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Comment on acp-2021-962

Anonymous Referee #2

Referee comment on "Kinetic study of the atmospheric oxidation of a series of epoxy compounds by OH radicals" by Carmen Maria Tovar et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-962-RC2, 2022

Review of: *Kinetic Study of the Atmospheric Oxidation of a Series of Epoxy Compounds by OH Radicals*

This paper summarizes several experiments in a pair of relative rate reactors to determine the rate constants of the OH reactions with a series of epoxides. The kinetics of epoxide reactions with OH have only been studied with a limited number of epoxides to this point. The literature values of those rate constants are compared, and are in good agreement with the values obtained in this study. This paper fills a gap in the literature as the kinetics of these reactions are currently understudied. The authors do a good job in their introduction outlining the importance of this class of compounds and how they are becoming more important through their role in carbon capture technologies. There are a few technical issues that need to be resolved in the specific comments below. My two large issues are as follows. There is a large section of the results/discussion dedicated to hybridization and ring strain. While interesting from a purely physical chemistry point of view I am not sure how much it actually adds to the paper and might be a bit too physical chemistry for the atmospheric chemistry community at large. Were this a J. Phys Chem. submission I think it would be fine, but I'm not sure about ACP. I think it would be more useful if the authors spent a little more time suggesting improvements/modifications to the Structure Activity Relationship (SAR) instead. This paper clearly demonstrates a scenario where SAR is lacking. It would be more informative to say something beyond "we need more data to properly capture the behaviour of the epoxide reactions with OH." Now it is possible that improvements to the five suggested methods are not possible, the authors could explain why this is the case. Overall, the paper fits within the scope of ACP and I recommend publication once the Results/Discussion section has been reworked and the technical issues below are addressed.

Specific Comments:

P4 L122: Were there any losses of reactants on their introduction into the chamber? If so how was this determined?

P5 L147: Perhaps I merely missed this in the description of the chambers, but why did the concentrations have to be 8 times higher in the smaller chamber? Is this a lamp intensity issue with the different chamber materials?

Table 1: There are formatting issues here. The column headers do not really describe what is in the columns. Column 1 is the species list not the initial mixing ratio. This needs to be fixed. What are the uncertainties on the initial conditions? This does not seem to stated anywhere and should be included in this table.

P6 L175: Was the linearity only for some compounds or all compounds? This sentence makes it seem like the relationship is not linear for all of the epoxides. This should be reworded, or the lack of linearity needs to be discussed.

Table 2: Why were different reference compounds used for the different epoxides? Was it initially merely a spot check on the kinetics of known reactions or something else? This should be mentioned/discussed.

P7 L192 should probably read “such as for cyclic ethers”.

P8 L215: The ordering of the SAR methods needs to be changed. The authors jump from (c) to (e) and then come back to (d). This leaves the reader confused and believing they missed something.

Figure 1: It is unclear to me which chamber these results came from. It should be indicated in the figure caption and/or panels.

P10 L243: This is where it would be helpful if the authors made some suggestions or at least discussed a better way to use SAR. Since all of the methods return varying degrees of accuracy for different compounds, it shows that it is not helpful without more data to constrain the SAR prediction. This of course probably is not shocking as with most models if you put either not enough information in (or garbage) you tend to get less than satisfactory results out.

Table 3: Column 2 needs to have the appropriate letter next to the SAR predicted rate constant. Currently it is up the reader to guess/assume.

P12 L285: The sentence should not start with brackets. I am guessing this is an Endnote formatting issue that the authors did not catch.

P13 L315: Perhaps it is my own ignorance but I would not have guessed that an epoxide would be less reactive to OH than its analogous alkane. This is a comment more on me than the authors.

P14 L339: This uncertainty is wrong. How can you potentially have a negative rate constant?

P14 L357: Are the chambers used in these experiments capable of temperature dependant measurements? How stable is the temperature in the reactor over the course of an experiment as I am guessing the lamps do add some heat.

P15 L372: Should be Cl atoms or radicals?

P15 L382: What are the aerosol uptake rates and how do they compare to oxidation by OH and Cl? A reference to this should be included.

P16 L400: The presentation of future work should either be put in a "Future Work" section or tacked on to the results discussion not the Conclusions section.