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.

A. Comments by Referee #1

R1: *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.

Reply from the authors: We gratefully appreciate the referee's comments. Our work has been indeed meant to contribute with additional rate coefficients to improve our current knowledge about the gas-phase reactivity of epoxides toward OH radicals. Kinetic studies with OH radicals on this group of compounds, widely spread in the atmosphere, have been limited to ethylene oxide and propylene oxide and just very recently the kinetic database has been updated with single studies of additional kinetic rate constants.

R1: 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.

Reply from the authors:

We agree with the reviewer that the theoretical basis and the experimental findings should be better linked in the text and decide to rewrite the section. The obtained rate coefficients from the present study together with existing literature data do 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, the discussion section has been improved organizing the information about the crucial factors in the improvement of a SAR estimation method for future work. Also, we include some recommendations since this are a common observation for both authors. We also add equations based on the log-log correlation fitting data between the kinetic rate coefficients for the reactions with OH and chlorine atoms and an extra figure to enrich the discussion.

Changes in the manuscript/supplementary text:

L235: *3.1 Correlation of the rate coefficients between the reaction of epoxides with OH radicals and chlorine atoms*

The abstraction route defines the main reaction pathway of the epoxides with OH radicals. For epoxides series it is likely to define a correlation of the rate coefficients from their reaction with OH radicals and chlorine atoms. Similar correlations have been observed for the series of alkanes, saturated alcohols and acyclic ethers (Calvert et al., 2011). Figure 3 presents a log-log correlation plot between the Cl atoms and OH radicals rate coefficients with epoxides for the series of propylene oxide, 1,2-epoxyhexane, 1,2-epoxybutane and both isomers of 2,3-epoxybutane. A very clear correlation (R^2=0.9935) described by the relation $\log_{10}[k_{(CL+epoxides)}] = 0.718 \times \log_{10}[k_{(OH+epoxides)}] - 1.685$ has been obtained. The ethylene oxide and cyclohexene oxide has been represented in the Figure 3 but have been not included into the correlation plot, although including the cyclohexene oxide, the log-log correlation would change to $\log_{10}[k_{(CL+epoxides)}] = 0.788 \times \log_{10}[k_{(OH+epoxides)}] - 0.852$ with (R^2=0.978). The reactivities of the epoxides with OH radicals and Cl atoms are clearly correlated for the series of epoxides. However, the log-log correlation for epoxides is different to the one presented by Calvert et al. (2011) described by the relation $\log_{10}[k_{(CL+alkanes)}] = 0.521 \times \log_{10}[k_{(OH+alkane)}] - 3.670$ with (R^2=0.85) for the series of alkanes with those two atmospheric oxidants. However, the log-log correlation for the series of ethers and alcohols with these two oxidants presented by Calvert et al. (2011) described by the relation $\log_{10}[k_{(CL+ether/alcohol)}]= 0.634 \times \log_{10}[k_{(OH+ ether/alcohol)}] - 2.710$ with (R^2=0.72) is in better agreement with those obtained in this study for epoxides.

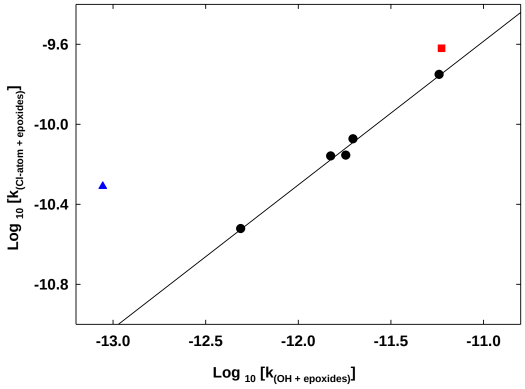


Figure 3. Double logarithmic plot ($\log_{10}$) of the rate coefficients for the reaction of Cl-atoms versus the reaction of OH-radicals with the epoxides (propylene oxide, 1,2-epoxybutane, *trans*-2,3-epoxybutane, *cis*-2,3-epoxybutane, 1,2-epoxyhexane). The solid line represents the unweighted least-squares fit to the data. Cyclohexene oxide is represented by the red square while ethylene oxide is represented by a blue triangle. Both were not included into the least squares fit.

