

Response to the reviewer's comments for manuscript acp-2021-962

Title: "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

Special Issue: Simulation chambers as tools in atmospheric research (AMT/ACP/GMD inter-journal SI)

We are very grateful for the valuable suggestions and comments of both reviewers, which were carefully considered and helped to improve the quality of our manuscript. The original comments from the reviewers are shown in black. Our answers are marked in blue while changes performed in the body of the manuscript are marked in red.

B. Comments by Referee #2

R2: 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.

Reply from the authors:



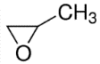
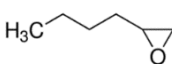
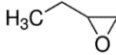
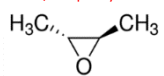
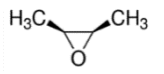
We very gratefully for the reviewer's comments. The reviewer clearly emphasize that there is a lack of knowledge for the kinetics of epoxide reactions with OH radicals. The new SAR method is beyond the scope of this paper but, as the reviewer mentioned, we intended to demonstrate where SAR is lacking and to provide with our work additional rate coefficients to improve the kinetic data base regarding the gas-phase reactivity of epoxides toward OH radicals.

As we already mentioned in a previous answer, the experimentally obtained rate coefficients from the present study together with existing literature data would not provide enough information to improve current SAR methods and more data are required to properly capture the behaviour of the epoxide reactions with OH radicals. However, more information has been added into the manuscript related to the comparison of the experimental vs SAR estimated rate coefficients. Furthermore, the discussion section has been improved with correlation equations based on the log-log correlation fitting data between rate coefficients for the reactions with OH and chlorine atoms. Besides, the manuscript has been modified by adding a new column in table 2 to emphasize the differences between various SAR methods and experimental rate constants for the reaction of epoxides with OH radicals. It is evident from Table 2 those different methods will work better for some epoxides than others and no SAR approach will cover satisfactorily all the epoxides investigated in present study.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

Table 3. Comparison of the rate coefficients for the reaction of OH radicals with the epoxides investigated in this study with the literature data and SAR predictions. $k_{\text{Epoxide}}/k_{\text{SAR}}$

Epoxide	k_{SAR}	$k_{\text{Epoxide}}/k_{\text{SAR}}$	k_{Epoxide} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
Cyclohexene Oxide 	(a) 6.37×10^{-12} (b) 6.14×10^{-12} (c) 6.31×10^{-12} (d) 5.81×10^{-12} (e) 1.02×10^{-11}	0.93 0.97 0.94 1.02 0.58	$(5.93 \pm 1.13) \times 10^{-12}$ $(6.51 \pm 0.65) \times 10^{-12}$	This work (El Othmani et al., 2021a)
Ethylene Oxide 	(a) 2.80×10^{-13} (b) 1.89×10^{-13} (c) 3.54×10^{-13} (d) 0.77×10^{-13} (e) 8.85×10^{-14}	0.31 0.47 0.25 1.14 0.99	$(0.88 \pm 0.25) \times 10^{-13}$	(Calvert et al., 2011)
Propylene Oxide 	(a) 0.59×10^{-12} (b) 0.46×10^{-12} (c) 0.67×10^{-12} (d) 0.28×10^{-12} (e) 5.43×10^{-12}	0.83 1.07 0.73 1.75 0.90	$(0.49 \pm 0.52) \times 10^{-12}$ $(0.30 \pm 1.00) \times 10^{-12}$ $(0.47 \pm 0.24) \times 10^{-12}$	(Wallington et al., 1988b) (Middala et al., 2011) (Virmani et al., 2020)
1,2-epoxyhexane 	(a) 4.64×10^{-12} (b) 4.48×10^{-12} (c) 4.15×10^{-12} (d) 3.97×10^{-12} (e) 6.34×10^{-12}	1.24 1.29 1.39 1.45 0.91	$(5.77 \pm 0.83) \times 10^{-12}$	This work
1,2-epoxybutane 	(a) 1.81×10^{-12} (b) 1.65×10^{-12} (c) 1.83×10^{-12} (d) 1.45×10^{-12} (e) 2.96×10^{-12}	1.09 1.20 1.08 1.37 0.67	$(1.98 \pm 0.29) \times 10^{-12}$ $(1.90 \pm 0.67) \times 10^{-12}$ $(2.20 \pm 0.02) \times 10^{-12}$	This work (Wallington et al., 1988a) (El Othmani et al., 2021b)
trans-2,3-epoxybutane 	(a) 0.92×10^{-12} (b) 0.73×10^{-12} (c) 0.99×10^{-12} (d) 0.49×10^{-12} (e) 9.98×10^{-13}	1.97 2.48 1.83 3.69 1.81	$(1.81 \pm 0.33) \times 10^{-12}$	This work
cis-2,3-epoxybutane 	(a) 0.92×10^{-12} (b) 0.73×10^{-12} (c) 0.99×10^{-12} (d) 0.49×10^{-12} (e) 9.98×10^{-13}	1.63 2.05 1.52 3.06 1.50	$(1.50 \pm 0.28) \times 10^{-12}$	This work

