Comment on acp-2022-119

Anonymous Referee #4

This paper presents aircraft measurements of peroxy radicals during the EMeRGe-Europe campaign. The authors compare their measurements to predictions from several iterations of a photostationary state analysis. The authors find that the predicted peroxy radical concentrations were lower than the measured concentrations and suggest that photolysis and oxidation of OVOCs not included in the steady-state expression were responsible for the discrepancies.
While the measurements likely provide important new information, the paper is difficult to read. In addition to an analysis of the ability of the photostationary state expression to reproduce the measured peroxy radical concentrations, the authors also provide an analysis of the rates and sources of radical production and the estimated rate of ozone production. Unfortunately, the main conclusions of the paper are lost in the extended discussion. There are also problems with their chemical mechanism and the form of the steady-state equations that they are using to estimate the peroxy radical concentrations.
Overall, this paper presents some interesting and valuable measurements of peroxy radical concentrations. The paper may be suitable for publication after correcting their photostationary state expressions and re-analyzing their results. The paper would also benefit from moving much of this analysis and the discussion of the rates of radical and ozone production to a supplement and focus the main discussion on their primary conclusions as outlined in the abstract and the summary.

Major comments

- *The authors need to correct and clarify their conclusions stated in the abstract and the text regarding loss of RO radicals (lines 120, 358 and 566 for example). I'm surprised that they are considering the RO + NO reaction an important loss mechanism for alkoxy radicals in the troposphere when the traditional understanding of the fate of these reactions in the atmosphere is reaction with O2 or isomerization and/or decomposition.*
  While the RO + NO termination reaction (reaction 22) may be important in laboratory studies, it is unlikely that this termination reaction for alkoxy radicals larger than methoxy or ethoxy could compete with reaction with O2 or isomerization/decomposition under atmospheric conditions (see Orlando et al., Chem. Rev. 103, 4657-4689, 2003). This would likely become apparent if they had included the rate of isomerization/decomposition of alkoxy radicals in their photostationary state expressions in addition to reaction with NO and O2 in their attempt to calculate the fraction of RO termination vs propagation (equations S12 and others).

Answer:

This is a misunderstanding. We have not explained role of the reaction of RO with NO adequately. In the atmosphere the rate of the reaction of RO with NO does not compete with the rate of reaction of RO with O_2. The ratio k_{22}[RO]NO] to k_{26}[RO][O_2] is typically < $1x10^{-4}$. In the introduction the reaction R22 was included for completeness.

The text has been revised to correct any potential misunderstanding. In line 96 the sentence

"The rate of R22 in the atmosphere compared to that of R26 is negligible"

has been included. In addition, a new figure (Fig. 9) has ben included to show the fractional contribution of loss reactions considered in this study.

- *Instead, termination of peroxy radicals through reactions with NOx leading to the formation organic nitrates such as the RO2 + NO -> RONO2 reaction are likely more important. Unfortunately, it appears that the authors are not including these reactions in their chemical mechanism.*
  As a result, their steady-state equations that attempt to incorporate the formation of organic nitrates as radical termination reactions are incorrect (equations 8 and 9). The authors should incorporate an average organic nitrate yield from the RO2 + NO reaction instead of incorrectly attempting to account for the formation of RONO relative to reaction with O2 using rate

constants for methoxy radical with NO and O2. It is not clear how this correction would impact their calculated peroxy radical concentrations, but their results should be recalculated and reanalyzed in a revision of their manuscript.

Answer:

The terminating reactions of peroxy radicals with NO_x were considered in the manuscript in the former Eq. 8 (Eq. 6 in the revised paper). In the old Eq. 8 the term :

$$\left(\left(\frac{k_{22}[NO]}{(k_{22}[NO]+ k_{26}[O_2])}\right) k_{25}(1-\delta)[NO]\right)$$

was correctly calculated. However, this term is negligible as the referee pointed out above and therefore it is not included in Eq 6 in the revised manuscript. This does not change the calculated peroxy radical concentrations.