The log-log correlation plot can be used to predict rate coefficients. For example, the rate coefficient for the reaction of propylene oxide with chlorine atoms which has not been measured to date, can be derived based on the proposed correlation, $k_{\text{(propylene oxide + Cl)}} = 3.04 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. However, the knowledge of rate coefficients for the reactions of epoxides with atmospheric oxidants is still very limited.

L270-324: *3.2 Structure-Activity relationship (SAR) calculations for epoxides*

L325-382: *3.2.1 Pseudo-ethylenic character in the epoxy ring as main factor affecting reactivity of epoxides and SAR*

The kinetics, reactivity trends and thermochemistry of cis/trans-2,3-epoxybutane, 1,2-epoxybutane, 1,2-epoxyhexane and cyclohexene oxide initiated by Cl atoms were discussed previously in Tovar et al. (2021). The series of epoxides were theoretically studied using density functional theory (DFT) applying the B3-LYP exchange-correlation function with Grimme´s GD3-BJ empirical dispersion corrections. The calculations showed that the abstraction channels of β-CH_2 sites are dominant for all epoxides studied.

As we explained in Tovar et al. (2021), the sites in the epoxide are more reactive in β-position when the carbon atoms in ethylene oxide approach the sp^2 state and its CH_2 units are pseudo-ethylenic in character. This conjugation does not occur if the π orbitals of the unsaturated groups cannot orient themselves with their axes parallel to the plane of the epoxide ring. Such a geometric arrangement in the epoxy molecule would be necessary to allow the abstraction of a hydrogen atom in the molecule in a preferential way, thus increasing the reactivity of the reaction.

In section 3.2 we discuss the rate coefficients experimentally calculated for the same series of epoxides towards OH radicals, and the estimated rate constants of epoxides with total of two to six carbon atoms by using different SAR approaches. In these estimations different substituent factors were applied. In the following discussion, we present the possible theoretical reasons why these SAR estimations could differ between them and with respect to the experimental values based in novel theoretical and experimental studies that confirms our previous findings.

From Table 4 we can assess the influence of the ring size over a series of epoxides. In this way, the cyclic ether reactivities towards OH radicals are increasing with the ring size (k in 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) ($k_{oxirane(C2H4O)}$ = (0.091± 0.023)) < ($k_{oxetane(C3H6O)}$ = (10.3±2.6)) < ($k_{oxolane(C4H8O)}$ = (17.0±2.6)); ($k_{oxaneC5H10O)}$ = (12.0±2.0)) < ($k_{oxepane(C6H12O)}$ = (18.0±5.0)).

From previous studies we know that the electron ability in hydrogen bonding can act as a measure of the relative electron density (Tamres et al., 1954). The very low electron donor ability of substituted ethylene oxides, compared with other cyclic ethers, in hydrogen bonding has already been shown in the past (Searles and Tamres, 1951; Searles et al., 1953). Thus, the oxygen in 3-membered ring ethers is more electronegative than in larger ring ethers or in acyclic ethers. This observation can be explained from Walsh´s proposal for the structure of ethylene oxide and cyclopropane (Walsh, 1949). Walsh's model imply a high electron density in the centre of the three-membered rings, which suggests that the exterior of such rings would have a lower electron density than normal for the atoms involved. This effect is explained for strained systems where the hybridized orbitals employed for a bonding attain maximum overlap in such a way that altered valence angles "bent bonds" are realized. Because the Walsh model does not correspond to the ground state of cyclopropane/epoxide, the description of bent bonds for cyclopropane by the Förster-Coulson-Moffitt model (Förster, 1939; Coulson and Moffitt, 1949, 1947) is the most frequently considered one (Wiberg, 1996). More recently, the topological analysis of the electron density method (ED) has been applied to describe the electron distribution within a compound (Kutzelnigg, 1993; Bader et al., 1994; Coppens, 2005; Koritsanszky and Coppens, 2001). However, the ED method provides information on concentration and depletion of electrons, but not on the pairing of electrons. In order to measure the electron pair localization the electron ability indicator (ELI) it is used (Kohout, 2004). A recent study presented by Grabowsky (2010), has introduced the ELI based on an X-ray diffraction experiment by means of the X-ray constrained wavefunction fitting procedure. The method was applied on a series of epoxides derivatives, and clearly indicated outwardly bent bonds according to the Förster-Coulson Moffit model.

