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Comment on acp-2021-962

Anonymous Referee #1

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-RC1, 2022

Kinetic Study of the Atmospheric Oxidation of a Series of Epoxy Compounds by OH Radicals by Carmen Maria Tovar et al. presents a series of measurements of epoxides using the relative rate technique with a variety of reference compounds. This work fills in gaps in the kinetic information on these compounds that are used in industrial chemistry and potentially CO_2 capture technology. This work also discusses the failings of the current structure activity relationships (SARs) used to estimate the rate constants of epoxides with OH radicals. This work adequately presents their laboratory results and comparison to the SARs, however it is unclear what actually needs to be adjusted to the current SARs from the presented results, as there was no attempt to create a more representative SAR. Because of the additional knowledge presented in this paper on the rate constants of these chemicals and potential to improve current SARs for epoxides, I recommend that this is reconsidered for publication after major revisions.

Major Comments:

L285-327: "(Tamres et al., 1954) stated…means of theoretical calculations." This seems beyond the scope of the paper. I think that it is useful to think of the reactivity of these compounds from a theoretical perspective in some situations. However, structure activity relationships are observationally/experimentally derived. In these paragraphs, there are many facts stated about the electronegativity, ring strain, hybridization, and other parameters of epoxides, but it is unclear how these relate to your results. Are these factors that can be put into a revised SAR? Can you obtain these from just knowing the structure of the molecule? As a concrete example, how does the suggestion "that the bonds are not saturated and can interact with π-electron systems" affect the OH rate constants with the epoxides? If you keep this section, it should be connected to the SAR and reaction rates more clearly.

Table 1: What is the error of your concentrations? I don't think the error on the 1ppm starting concentration is the same as the 84ppm, which is what this table implies. Were the initial concentrations assumed from the known amount injected? If so, how do you know it all made it into the chambers without decaying? How did you actually manage to get these chemicals into the gas-phase consistently?

Table 2: The final errors on the rate constants do not seem to make sense. The error on the Ethylene rate constant is ~1.5% and the error of your measured slope is ~5% (is this just the error on the slope? Do you force the fit through zero? Does that change the error?). How does the reported rate constant error for CHO come out to be ~16%? You say "up to 35% contribution in the recommended values of the rate coefficients for reference compounds" is accounted for in the error, but not all of your reference compounds have this large of errors. Also, unless you have a valid justification, it does not make sense for reported errors to have more than one significant figure. On a similar note, the error should also determine the significant figures of the reported value. This might end up affecting your claim that the trans- and cis- isomers have duifferent rates, since the reported rates are within each other's errors.

Table 4 (and corresponding discussion): There should be more discussion about what a homologous compound is. Potentially having the structures drawn would help with this. From my perspective, I just see that CHO is C6H10O, methylcyclohexane is C7H14, and di-n-propyl ether is C6H14O which have different numbers of total atoms. I expect the rate constant for these other compounds to be faster because there are more hydrogens to abstract, so I am not sure if your point is coming across with this table and discussion. It is difficult to see how the addition of the 3-membered ring or additional oxygen actually affects the rates when the molecules could have other factors changing their rate constants.

Minor Comments:

L162: Why are only some reference compounds used for some of the epoxides? Why did you not use all 6 reference compounds?

L169: Keep names the same for compounds (e.g. propene vs propylene) throughout the paper.

Figure 1: I think one panel will show the fact that your results are linear adequately. I would recommend putting most of this figure in the SI.

L339: A range of (2.0±5.7) ×10-12 cm3 molecule-1 s-1 does not make physical sense. The way the error is written includes negative rate constants.

L344: You mention a theoretical structural analysis but have no basis sets or computational details in the methods for this.

Section 4: There are more recent references for the 24-hr average concentration of OH, Cl, and peak Cl atom concentrations during CalNex that probably should be used:

Young et al. ACP 10.5194/acp-14-3427-2014

Wang et al. ACP 10.5194/acp-19-3981-2019

Lelieveld et al. ACP 10.5194/acp-16-12477-2016

L385: How does the timescale for aerosol partitioning compare to oxidation by OH?

L400-401: There should not be any new information in the conclusion - potential future work should not be included.

Technical Comments:

The L in 480*L* or 1080*L* should be consistently formatted through the paper (i.e. capitalization, italicization, space after the numbers, etc.)

Numbering of equations is inconsistent.

There are subject/verb disagreements, grammar and punctuation errors, and extra spaces and carriage returns that should be checked for.