Concerning the formation of nitrates, as stated in the text, CH_3O_2 is the only RO_2 considered in the analysis:

Line 355: “As a first approach, RO_2 is assumed to consist only of CH_3O_2 to reduce the complexity of the calculations by considering only CH_3O_2 reaction rate constants”

We agree with the referee that larger RO_2 react with NO to make $RONO_2$ as is well documented. However, our RO_2^* is the sum of HO_2 and those RO_2 which react with NO to form NO_2. We use CH_3O_2 to represent the RO_2, as we wrote. According to JPL, the yield of the formation CH_3ONO_2 is <0.5% while 99.5% leads to $CH_3O + NO_2$. Therefore, this formation path has not been further considered in the analysis (see table note (l) in the Table S1 in the supplementary information).

In order to reduce the complexity and the assumptions about the unknown RO_2 composition, the formation of organic nitrates for longer RO_2 than CH_3O_2 (as e.g. investigated by Atkinson and Carter and Butkovskaya et al, see references below) has not been considered in the calculations. These studies show that generally the pressure dependent yield of alkylnitrates for the reaction of alkylperoxy radicals with NO increases from ca. 4% for C3 to ca. 30% for C>8. For the case that the mixing ratios of long alkylperoxyradicals is higher than the CH_3O_2 mixing ratio, the RO_2^* calculated in this study will overestimate the ambient RO_2^*.

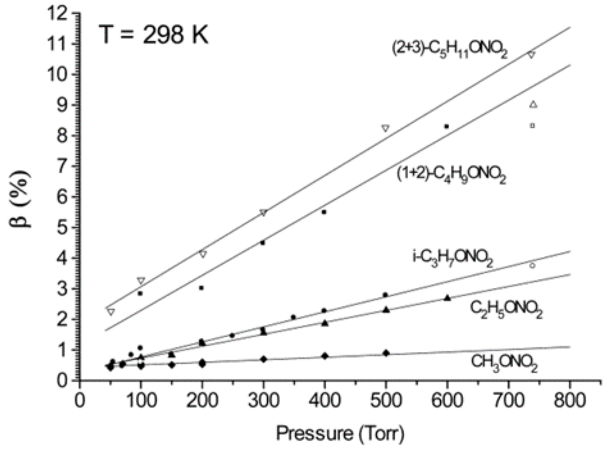

Figure 4. Comparison of the branching ratios k_b/k_a of alkyl nitrate formation in RO_2 + NO reactions for small alkylperoxy radicals: ▽, ref 14; ■, this work; ●, ref 18; ▲, ref 17; ◆, ref 16; atmospheric pressure data for propyl nitrate (○) and butyl nitrate (□) are from ref 10, and those for *n*-pentyl (Δ) nitrate are from ref 43. The open circle at 100 Torr is the branching ratio for isopropyl nitrate from ref 44.

(Butkovskaya et al., 2015)

Atkinson, R.; Carter, W. P. L.; Winer, A. M. Effects of Temperature and Pressure on Alkyl Nitrate Yields in the NOx Photooxidations of n-Pentane and n-Heptane. J. Phys. Chem., 87,2012-2018, 1983.

Carter, W. P. L.; Atkinson, R. Alkyl Nitrate Formation from the Atmospheric Photooxidation of Alkanes; A Revised Estimation Method., J. Atmos. Chem., 8, 165-173, 1989

Butkovskaya, N.; Kukui, A.; Le Bras, G. Pressure and Temperature Dependence of Ethyl Nitrate Formation in the $C_2H_5O_2$ + NO Reaction. J. Phys. Chem. A 2010, 114, 956-964.

Butkovskaya, N.; Kukui, A.; Le Bras, G. Pressure Dependence of Iso-Propyl Nitrate Formation in the i-$C_3H_7O_2$ + NO Reaction. Z. Phys. Chem. 2010, 224, 1025-1038

Butkovskaya, N. I., Kukui, ⊥ A., Le Bras, G., Rayez, M.-T., and Rayez J.-C., Pressure Dependence of Butyl Nitrate Formation in the Reaction of Butylperoxy Radicals with Nitrogen Oxide, JPCA, 119, 4408-4417,2015.

