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

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Abstract. The kinetics of the gas-phase reactions of hydroxyl radicals with cyclohexene oxide (CHO), 1,2-epoxyhexane (EHX), 1,2-epoxybutane (12EB), *trans*-2,3-epoxybutane (*t*EB) and *cis*-2,3-epoxybutane (*c*EB) have been investigated using the relative rate technique. The experiments have been performed at (298±3) K and (760 ± 10) Torr total pressure of synthetic air using different reference compounds in a 1080 l Quartz Reactor (QUAREC) and a 480 l Duran glass chamber. The following room temperature rate coefficients (cm^3 molecule^{-1} s^{-1}) were obtained: k_1 (OH+CHO) = (5.93±1.78) × 10^{-12}, k_2 (OH+EHX) = (5.77±1.29) × 10^{-12}, k_3 (OH+12EB) = (1.98±0.39) × 10^{-12}, k_4 (OH+cEB) = (1.50±0.26) × 10^{-12}, k_5 (OH+tEB) = (1.81±0.42) × 10^{-12}. With the exception of previous studies for 1,2-epoxybutane and cyclohexene oxide, this is to the best of our knowledge the first kinetic study of the reaction of these compounds with OH radicals. Atmospheric lifetimes, reactivity trends and atmospheric implications are discussed considering the epoxy compound rate coefficients obtained in the present study. In addition to a direct comparison with the literature data where possible, the results from the present study are compared with values estimated from the Structure Activity Relationship method.

1 Introduction

Oxygenated volatile organic compounds (OVOCs) play an important role in atmospheric chemistry and have an impact on climate and human health (Calvert et al., 2011). From those OVOCs emitted from either biogenic or anthropogenic sources, cyclic ethers, with the exception of furans (Villanueva et al., 2009; Li et al., 2018) have received very little attention. Epoxides, as simplest cyclic ethers, are an important and valuable class of raw materials and intermediates for chemical industry. They can polymerize for the production of homo- and copolymers as polyethers, polyols and polycarbonates (Hereijgers et al., 2012). Epoxides are considered a key element in "click-chemistry" (Kolb et al., 2001; Fokin and Wu, 2006). They are also relevant

30 in the field of pharmaceutical applications because of their potential as protease inhibitors against several diseases like cancer, stroke, and parasitic or viral diseases (Powers et al., 2002; Otto and Schirmeister, 1997; Schirmeister and Klockow, 2003). A relatively new utilization of epoxides, which could have huge atmospheric implications and an impact on climate change is their potential use for carbon capture and storage, i.e. the chemical fixation of CO_2 in the form of cyclic carbonates in the presence of various catalysts (Zou and Hu, 2017; Zhang et al., 2020; Guo et al., 2021; Andrea and Kerton, 2021; Appaturi et

35 al., 2021).

Epoxides are known to be formed from the reaction of $O(^3P)$ with isoprene at nearly 80% yield (Atkinson et al., 1994b; Paulson et al., 1992). In the atmospheric ozonolysis of isoprene epoxide yields of about 2-3% have been observed (Atkinson et al., 1994a). A few percent of epoxide formation have been reported from α-pinene ozonolysis as well as from the reaction of 1,2-dimethyl-1-cyclohexane with ozone (Alvarado et al., 1998). Atkinson (Atkinson et al., 1994a) concluded that epoxides

40 formation is a process occurring in the ozonolysis of most terpenes and cycloalkenes. Low yields of isoprene derived epoxides have been observed also from the gas phase nitration of isoprene (Skov et al., 1994).

Furthermore, in indoor pollution studies the formation of epoxides from the heterogeneous oxidation of VOCs with gas phase ozone has been reported (Zhou et al., 2017). Other compounds could also form epoxides during their gas phase chemical degradation by OH radicals and ozone. More recent theoretical and mechanistic studies report epoxide formation during the

45 gas phase ozonolysis of methylbutenol and sabinene via the Criegee degradation mechanism (Calvert et al., 2000; Almatarneh et al., 2019a, b).

Epoxides are responsible for up to 10% of the open ring products from the degradation of aromatic hydrocarbons in the presence of OH radicals according to the MCM model (Master Chemical Mechanism) (Jenkin et al., 2015). In the past, benzene oxide has been reported as an epoxide type product in the reaction of benzene with OH radicals (Klotz et al., 1997, 2000).