Calculated using the SAR estimation of (a) (Kwok and Atkinson, 1995), (b) (Calvert et al., 2011), (c) (Calvert et al., 2015), (d) (Middala et al., 2011), (e) (Jenkin et al., 2018).

R2: Specific Comments: P4 L122: Were there any losses of reactants on their introduction into the chamber? If so how was this determined?

Reply from the authors:

There are no wall losses for neither the epoxides nor the reference compounds. Preliminary tests for potential photolysis have been also performed and no loss by photolysis has been observed over a period of 15 minutes.

R2: 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?

Reply from the authors:

The concentrations are approximately 8 times higher in the smaller chamber because there is a similar ratio between the optical path lengths of the White type optical system in the chamber. In order to have similar absorbance with respect to Lambert-Beer law there should be an increase in concentration when the optical path is decreasing. For methyl nitrite the higher concentration would be necessary to provide a high enough steady-state OH radical concentration to react with both the epoxides and reference compounds, respectively.

R2: 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 be stated anywhere and should be included in this table.

Reply from the authors:

We have already answered replied to a similar comment from reviewer 1. The header of table 1 has been modified. We agree that usually the concentrations (mixing ratios in Table 1) should be represented by a value with a range of uncertainties. However, the mixing ratios in table 1 are indicative and are not included in any calculations. A sentence has been introduced into the text to show how these mixing ratios have been obtained. We follow in our determinations the subtraction factor of a reference IR spectrum from all IR spectra recorded during a kinetic experiment. For equation (I) there is a direct dependence between the ratios of concentrations with the ratio of subtraction factors and such later ratios are considered in the relative rate coefficient determinations.

R2: 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.

Reply from the authors:

It is evident from figure 1 that we obtained linear plots with almost “zero” intercept for all compounds investigated in present study. This indicates the missing interferences and secondary reactions and proves that our investigations provide high quality data. The sentence has been re-formulated accordingly: “The linearity has been observed for all the investigated epoxides in both reactors.”

R2: 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.

Reply from the authors:

The selection of the reference compounds employed in the kinetic study has been constrained by the experimental technique. Prior to the use of one reference compound, its reference spectrum has been recorded and compared with the reference spectrum of the epoxide compound and methyl nitrite and in a lesser extent with product spectra resulting from the initiated oxidation of epoxides/reference compound with OH radicals. The comparison has been made to identify the infrared absorption bands, which do not overlap with other infrared absorptions features from reaction mixture to allow subtraction procedure without interferences from IR absorptions of other compounds. Another more permissive criterion is to find a reference compound, which has a rate coefficient toward OH radicals, which is not very different than that one of the epoxides. Usually, up to three reference compound are enough to derive an average reaction rate coefficient value.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

Line 170: The selection of the reference compounds employed in the kinetic study has been constrained by the experimental technique since there is required to identify the infrared absorption bands which do not overlap with other infrared absorptions features from reaction mixture.

R2: P7 L192 should probably read “such as for cyclic ethers”.

Reply from the authors:

The sentence has been modified in the revised manuscript

R2: 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.

Reply from the authors:

Thank you for the comment. The entire Results and Discussion section has been re-written.