Also, this study shows that the maxima of deformation density and the valence shell charge concentrations (VSCCs) in the Laplacian maps are located clearly outside the bond axes for both the C-O and C-C bond, and there are no maxima inside the ring. The Förster-Coulson Moffit model makes use of hybrid orbitals with a relation between s- and p- character like sp2-hybridization. This conducts to an orbital overlapping outside the direct bond axis forming three σ-type bonds. The orbitals used in these exterior bent bonds of the ring are in a favourable position for some overlap with p-orbitals from adjacent atoms (Searles et al., 1953). The involvement of sp2-type orbitals in the epoxide ring instead of sp3 like in normal single bond suggests that the bonds are not saturated and can interact with π-electron systems (Grabowsky et al., 2010). Our recent study on the reactivity of a series of epoxides towards chlorine atoms in gas phase using quantum mechanical calculations agrees with these findings. As we discussed in Tovar et al. 2021, If we consider the case of cis/trans-epoxybutane, when the compound has lost one H of the CH_3 group, it becomes trigonally (sp^2) hybridized, facilitating the possible formation of a double bond with the singly occupied p-orbital after abstraction of H. This effect could explain the formation of acrolein from Cl-initiated oxidation of both *cis*-2,3-

dimethyloxirane and *trans*-2,3-dimethyloxirane with yields of 36.49±0.55 and 49.08±1.29 at 650K and 800k, respectively in the work presented by Doner et al. (2020). The formation of the vinyl oxirane from beta hydrogen abstraction and the subsequent formation of the keto hydro peroxy radical reported by Christianson et al. (2020) for the oxidation of 1,2-epoxybutane also confirms this theory. In addition, one of the most abundant products reported in the same work, 2,2-bioxirane (31.44±6.49) at 640K, would also respond to the same reactivity trend, with abstraction in the beta position being the most predominant.

This structural effect has been observed also experimentally with cyclopropyl ketones (Rogers, 1947), α,β-epoxyketones (Walsh, 1949; Cromwell and Graff, 1952), ethylenimine ketones (Cromwell and Graff, 1952) and more recently in the acid catalysed ring opening of epoxides (Oshima et al., 2008). Moreover, there is some evidence of a conjugation of the epoxy ring with substituents using methods like UV spectroscopy, heat of combustion and MO calculations (Parker and Isaacs, 1959; Starit et al., 1964).

L385-406: *3.2.2 Ring strain in epoxides*

From Table 4 we can see that the epoxides are less reactive towards OH radicals than the analogous alkanes with the same number of carbon atoms: (k in 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) ($k_{cEB(C4H8O)}$ = (1.50±0.28)), ($k_{tEB(C4H8O)}$ = (1.81±0.33)), ($k_{12EB(C4H8O)}$ = (1.98±0.29)) < ($k_{butane(C4H10)}$ = (2.38±0.24)). The effect is more pronounced for epoxides with 4 carbon atoms than for those with 6 carbon atoms: ($k_{12EHX\ (C6H12O)}$ = (5.77±0.83)) < ($k_{(C6H14)}$ = (5.86±1,17)). The presence of a six-membered ring next to the epoxide group increases its reactivity ($k_{CHO(\ C6H10O)}$ = (5.93±1.13))> ($k_{(C6H14)}$ = (5.86±1,17)). Grabowsky (2010) derived the experimental electron density of ethylene oxide from a multipole refinement of 100 K X-ray data and complemented by density-functional calculations at experimental and optimized geometry. This study found that despite the high strain in the three-membered ring of ethylene oxide, most atomic and bond topological properties do not differ from comparable fragments in unstrained molecules. Grabowsky (2010), concluded that the strained and unsaturated character of the epoxide ring is reflected in the populations of the bonds.
The three-membered ring strain is considered in the SAR estimations for its influence on the reactivity of epoxides. However, this factor itself does not play a dominant role for the rate coefficients of the epoxides. The presence of the epoxy ring would affect the reactivity of epoxides because the CH group attached favours the pi overlap (Fig. 4). For this reason, the factors (F(O), F(3m-ring)) need to be treated specially in SAR and possibly as one single factor F (epoxy ring-β-C_X) since their influence on the beta carbon is very pronounced. Only then, see the contributions of other groups, linear, branched, rings etc. on this basic structure. The reactivity trends observed in our previous and present work Tovar et al. 2021 suggests that the rate constant of the β-channel could be the closest to the k_{total} determining the overall reaction rate. These aspects had not been considered in SAR estimates to date, therefore new factors that includes these complicated bond structures in epoxides need to be developed.