50 Besides, a theoretical study has reported epoxide formation in the OH radical initiated oxidation of dimethylphenol isomers (Sandhiya et al., 2013).

Secondary organic aerosols (SOA) constitute a substantial portion of the total ambient aerosol particles, which are mainly originating from biomass burning and atmospheric reactions of volatile organic compounds (VOCs) (Kanakidou et al., 2005). Epoxides can polymerize easily, leading to the growth of SOA (Gao et al., 2004). A recent study shows that the yield of

55 epoxides from the reaction of aromatic compounds with OH radicals is probably dependent on the abundance of NO, HO_2 and RO_2 in the reaction system (Vereecken, 2018). This aspect represents an uncertainty in atmospheric models to reliably estimate the expected SOA formation from reactive epoxide uptake by aerosols (Paulot et al., 2009). The presence of epoxides in SOA are highly probable for conditions prevailing in the atmosphere leading to higher hygroscopicity of particles with potential cloud condensation nuclei activity by conversion to organosulfates through an acid catalysed mechanism (Fuzzi et al., 2015).

60 Isoprene derived epoxides are very important intermediates, which could explain at least in part the composition of ambient SOA both in urban areas (Lin et al., 2013) and remote regions (Jacobs et al., 2013; Stropoli et al., 2019; Paulot et al., 2009; Jacobs et al., 2013; Shrivastava et al., 2019).

The toxicity of ultrafine particles such as SOA is not only related to their atmospheric concentration but also to the nature and chemical properties of both the precursors and the formed SOA components (Jiang et al., 2019). In this sense, epoxides are of

65 great concern because the epoxy functional group can act as an electrophile in its interaction with DNA and nucleosides, producing carcinogenic and mutagenic damages (Ehrenberg and Hussain, 1981).

The kinetic and mechanistic database available on the gas-phase reactions of epoxy compounds with the atmospheric oxidants OH and NO_3 radicals, O_3, and chlorine atoms are very scarce. For the compounds investigated in the present study, there is only one previous relevant study towards chlorine atoms at 298K (Tovar et al., 2021) . Two studies have reported the rate

70 coefficients of the reaction of 1,2-epoxybutane towards OH radicals (Wallington et al., 1988a; El Othmani et al., 2021a) and more recently cyclohexene oxide with OH radicals have been measured as a function of temperature (El Othmani et al., 2021a). In the present study we have performed for the first time a kinetic study of the reaction of OH radicals with 1,2-epoxyhexane, *trans*-2,3-epoxybutane and *cis*-2,3-epoxybutane at 298 K using the relative rate method.

Since several of the rate coefficients for the reactions of epoxides with OH radicals have been measured in the present study

75 for the first time and cannot be compared with literature values accordingly, we have applied different approaches for the estimation of structure-activity relationship (SARs) for the compounds studied in this work.

2 Methods

The experiments were performed in two different environmental chambers, namely a 1080 *l* quartz-glass photoreactor and a 480 *l* Duran glass chamber. These two photoreactors are briefly described below.

80 ### 2.1 480 l reactor

This reaction chamber consists of a cylindrical Duran glass vessel (3m length, 45 cm dia.) closed at both ends by Teflon coated aluminium end flanges. Integrated on the metal flanges are ports for the inlet of reactants into the chamber and for the collection of samples from the reaction mixtures for further analyses. Other accessories, like a mixing fan to ensure homogeneity of the reaction mixtures and a capacitance manometer, are also located on the flanges. Arranged concentrically around the outside of

85 the reactor are 32 super actinic fluorescent lamps (Philips TLA 40 W, $300 \leq \lambda \leq 460$ nm, $\lambda_{max} = 360$ nm. The vacuum (ca. 10^{-3} mbar) is maintained by means of a Leybold turbo-molecular pump, model RUVAC WZ 151 (500 m^3/h), backed by a Leybold double stage rotary fore pump, model D40B (200 m^3/h). A White-type mirror system mounted inside the reactor is set to an overall optical path length of 51.6 m. The analysis of the reactants was done, during the experiments by *in situ* FTIR (Fourier Transform Infrared) long path spectroscopy using a resolution of 1 cm^{-1}. The FTIR spectrometer (Nicolet Magna 520) and the

90 transfer mirror system are covered with a protective box and are permanently purged with dry air to remove water vapour. The spectrometer is directly controlled by the OMNIC software, which is provided by Nicolet.