Specific comments

- *The authors seem to confuse radical initiation and termination processes with radical production and loss through propagation in several places in the manuscript. For example, it appears that the authors intended to calculate the rate of OH, HO2, and RO2 radical initiation using equation 2, but the equation incorrectly includes the rate of radical propagation by the OH + VOC reaction. Even though they neglect this term in their analysis, they should remove it from the equation and clarify their use of radical production vs. initiation throughout the manuscript and supplement.*

Answer:

This has been identified and corrected all over the text and the supplementary information.

- *In their revision, the authors should consider only including the results of their overall photostationary state calculations (after correction) in the main text and include the incremental analysis in the supplement (Figures 9-11). This would reduce the length of this discussion and the number of similar plots, making the discussion easier to follow.*

Answer:

The text has been shortened and modified for clarification following the comments of all referees. Some equations have been simplified or removed and a few figures have been moved to the supplementary information.

- *In addition to the correlation plots shown in Figure 12, it would be useful to include the calculated RO2* concentrations in the plots of the measured RO2* concentrations as a function of altitude (Figure 3 and perhaps Figure 4), illustrating the agreement/disagreement as a function of height.*

Answer:

The figure 11 in the revised manuscript has been included as proposed by the referee.

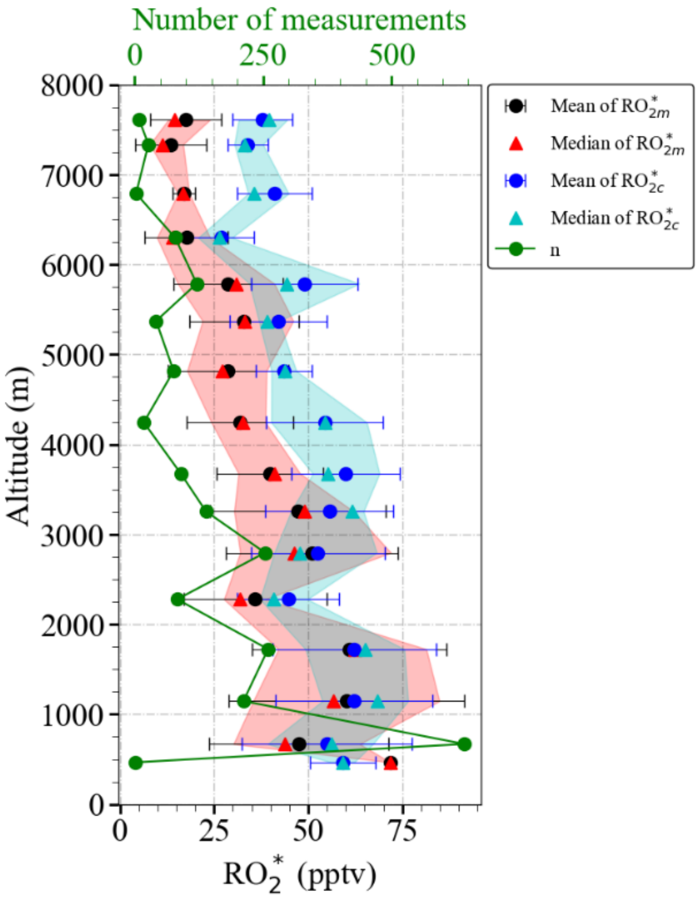

Figure 11: Vertical distribution of the mean $RO_2^*{}_m$ and mean $RO_2^*{}_c$ using Eq. 7 for δ = 0.5 for the EMeRGe data set in Europe. The measurements are binned over 500 m altitude. The error bars are the ± 1σ standard deviation of each bin. Median values (red and green triangles) the interquartile 25-75% range (red and blue shaded areas) and the number of individual measurements, n, for each bin (in green) are additionally plotted.