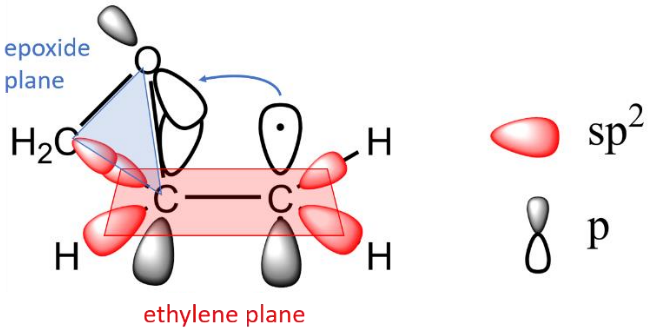


Fig. 4. Involvement of sp^2-type orbitals in the epoxide ring

L409-444: *3.3 Improving SAR estimation for epoxides*

In order to provide a new set of “corrected” factors, especially for F(epoxy ring-β-C_X) that can be used for an improved SAR estimation for epoxides a new set of theoretical calculations with OH radicals are recommended. This kind of

calculations are beyond of the scope of this work. However, a possible approach should conduct to expanding the kinetic database of epoxides (experimental and theoretical) in a wide temperature range. Experiment and theory are highly complementary in this regard, and their combined application allows for alleviation of some of the shortcomings in both approaches; for theoretical work specifically, even a single experimental datum point often allows for the optimization of the PES or energy transfer parameters to allow T, P-extrapolations with strongly enhanced reliability Vereecken et al. (2015).
A recent work by Wang et al. (2022) proposed a concept of experiment-SAR-DFT combined to theoretically discuss the abstraction reaction of a series of alcohols and ketones. Similar approach could be used for epoxides with some considerations.

As has been shown in Tovar et al. (2021) the potential energy surface of chlorine atoms reacting with the series of epoxides possess barrierless reaction. For these cases, Bartolotti et al. (2017) proposed to use the Master Equation Solver for Multi-Energy Reactions (MESMER v.4.0) in order to compute the energy dependent microcanonical rate constants for all forward and reverse reactions on the PES with the option of computing the k(E)s using an inverse Laplace transform (ILT) technique. The k(E)s may be calculated by using Arrhenius parameters from a fit of the temperature dependent high pressure rate coefficients.

A second method could include a semi-empirical method using the Arrhenius parameters in MESMER to fit phenomenological rate constants that are consistent with the experimentally measured rates. Our preliminary exploration of the PES of the series of epoxides towards chlorine atoms Tovar et al. (2021) provide a hint of the complex structural analysis that must be developed in order to assure more accurate rate coefficients and capture the reactivity trends of epoxides by SAR estimation method.

Some studies have evaluated the temperature dependence for 1,2- epoxypropane and 1,2-epoxybutane towards OH radicals. Virmani et al. (2020) found for the reaction with 1,2-propylene oxide a very small (or possibly no) dependence on temperature within the temperature range between 261-355 K. El Othmani et al. (2021b) showed for the reaction with 1,2-epoxybutane a very weak negative temperature dependence at T≤285 K and a transition toward a positive temperature dependence at T≥295K. (El Othmani et al., 2021a) measured a stronger negative temperature dependence in the case of cyclohexene oxide. This behaviour could suggest the existence of van der Waals complexes that can play a role in the reaction mechanisms of epoxides at lower temperatures. More theoretical research is needed to further elucidate these findings.