2.2 1080 l reactor

A detailed description of the reactor can be found in the literature (Barnes et al., 1994). Briefly, the reactor consists of the two quartz glass tubes with an inner diameter of 47 cm and a wall thickness of 5 mm. The reactor has a total length of 6.2 m. Silicone rubber rings are used for all the glass-metal connections as well as for metal-metal connections. The reactor is connected to a turbo molecular pump system by which an end vacuum of 10^{-3} mbar can be achieved. A total of three fans are used for homogeneous mixing of compounds within the reactor. Different types of inlets are mounted on the end flanges for the introduction of chemicals and for pressure measurements.

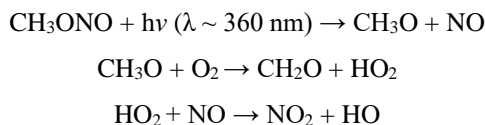
The beam from an FT-IR spectrometer is coupled via a transfer mirror system into the reactor through KBr windows located in one of the end flanges. A White-type mirror system (base path length (5.91 ± 0.01) m), mounted inside the reactor, is used for multiple-reflection of the infrared beam within the reactor before it reaches the detector. Reactants were monitored *in situ* in the reactor in the infrared using 82 traverses of the beam, which is equivalent to a total optical path length of (484.7 ± 0.8) m. All spectra in this work were recorded with a spectral resolution of 1 cm^{-1}. The FT-IR spectrometer NICOLET NEXUS was used, which is equipped with a liquid nitrogen cooled (77 K) mercury-cadmium-tellurium (MCT) detector. A Globar was used as IR light source. All mirrors are gold coated to achieve optimum reflectivity.

Two different types of lamps (32 each) are installed around the reactor. They are mounted alternatively around the reactor to ensure homogeneity of the light intensity within the reactor. The first type, 32 superactinic fluorescent lamps (Philips TL05 40W: 300– 460 nm, max. intensity at ca. 360 nm) and 32 low-pressure mercury vapour lamps (Philips TUV 40W: max. intensity at 254 nm) can be used to irradiate the reaction mixture.

Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 minute and 15-20 such spectra were recorded per experiment.

2.3 Relative Rate Method

The relative rate method was used to determine the rate constant of the OH radical induced oxidation of the epoxy compounds. The photolysis of CH$_3$ONO in the presence of NO was used for the production of OH radicals:

$$CH_3ONO + h\nu\ (\lambda \sim 360\ nm) \rightarrow CH_3O + NO$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$
$$HO_2 + NO \rightarrow NO_2 + HO$$

Reaction mixtures consisting of a reference organic compound, the sample organic reactant and the radical precursor compounds, diluted in synthetic air, were prepared in the reaction chamber and left for mixing prior to photolysis for approximately 15 min. Known amounts of the reagents were flushed into the reaction chamber by a stream of nitrogen or synthetic air and the reactor was then filled with synthetic air to atmospheric pressure.

Typical photolysis times ranged from 15 to 20 min. In the presence of the OH radical the corresponding epoxide and reference compound are consumed by the following reactions:

$$OH + Epoxides \quad \rightarrow \quad Products \qquad (k_{Epoxide}) \ (1)$$
$$OH + Reference \quad \rightarrow \quad Products \qquad (k_{Reference}) \ (2)$$

Provided that the reference compound and the epoxide are lost only by reactions (1) and (2), then it can be shown that:

$$ln\left\{\frac{[Epoxide]_0}{[Epoxide]_t}\right\} = \frac{k_{Epoxide}}{k_{Reference}} ln\left\{\frac{[Reference]_0}{[Reference]_t}\right\} \ (I),$$

where, $[Epoxide]_0$, $[Reference]_0$, $[Epoxide]_t$ and $[Reference]_t$ are the concentrations of the corresponding epoxy compound and reference compound at times $t=0$ and t, respectively and $k_{Epoxide}$ and $k_{Reference.}$ are the rate coefficients of reactions (1) and (2), respectively.

In order to test for a possible loss of the reactants through photolysis, mixtures of the reactants in air in the absence of methyl nitrite were irradiated for 30 min and photolysis were found to be negligible for both the epoxide and the reference compounds. Additionally, various tests were performed to assess possible loss of the reactants via deposition on the chamber walls, and no significant wall loss of the epoxy compounds and references was observed leaving the compounds in the dark in the reactor.