The vertical profiles comprise measurements from different flights on different days and different geographical areas over Europe, which are taken under very heterogeneous conditions and only have in common the altitude. Please also note that the number of measurements decrease with the altitude due to the own nature of the EMeRGe campaign.

In order to analyse the agreement/disagreement between $RO_2^*{}_m$ and $RO_2^*{}_c$ with the altitude in more detail, the Fig. S4 showing the mixing ratios as a function of latitude and altitude has additionally included in the supplementary information

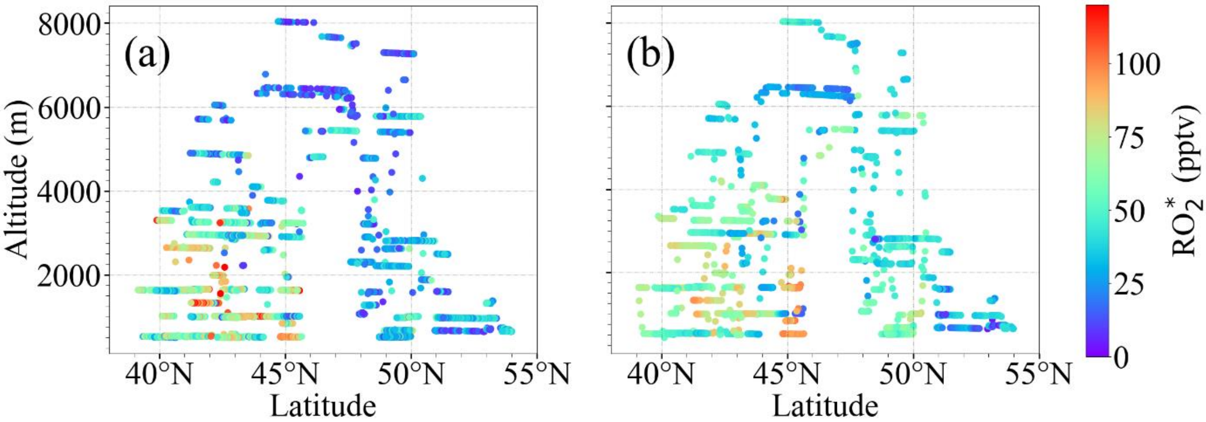

Figure S4: Latitudinal and altitudinal distribution of a) $RO_2^*{}_m$ and b) $RO_2^*{}_c$ mixing ratios calculated using Eq. 7 for $\delta = 0.5$.

Further information about the agreement/disagreement between $RO_2^*{}_m$ and $RO_2^*{}_c$ can be seen in the former Fig. 11 (in the revised manuscript moved to the supplementary information as Fig. S5) where $RO_2^*{}_m$ is plotted versus $RO_2^*{}_c$ and the data points are coloured-coded for altitude:

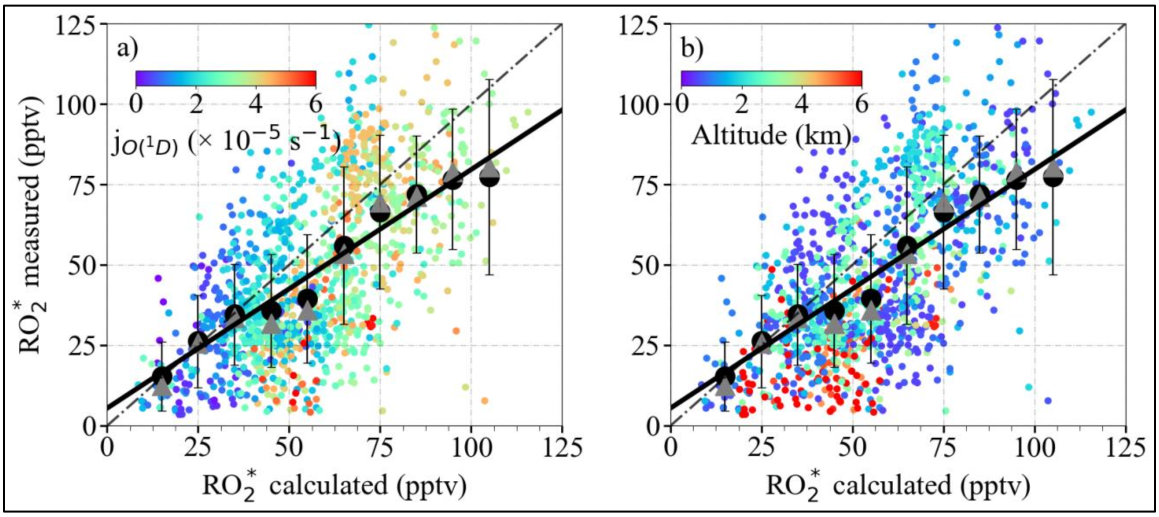

Figure S5: $RO_2^*{}_m$ versus $RO_2^*{}_c$ calculated using Eq. 7 for $\delta = 0.5$. The data points are colour-coded for a) photolysis frequency of O_3; b) altitude. The 1-minute (small circles), the mean of the binned $RO_2^*{}_m$ over 10 pptv $RO_2^*{}_c$ intervals (large circles), and the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear regression for the binned values (solid line) and the 1:1 relation (dashed line) are also depicted for reference

as well as in the figure 14 by the $RO_2^*{}_m/RO_2^*{}_c$ ratio as a function of altitude and latitude for all the EMeRGe flights over Europe.

Generally, there is no obvious relation only with the flight altitude except for the measurements above around 4000 m, which are all overestimated, as states in the text:

The text has been modified as follows (from Line 429 in the revised manuscript):

"Figure 11 shows the vertical profiles of $RO_2^*{}_m$ and $RO_2^*{}_c$ mixing ratios calculated for $\delta = 0.5$, averaged for the EMeRGe flights over Europe in 500 m altitude bins. $RO_2^*{}_c$ seems to overestimate $RO_2^*{}_m$ for altitudes above 4000 m. As mentioned in Sect. 4.1, the vertical profiles are a composite from averaging flights with legs carried out at different longitude and latitudes. Therefore, the differences between $RO_2^*{}_m$ and $RO_2^*{}_c$ have been studied in more detail respect to the composition of the individual air masses (see the $RO_2^*{}_m$ and $RO_2^*{}_c$ mixing ratios as a function of latitude and altitude in Fig. S4 in the supplementary information).

Figure 12 shows the data for δ = 0.5 colour-coded with NO, NO_x, the sum of HCHO, CH_3CHO, CHOCHO, CH_3OH, and $CH_3C(O)CH_3$ (from now on referred to as ΣVOCs), as a surrogate for the amount of OVOCs acting as RO_2^* precursors, and the ΣVOCs to NO ratio. The largest differences between $RO_2^*{}_m$ and $RO_2^*{}_c$ are observed for the bins around 50 pptv. The $RO_2^*{}_c$ overestimate the $RO_2^*{}_m$ mostly for $RO_2^*{}_m < 25$ pptv observed above ≈4000 m. These air masses are characterised by NO < 50 pptv, ∑VOCs typically below 4 ppbv, high ΣVOCs/NO ratios (> 50), and low insolation conditions , i.e. $j_{O(^1D)} < 2 \times 10^{-5}$ s^{-1} (see Fig. S5 in the supplementary information). Under these insolation conditions, the radical production rate is expected to be low, and the RO_2^* – RO_2^* reactions are expected to dominate the RO_2^* loss processes. As OH and H_2O_2 were not measured during the EMeRGe campaign in Europe, Eq. 7 does not include the loss reactions R17 and R18, which might be significant under such conditions (Tan et al., 2001) and explain the overestimation of $RO_2^*{}_m$.“

- *The data shown in Figure 4 is not consistent with their reported binning as there appears to be a point below 500 m even though there are no reported measurements at this altitude.*

Answer:

The point indicated by the referee below 500 m was measured in a stable flight leg just after the take-off of one of the flights (as indicated by the number of points) and has been removed in the revised figure.