All the electronic structure calculations will serve as input for the kinetic rate calculations using MESMER o another similar approach.

Even with the clear correlation between the rate coefficients of epoxides with OH radicals and chlorine atoms showed in section 3.1, a detailed structural optimizations and vibrational frequency calculations are also recommended for the reactions of the epoxides towards OH radicals.

R1: 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?

Reply from the authors: We agree that usually the concentrations (mixing ratios in Table 1) should be represented by a value with a range of uncertainties. A statement has been introduced in the text to show how this concentration has been obtained. However, we decided, deliberately, not to provide uncertainties for the concentrations since they are not required for the experimental approach applied in our study. The exact concentrations are not representative for a relative rate kinetic measurement and are not included in any calculations since we follow in our evaluations 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, accordingly, such ratios are considered in the relative rate coefficient determinations.

From Table 1 the highest initial mixing ratios (ppmv) for both reactors are representative for the precursor of OH radicals (i.e. methyl nitrite), which is added to ensure the formation of OH radicals through its photolysis. Usually, methyl nitrite is not completely consumed during the duration of the experiment. Also, we stated (line 144) that a conversion of maximum 50% was achieved through the kinetic reactions for epoxides and reference compounds.

Our previous work on the determination of the kinetic rate coefficients of same group of epoxides with chlorine atoms has been very helpful to handle the different epoxides in the present study.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

Line 120: The concentrations or mixing ratios were measured from the exact amount of the compound added to the chamber. The liquids and gases have been injected into the chamber via a septum using a gas-tight syringe in a flow of air with the reactor being under reduced pressure. The glass-steel inlet system has been heated up to 60^{o}C to ensure the addition of the entire amount of epoxides and reference compounds into the reactor. After addition and filling the chamber to 760±10 Torr pressure of synthetic air, up to 15 infrared spectra (15 min) have been recorded to prove the constant concentration of the compounds in the chamber. These tests have been performed not only to check if there is a diffusion of the injected compounds from the inlet into the chamber but also to evaluate the potential wall deposition of the added compounds in order to correct the rate coefficients for additional loss processes. Any diffusion from the inlet would affect the linearity of the kinetic plots, which otherwise would not have been obtained. The different epoxides and reference compounds employed in the present study did not show a wall loss during the time of the experiment.

Line 160: **Table 1.** Initial mixing ratios used in the 1080 l reactor and 480 l reactor for the epoxide and reference compounds in ppmv (1 ppm = 2.46 x 10^{13} molecule cm^{-3}) at 298 K and 760 Torr of total pressure. The mixing ratios have been estimated from injections of the compounds into the reaction chambers and provide information about the amount of compounds used in this study.

	Initial mixing ratios (ppmv)	
Compounds	*Reactor (1080 L)*	*Reactor (480L)*
Epoxides		
cyclohexene oxide	6	17
1,2-epoxyhexane	6	28
1,2-epoxybutane	6	23
cis-2,3-epoxybutane	3	28
trans-2,3-epoxybutane	3	23
Reference compounds		
Propylene	4	8
Butane	4	-
iso-propyl acetate	1	9
sec-butyl acetate	1	9
Ethylene	4	21
methyl nitrite (OH radical precursor)	8	84

R1: 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 different rates, since the reported rates are within each other's errors.

Reply from the authors:

We did not force the fit through zero since the data plotted in the form of equation ”I” should be with almost "zero" intercept and our intention was to show that there is not a significant deviation from "zero". The linearity of the plots indicates the absence of interferences and secondary reactions, which can affect the ratio of the rate coefficients $k_{Epoxide}/k_{reference}$.

In order to provide an unitary answer regarding the error calculation for all rate constants obtained in the present study, we revised the errors for all measured rate constants. The epoxides rate constants are placed on absolute basis by use of different reference rate constants. Since there are various modes for error calculations for these reference rate coefficients from simple standard deviation to average values from different sources, it is recommended to use a uniform representation of the error. The reviewer is correct and the consideration of "up to 35%" for the reference rate constant does not represent all rate constants. We decided to use a more representative error calculation for the epoxide's rate constants. Accordingly, we have adopted the following procedure and the manuscript has been changed in agreement with new assumptions.