A minimum of two experiments for each epoxide compound has been performed in this study and up to three references compounds have been used. Reference compounds have been chosen based on similar reactivity as epoxides and suitability for FTIR subtraction procedures. Conversion of epoxides and reference compounds through the reaction with OH radical has been achieved up to 50%. Initial mixing ratios used in the 1080 l reactor for the epoxides and reference compounds have been as follow (in ppmv with 1 ppmv = 2.46 x 10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure of synthetic air): epoxides between 3-6 ppmv and reference compounds between 1 and 4 ppmv as shown in Table 1. Concentrations used for the reactions performed in 480 l reactor have been up to 8 times higher. Around 8 ppmv CH$_3$ONO has been added in 1080 l reactor and up to 10 times more in 480 l reactor.

All epoxy and reference compounds used in this study were obtained from Sigma Aldrich and used without further purification. The stated purities were as follows: cyclohexene oxide, 98%; 1,2-epoxyhexane, 97%; 1,2-epoxybutane, 99%; *trans*-2,3-epoxybutane,97%; for *cis*-2,3-epoxybutane, 97%; propylene, 99%; butane, 99%; *iso*-propyl acetate, 99.6%; *sec*-butyl acetate, 99%; ethylene, 99.5% and 99.985% for synthetic air, respectively, which was from Messer.

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.

Initial mixing ratios (ppmv)	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	8	84

3 Results and Discussion

The experimental data from the kinetic experiments are plotted according to equation (I). Figure 1 shows the results obtained for the rate coefficient determinations from the OH radical initiated oxidation of: cyclohexene oxide using ethylene, propylene and isobutene as reference compounds; 1,2-epoxyhexane using ethylene and propylene as reference compounds; 1,2-epoxybutane using ethylene and iso-propyl acetate as reference compounds; trans-2,3-epoxybutane using sec-butyl acetate, ethylene and propylene as reference compounds, and cis-2,3-epoxybutane using sec-butyl acetate, iso-propyl acetate and butane as reference compounds. All plots showed very good linearity despite the difficulties from handling the epoxides and subtracting the IR spectra.

The rate coefficients $k_{Epoxide}$ given in Table 2 were put on an absolute basis using the following values for the reactions of the reference compounds (cm^3 molecule^{-1} s^{-1}): k(OH+propene): $(2.44\pm0.37) \times 10^{-11}$ (IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, 2021), k(OH+ethylene): $(8.52\pm0.13) \times 10^{-12}$ (Calvert et al., 2015), k(OH+isobutene): $(5.10\pm1.33) \times 10^{-11}$ (IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, 2021), k(OH+*iso*-propyl acetate): $(3.72\pm0.29) \times 10^{-12}$ (Wallington et al., 1988c), k(OH+*sec*-butyl acetate): $(5.65\pm0.59) \times 10^{-12}$ (Wallington et al., 1988c), k (OH+ butane): $(2.38\pm0.24) \times 10^{-12}$ (McGillen et al., 2020).

The rate coefficients obtained by using two simulation chambers are in perfect agreement as shown in Figure 2, which is a comparison of the data for EHX using propylene as reference compounds. The similar linearity has been observed for other

compounds in both reactors. Accordingly, the data have been plotted together for all the epoxides regardless the reactor where the experiment has been performed.

The rate coefficient ratios $k_{Epoxide}/k_{Reference}$ obtained from linear regression analyses of these plots are summarized in Table 2. The rate coefficients are averages from the experiments with each reference compound from the experiments performed in both reactors (cm^3 molecule^{-1} s^{-1}): k_1(OH+CHO) = (5.93±1.78) × 10^{-12}, k_2(OH+EHX) = (5.77±1.29) × 10^{-12}, k_3(OH+12EB) = (1.98±0.39) × 10^{-12}, k_4(OH+cEB) = (1.50±0.26) × 10^{-12}, k_5(OH+tEB) = (1.81±0.42) × 10^{-12}.

Since all rate coefficients obtained in this study, except those for 12EB and CHO, were measured for the first time; the errors quoted for the rate coefficients include the 2σ statistical error from the linear regression analyses for $k_{Epoxide}/k_{Reference}$ ratios and up to 35% contribution in the recommended values of the rate coefficients for reference compounds with OH radicals. The ratios $k_{Epoxide}/k_{Reference}$ given in Table 2 could be used for future re-evaluation of the corresponding epoxides rate coefficients if the reference compounds rate coefficients would change.