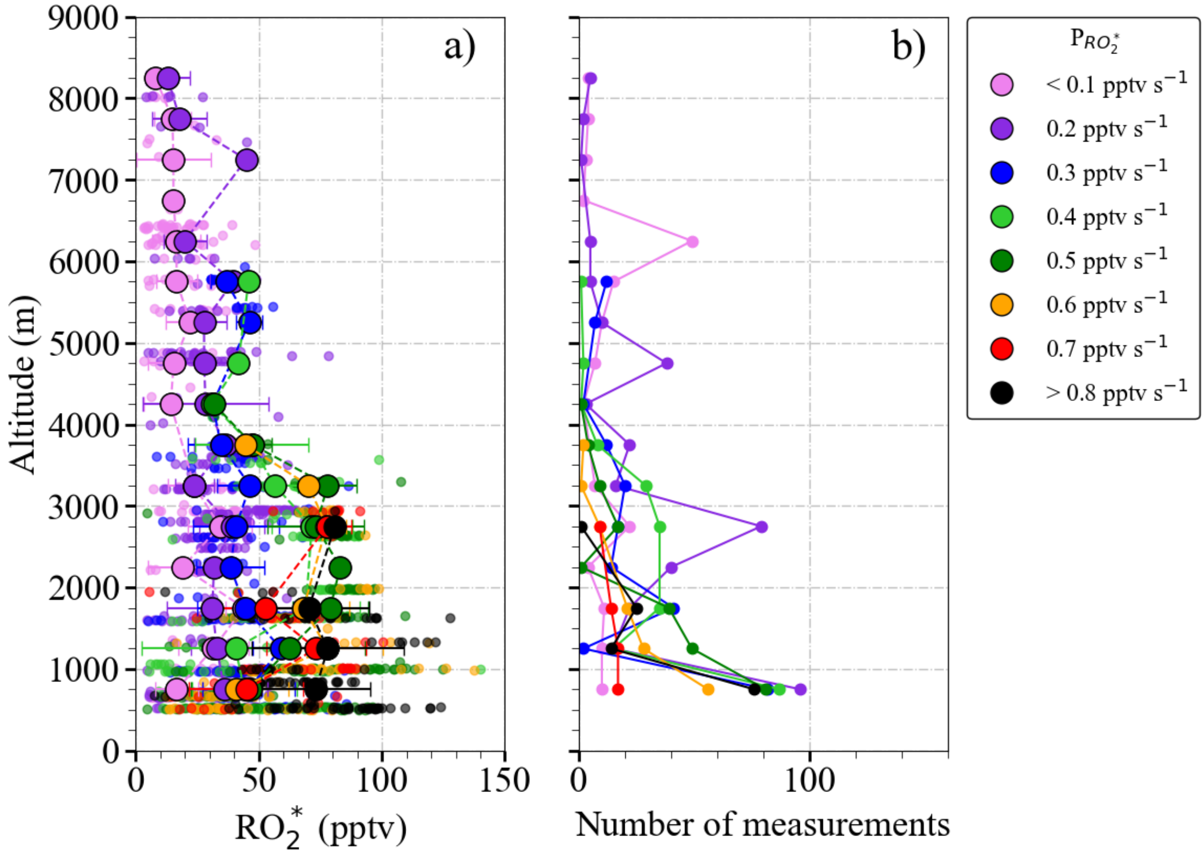

Figure 4: a) Composite averaged vertical distribution of measured RO_2^* colour-coded according to the value of $P_{RO_2^*}$, b) the number of measurements in each altitude bin. Small circles are 1-minute individual measurements binned with $P_{RO_2^*}$ values in 0.1 pptv s^{-1} intervals. Larger circles result from a further binning over 500 m altitude steps. All the production rates below 0.1 pptv s^{-1} and above 0.8 pptv s^{-1} are binned to 0.1 pptv s^{-1} and 0.8 pptv s^{-1}, respectively. The error bars are the standard deviation for each altitude bin.