The errors presented in Table 2 for the individual value of the slope $k_{Epoxide}/k_{reference}$.are 2 times the standard deviation of the least-squares fit of the data. The epoxides rate constants are placed on an absolute basis by using different reference rate constants for which we have considered a uniform error of 10%. The final rate constant has been calculated with the expression:

$$k_{average} = \frac{\sum_{i=1}^{n} k_i}{n}$$

while the errors have been calculated using the arithmetic calculation of the error propagation

$$\Delta k_{\text{average}} = \sqrt{\sum\nolimits_{\text{i=1}}^{\text{n}} (\Delta \text{k}_i)^2}$$

where k_i are the individual rate constant obtained using one reference compound and Δk_i and $\Delta k_{average}$ are the associated errors for k_i and $k_{average}$, respectively.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

Line 201 All the rate coefficients obtained in this study, except those for 12EB and CHO, were measured for the first time. The errors presented in Table 2 for the individual value of the slope $k_{Epoxide}/k_{reference}$.represent two times the standard deviation of the least-squares fit of the data. The error of the slope is the most representative for the quality of the data from a relative kinetic study since the reference rate coefficient could be later reconsidered once new studies would be performed. The epoxides rate constants are placed on an absolute basis by using different reference rate constants for which a uniform error of 10% has been considered. The final rate constant has been calculated as an average of the individual rate constant with the error calculated using the arithmetic calculation of the error propagation.

Table 2. Measured rate coefficient ratios, $k_{Epoxide}/k_{Reference.}$, and the rate coefficients for the reactions of OH radical with epoxides at (298±3) K derived from these ratios.

Epoxide	Reference compound	$k_{Epoxide}/k_{Reference.}$	$k_{Epoxide}$ (cm^3 molecule^{-1} s^{-1})
CHO	Propene	0.258±0.009	$(6.28\pm0.66)\times10^{-12}$
	Ethene	0.751±0.038	$(6.40\pm0.72)\times10^{-12}$
	Isobutene	0.099±0.005	$(5.13\pm0.57)\times10^{-12}$
		Average	**$(5.93\pm1.13)\times10^{-12}$**
EHX	Propene	0.259±0.004	$(6.33\pm0.64)\times10^{-12}$
	Ethene	0.612±0.009	$(5.21\pm0.53)\times10^{-12}$
		Average	**$(5.77\pm0.83)\times10^{-12}$**
12EB	*iso*-Propyl acetate	0.406±0.011	$(1.51\pm0.16)\times10^{-12}$
	Ethene	0.286±0.006	$(2.43\pm0.25)\times10^{-12}$
		Average	**$(1.98\pm0.29)\times10^{-12}$**
*t*EB	*sec*-Butyl acetate	0.398±0.009	$(2.25\pm0.23)\times10^{-12}$
	Ethene	0.190±0.007	$(1.62\pm0.17)\times10^{-12}$
	Propene	0.064±0.002	$(1.56\pm0.16)\times10^{-12}$
		Average	**$(1.81\pm0.33)\times10^{-12}$**
*c*EB	*iso*-Propyl acetate	0.518±0.012	$(1.93\pm0.20)\times10^{-12}$
	sec- Butyl acetate	0.142±0.001	$(0.80\pm0.08)\times10^{-12}$
	Butane	0.745±0.022	$(1.77\pm0.18)\times10^{-12}$
		Average	**$(1.50\pm0.28)\times10^{-12}$**

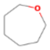
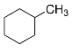
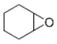
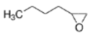
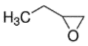
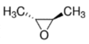
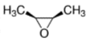
R1: Table 4 (and corresponding discussion): There should be more discussion about what a homologous compound is. Potentially having the structures drawn would help with this. From my perspective, I just see that CHO is C6H10O, methylcyclohexane is C7H14, and din-propyl ether is C6H14O which have different 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.

Reply from the authors:

We agree with the reviewer's suggestions and Table 4 and the corresponding discussions have been changed. Also, we have added the structures drawn to the Table.