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	Propylene	0.258±0.009	(6.28±1.04)×10^{-12}
	Ethylene	0.751±0.038	(6.40±1.02)×10^{-12}
	Isobutene	0.099±0.005	(5.13±1.03)×10^{-12}
	Average		**(5.93±1.78)×10^{-12}**
EHX	Propylene	0.259±0.004	(6.33±1.02)×10^{-12}
	Ethylene	0.612±0.009	(5.21±0.78)×10^{-12}
	Average		**(5.77±1.29)×10^{-12}**
12EB	iso-Propyl acetate	0.406±0.011	(1.51±0.24)×10^{-12}
	Ethylene	0.286±0.006	(2.43±0.37)×10^{-12}
	Average		**(1.98±0.39)×10^{-12}**
tEB	sec-Butyl acetate	0.398±0.009	(2.25±0.24)×10^{-12}
	Ethylene	0.190±0.007	(1.62±0.25)×10^{-12}
	Propylene	0.064±0.002	(1.56±0.24)×10^{-12}
	Average		**(1.81±0.42)×10^{-12}**
cEB	iso-Propyl acetate	0.518±0.012	(1.93±0.16)×10^{-12}
	sec- Butyl acetate	0.142±0.001	(0.80±0.08)×10^{-12}
	Butane	0.745±0.022	(1.77±0.19)×10^{-12}
	Average		**(1.50±0.26)×10^{-12}**

190

To date, the rate coefficients of hundreds of new compounds have been studied under laboratory conditions with different atmospheric oxidants. However, there are still many compounds for which the database is still very scarce, as for cyclic ethers. There are several methodologies to estimate the rate coefficients towards OH radicals. One of them is quantum theoretical calculations useful for reactions, which are very difficult to study directly in the laboratory. Another approach is the Structure-

195   Activity Relationship (SAR) method, which rely solely on the structure of the organic compounds and the effect of this structure on the reactivity. Both methodologies are critical to predict the chemical reactivity and physical behaviour of compounds where direct data are not available. The SAR estimation method applied for the epoxide type compounds studied in the present work treats the rate of abstraction from a group within an epoxide molecule. In the case of H atom abstraction from C-H bonds, the calculation of the overall H atom abstraction rate constants is based upon the estimation of $-CH_3$, $-CH_2-$,

200   $>CH-$, group rate constants.

The $-CH_3$, $-CH_2-$, and $>CH-$ group rate constants depend on the substituents around those groups.

For example, in the case of an α position: $k(CH_3-X) = k_{prim} F(X)$; $k(X-CH_2-Y) = k_{sec} F(X) F(Y)$; and $k(X-CH(Y) (Z)) = k_{tert}$ $F(X) F(Y) F(Z)$. Where k_{prim}, k_{sec} and k_{tert} are the rate constants per $-CH_3$, $-CH_2-$, and $>CH-$ group for a "standard" substituent, X, *Y,* and Z are the substituent groups; and *F(X), F(Y),* and *F(Z)* are the corresponding substituent factors (Atkinson, 1987,

205   1986a, b). The validity and usefulness of a SAR depends on many factors, such as the amount and type of input data, reliability of prediction, scope of applicability, and ease of implementation (Vereecken et al., 2018).

The rate constants of the reactions with OH radicals obtained in this work were used to derive reactivity trends towards the OH radical. Also, five different approaches have been used in the SAR estimations in order to evaluate the most suitable method to predict the reactivity of this series of epoxides towards OH radicals. The results obtained are described in more

210   detail below.

For isomers it has been observed that within the experimental error limits, the rate coefficients for the reaction of *trans*-2,3-epoxy butane with OH radicals are slightly different than that for *cis*-2,3-epoxybutane. Table 3 shows the result of the SAR calculations for the epoxide reactions by using different factors from the literature for the total rate constant estimation. Method (a) Kwok and Atkinson (1995) used the substituent factor F(-OR)=6 to describe the effect of one or two α-ether linkages, with

215   the influence of a β-ether linkage. Method (b) Calvert (2011) also took into consideration the influence of a β-ether linkage and a factor F(-OR)=4.13. Method (c) Calvert (2015) is similar to method (a) and (b) but assuming a factor F(-OR)=8.4. Comparing these approaches with the experimental results, for 1,2-epoxybutane the estimated value using the method (a) Kwok and Atkinson (1995) is the closest to the experimental value. However, it is not the case for cis / trans isomers where a small deviation is observed.

