k[O_3][alkenes_k]$ – the ROx yield from this reaction should be included (i.e., 2 × the OH yield).

Answer:

The equation 2 has been corrected as the referee pointed out with an effective RO_2^* yield, denoted by γ, from ozonolysis of alkenes.

Anonymous Referee #4

In this revision, the authors have addressed many of my concerns outlined in my original review. Specifically, they have corrected equation 8 (now equation 6) by excluding radical termination by the RO + NO reaction, which may be important in their chemical amplifier, but not in the atmosphere.

However, they still have not adequately addressed potential peroxy radical loss by the RO_2+NO_x reactions. While they are assuming that all RO_2 radicals are CH_3O_2 and as a result the termination by this reaction is negligible, they should include the RO_2+NO-> $RONO_2$ reaction in their generic reaction mechanism in the Introduction. They should also include it in their steady-state equation for completeness and can then make it clear that by assuming all RO_2 is CH_3O_2 that this term is negligible. They should also clarify that ignoring organic nitrate formation from these reactions may result in an overestimation of the peroxy radical concentrations in their calculations and could explain the some of the model overestimation highlighted in Figures 10 and 12.

Answer:

The reaction RO_2 + NO → $RONO_2$ has been included in the generic reaction mechanism in the Introduction as R25b. Additional text has been included in line 364 as:

”The reaction channel R25b is not considered in the calculation since the yield of this channel is < 5 % (Burkholder et al., 2020) for CH_3O_2 + NO reaction.”

for the explanation of Eq. 6.

An extra paragraph has been added in line 464 to address the overestimation in Figures 10 and 12 as pointed out by the referee.

“In addition, Eq. 7 does not consider the loss of RO_2 through the organic nitrate formation (reaction R25b) which results in an underestimation of radical loss in the presence of RO_2 with higher organic group. Tan et al., 2019 reported changing the yields for organic nitrate formation channel in reaction R25 from 5% to 20% has a small but notable influence on their experimental budget analysis. Similarly, the RO_2 loss through organic nitrate formation which are not included in Eq. 7 might explain the $RO_2{}^*{}_m$ overestimations for $\sum$VOC < 2ppb and $\sum$VOCs/NO < 20, and for NO > 200 pptv.”

Summary and conclusion section is also extended on line 603 as:

“Similarly, the RO_2 loss through organic nitrate are also excluded from the analytical expression. These reactions may become significant RO_2^* loss processes in the presence of RO_2 with higher organic groups. This might explain some of the RO_2^* overestimations by the analytical expression observed for NO > 200 pptv.”

The authors should also comment on whether ignoring radical termination by RO_2+NOx reactions their calculated RO_2 leads to the apparent discrepancy with that predicted by equation 10 for PROx > 0.7 ppt s^{-1} as shown in Figure 16a and discussed on lines 536-538. As the authors note, the measured RO_2 does show a decrease with increasing NO_x (Figure 16b, line 539), suggesting greater RO_2 radical termination by NO_x than accounted for by their model.

Answer:

To address this point, the text in line 545 has been modified as:

"$RO_2{}^*{}_c$ does not show the decrease with increase in NO_x for $P_{RO_2^*} \geq 0.7$ pptv s^{-1}. This might be explained by the under estimation of radical losses through organic nitrate formation in Eq. 7 as explained in section 4.3."

The revised manuscript also adds some confusing language related to their steady-state calculations. In particular, the new description of the terms in Equation 6 on page 17 (lines 365-369) is confusing. The authors state "ρ accounts for the effective yield of HONO, HNO3 and H2O formation through reactions R19 to R21 and the HO_2 + NO and HO_2 + O_3 reactions (R23 and R24 respectively) on the right hand side of Eq. 6." Rather than stating that they are account for the effective yield of H_2O (which is a product of many OH + VOC reactions in addition to R21), the authors should clarify that they are attempting to account for the fraction of OH radical termination through the OH+NO, OH+NO_2, and OH+HONO reactions relative to OH radical loss by the OH+VOC, OH+HO_2, and other OH loss reactions. In this term, it also appears that they are assuming that OH production by reactions 23 and 24 is much greater than OH initiation. More details on how they have derived this equation should be provided for clarification.

Answer:

The explanation of terms in Eq. 6 has been modified in line 374 onwards as:

"On the left-hand side of Eq. 6, 1-ρ accounts for the effective yield of HO_2+RO_2 through the radical initiation reactions R2a and R3 and reactions R5 to R7 and reaction R12. As the calculation is constrained with on-board measurements, only the reactions of measured VOCs were considered in reaction R12. Similarly, on the right-hand side of Eq. 6, ρ accounts for the radical termination through the OH + NO, OH + NO_2, and OH + HONO reactions (reactions R19 to R21) relative to the radical undergoing OH to peroxy radical conversion."

As now explained, the ρ account for radical termination relative to radical undergoing OH to peroxy radical conversion. The detailed derivation of Eq. 6 and Eq. 7 are already given in the supplementary information.