Concerning Fig 1: The rate coefficients obtained by using two simulation chambers are in perfect agreement as shown in Fig. 2. Accordingly, the data have been plotted together for all the epoxides regardless the reactor where the experiment has been performed.

R2: 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.

Reply from the authors:

We have mentioned as the reviewer suggested that the rate coefficients from the present study together with existing literature data does not provide enough information to improve current SAR methods. All SAR methods report difficulties regarding the agreement of the rate constant with those reported in present study and the literature for the entire series of compounds. Even a factor of 3 has been observed between estimated and observed rate constant values. However, the discussion concerning the factors used in the SAR estimates has been expanded and restructured, in order to have a better view of why structural analysis of epoxides is so important in improving these factors.

R2: 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.

Reply from the authors:

Table 3 has been modified and the appropriate letter has been placed next to the SAR predicted rate constants.

R2: P12 L285: The sentence should not start with brackets. I am guessing this is an Endnote formatting issue that the authors did not catch.

Reply from the authors:

We agree with the reviewer's comment. The manuscript has been corrected accordingly.

R2: 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.

Reply from the authors:

The discussion derived from Table 4 has been re-written in the revised manuscript and more information has been added.

R2: P14 L339: This uncertainty is wrong. How can you potentially have a negative rate constant?

Reply from the authors:

This is actually a typo where “-” was replaced by “±”. The correct sentence is “the range of $(2.0-5.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ”. However, this section has been reworked and new data added.

R2: 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.

Reply from the authors:

The chambers have a permanent monitoring system of the temperature. All experiments have been performed in the range of $(298 \pm 3) \text{ K}$. The lamps, placed evenly around the chamber, could heat up the air inside the reactor if long time experiments are performed. However, our experiments have been performed over a time period of around 30 min irradiation time, not long enough to heat the chamber over the indicated temperature range.

The 1080 L chamber has an additional temperature control system which could maintain the constant temperature from 278K to 341K and usually is used for temperature dependent kinetic studies. However, the system was not activated during the experiments since the temperature was not out of the $(298 \pm 3) \text{ K}$ range.

R2: P15 L372: Should be Cl atoms or radicals?

Reply from the authors: We would like to keep “chlorine atoms”. This is very often used in the scientific community, although it is well known that the chlorine atom could be a significant reactive free radical in the troposphere (Ravishankara, 2009).

R2: P15 L382: What is the aerosol uptake rates and how do they compare to oxidation by OH and Cl? A reference to this should be included.

Reply from the authors:

We have discussed the epoxides atmospheric implication in a large context including the most important isoprene derived epoxides. We have already pointed out in the revised version of the manuscript that Minerath et al. (2009) have shown the effect of particles acidity on the 1,2-epoxy butane uptake. The text been modified accordingly in the revised manuscript.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

Line 478: In the laboratory and ambient SOA, epoxides are considered as potential precursors for sulphate esters, polyols, hydroxy nitrates and halides. Epoxide concentrations in the aerosol composition will be limited by the rates of the gas uptake process, which will be largely determined by the gas phase epoxide concentration levels (Minerath and Elrod, 2009; Minerath et al., 2009), the uptake process and particles acidity. Higher acidity of aerosol particles would produce more efficient heterogeneous reactions of epoxides. A recent study suggests that heterogeneous reaction of some epoxides on acidic aerosols are faster and more efficient than gaseous reactions with atmospheric oxidants, and thus these reactions could represent the major removal pathway for epoxides (Lal et al., 2012). Besides, in urban environments the particle acidity can be significantly high, with pH between 0-5. Under such conditions, epoxides can react rapidly, and the reaction products of the heterogeneous reactions could contribute to the growth of the SOA particles and to the possible modification of their physical and chemical properties (Zhang et al., 2007).

Minerath et al., (2009) has shown that 1,2-epoxybutane, which possess slower hydrolysis, has an increasing lifetime with increasing pH. It is expected that even at higher pH most of the epoxides will have time to react on SOAs. The monitoring and evaluating of emissions of this kind of compounds in different ambient conditions, as pH and different regimens of NO_x, is recommended in rural and urban locations.

R2: 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.

Reply from the authors: The suggestion of the reviewer has been taken into account and the manuscript has been modified accordingly