220   The SAR estimation using (e) Jenkin (2018) propose an improved new set of three rate coefficients for H atom abstraction for C atoms adjacent to ether linkages. These new sets of the rate coefficients are applied independently of neighbouring group substituent factors. Our experimental results show that the rate coefficient of 1, 2-epoxybutane is lower than the rate coefficient calculated with this approach. The rate coefficient calculated for cyclohexene oxide with this approach is the lowest with respect to all experimental values and by other SAR estimation methods.

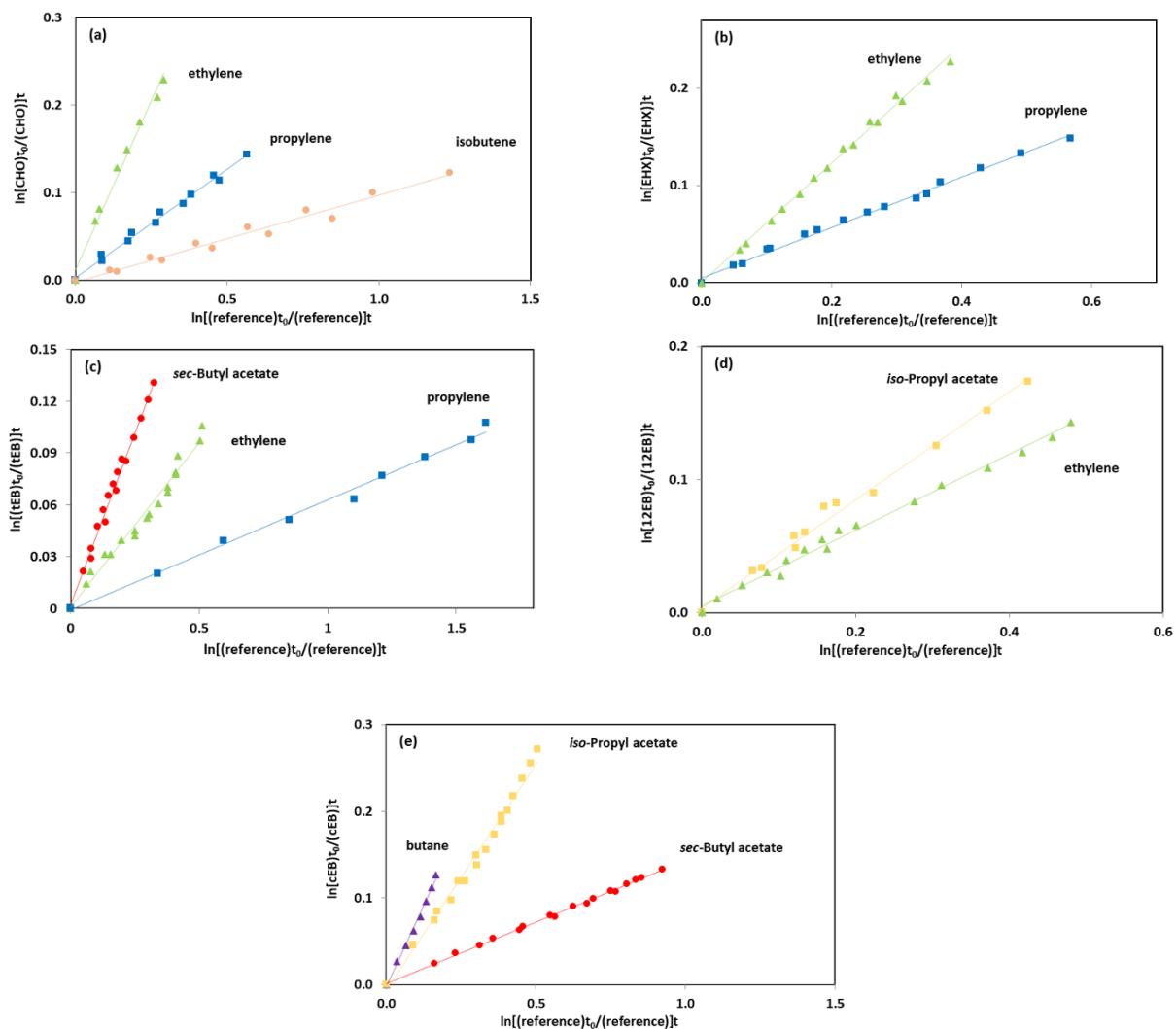
225   The influence of the ether group seems not be the same for epoxides of the same number of carbon atoms with differences in the symmetry. Factors like geometrical disposition and neighbour groups could explain the H atom abstraction in places far from the ether linkage.