Changes in the manuscript/supplementary text:

Changes in the manuscript: Table 4 - Reactivity trends of the epoxy compounds towards OH radicals compared with their homologous alkanes, acyclic ethers and cycloalkanes with the same number of carbon atoms.

	Cyclic ether			Alkane/cycloalkane			Acyclic ether	
Ring size	Structure	$k_{OH}\times10^{12}$ †	C atoms	Compound	$k_{OH}\times10^{12}$ †	C atoms	Compound	$k_{OH}\times10^{12}$ †
7 member	Oxepane 	18.0[1]						
6 member	Oxane 	12.0[1]	7	Methylcyclohexane  heptane	9.26[1] 6.23[1]			
5 member	Oxolane 	17.0[1]	6	2,3-dimethylbutane Hexane	5,86[1] 4.97[1]	6	di-n-propyl ether	20.0[1]
4 member	Oxetane 	10.3[1]	5	2-methylbutane Pentane	3.74[1] 3.76[1]	5	methyl-s-butyl-ether	9.67[1]
3 member	CHO  EHX  12EB  *t*EB  *c*EB  oxirane 	5.93 5.77 1.98 1.81 1.50 0,09	4	Butane	2.38[1]	4	1-metoxypropane	9.91[1]

(*) ×10^{12}units: $cm^3 molecule^{-1} s^{-1}$; [1](McGillen et al., 2020)

R1: Minor Comments: L162: Why are only some reference compounds used for some of the epoxides? Why did you not use all 6 reference compounds?

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 less extent with product spectra resulted from the initiated oxidation of epoxides/reference compound with OH radicals. The comparison should be 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 not very different than that one of the epoxides. Usually, up to three reference compounds are enough to derive an average reaction rate coefficient.

R1: L169: Keep names the same for compounds (e.g. propene vs propylene) throughout the paper.

Reply from the authors:

The manuscript has been corrected accordingly.

R1: 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.

Reply from the authors:

Figure 1 represents the proof for each epoxide that our work has been performed in a proper scientific manner with a good quality of the results. The linearity of the plots does not only show that the methods work adequately but provides information of the missing interferences and secondary reactions for each of the investigated epoxides and selected reference compound. We would prefer to keep Figure 1 in the main manuscript and not to move it to the SI.

R1: L339: A range of (2.0±5.7) ×10^{-12} cm^3 $molecule^{-1}$ s^{-1} does not make physical sense. The way the error is written includes negative rate constants.

Reply from the authors:

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

R1: L344: You mention a theoretical structural analysis but have no basis sets or computational details in the methods for this.

Reply from the authors:

The sentence has been removed from the article. We did not perform theoretical calculations in the present work. However, the discussion section has been reorganised and rewritten following the reviewer's suggestions.

R1: 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

Reply from the authors:

The new 24-hr average concentration of OH, Cl, and peak Cl atom has been assumed and the proper lifetimes have been re-calculated in Table 5

R1: L385: How does the timescale for aerosol partitioning compare to oxidation by OH?

Reply from the authors:

No studies have been reported so far for secondary organic aerosol formation from the OH radical initiated oxidation of the epoxides compounds studied in the present work. However, recent studies show that under determinated ph conditions, most epoxides will have time to react on SOAs (particularly those with tertiary carbon atoms) (Minerath et al 2009). We have discussed the atmospheric implications of epoxides in a large context including the most important isoprene derived epoxides. The manuscript has been modified accordingly.

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.

R1: L400-401: There should not be any new information in the conclusion - potential future work should not be included.

Reply from the authors: The manuscript has been revised accordingly.

R1: Technical Comments: The L in 480L or 1080L should be consistently formatted through the paper (i.e. capitalization, italicization, space after the numbers, etc.)

Reply from the authors: The manuscript has been modified accordingly.

R1: Numbering of equations is inconsistent.

Reply from the authors: The numbering of equations and reactions has been corrected accordingly.

R1: There are subject/verb disagreements, grammar and punctuation errors, and extra spaces and carriage returns that should be checked for.

Reply from the authors: The manuscript has been thoroughly checked for grammar and English errors as well as for technical errors.