

Atmos. Chem. Phys. Discuss., referee comment RC4
<https://doi.org/10.5194/acp-2022-119-RC4>, 2022
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Comment on acp-2022-119

Anonymous Referee #4

Referee comment on "On the understanding of tropospheric fast photochemistry: airborne observations of peroxy radicals during the EMERGe-Europe campaign" by Midhun George et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-119-RC4>, 2022

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). Instead, termination of peroxy radicals through reactions with NO_x 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.

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.

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.

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. 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.

Figure 6 is confusing and difficult to read. It is unclear how this figure adds to the discussion compared to Figure 5. It too could be moved to the supplement, perhaps separating some of the different plots to make it easier to read.

Much of the discussion in section 4.3 may change after the authors have corrected their photostationary state equations and recalculated their RO₂* concentrations. In any case, the authors should consider dividing this section into more subsections to improve readability, including moving some supporting figures and discussion to the supplement (Figures 13 and 16 for example).

I expect that the main conclusions would also change, as RO₂ loss due to organic nitration formation during radical propagation is likely to be much more important than loss of RO radicals. The authors should consider including calculations of the fractional contributions to radical termination as a function of height similar to the fractional contributions to radical initiation illustrated in Figure 5.

The new calculations could also impact the NO_x dependence of the calculated RO₂* as shown in Figure 17. While the authors comment on the agreement of the measured RO₂* with the expected trend, there is no discussion of the agreement with the calculated RO₂*. The authors should expand this discussion after correcting their calculated RO₂* concentrations.