230

Figure 1. Kinetic data for the reaction of OH radicals with (a) CHO; (b) EHX; (c) *t*EB; (d) 12EB; (e) *c*EB using ethylene, butane, *sec*-butyl acetate, *iso*-propyl acetate and propylene as reference compounds.

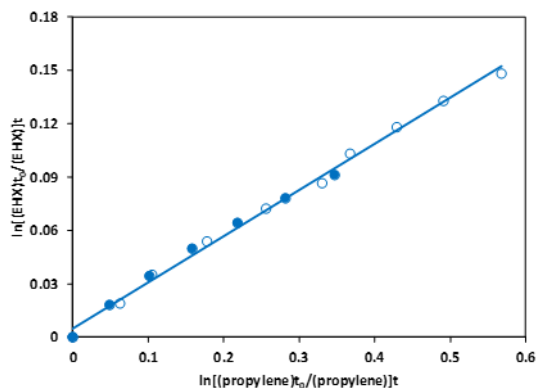



Figure 2. Kinetic data for the reaction of OH radicals with EHX using propylene as reference compound performed in 480 l reactor (●) and
1080 l reactor (○).

In less substituted epoxides, such as propylene oxide the approaches presented by Kwok and Atkinson (1995), Calvert (2011),
and Calvert (2015) are the closest to the experimental values determined in this work.

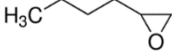
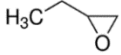
The SAR estimation (d) Middala (2011) proposed a corrected factor for ring strain, assuming that the effect of the presence of
oxygen on the ring might have been underestimated. However, as shown in Table 3, the experimental data obtained in this
work differ in most of the cases from the values predicted by SAR using this approach.

There are discrepancies between the values calculated by different approaches of the SAR estimation method, as is shown in
Table 3. In addition, there is no SAR estimation method that consistently generates a value close to the experimental value for
all compounds, which have been studied in the present work. These discrepancies had already been observed since the first
SAR approximations for cyclic ethers and they could be attributed to the limited database that still exists for this kind of
compounds (Kwok and Atkinson, 1995; Jenkin et al., 2018). In general, all these approaches have been developed to fit the
behaviour of cyclic alkanes, with one factor being attributed to ring strain and the presence of an ether group.

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.

Epoxide	k_{SAR}	$k_{Epoxide}$ (cm^3 molecule^{-1} s^{-1})	Reference
Cyclohexene Oxide	$6.37\times10^{-12(a)}$	$(5.93\pm1.78)\times10^{-12}$	This work
	$6.14\times10^{-12(b)}$	$(6.51\pm0.65)\times10^{-12}$	(El Othmani et al., 2021a)
	$6.31\times10^{-12(c)}$		
	$5.81\times10^{-12(d)}$		
	$3.60\times10^{-12(e)}$		
Ethylene Oxide	$2.80\times10^{-13(a)}$	$(0.88\pm0.25)\times10^{-13}$	(Calvert et al., 2011)
	$1.89\times10^{-13(b)}$		
	$3.54\times10^{-13(c)}$		
	$0.77\times10^{-13(d)}$		
	$3.09\times10^{-13(e)}$		
Propylene Oxide	$0.59\times10^{-12(a)}$	$(0.49\pm0.52)\times10^{-12}$	(Wallington et al., 1988b)
	$0.46\times10^{-12(b)}$	$(0.30\pm1.00)\times10^{-12}$	(Middala et al., 2011)
	$0.67\times10^{-12(c)}$	$(0.47\pm0.24)\times10^{-12}$	(Virmani et al., 2020)
	$0.28\times10^{-12(d)}$		
	$1.16\times10^{-12(e)}$		
1,2-epoxyhexane	$4.64\times10^{-12(a)}$	$(5.77\pm1.29)\times10^{-12}$	This work
	$4.48\times10^{-12(b)}$		
	$4.15\times10^{-12(c)}$		
	$3.97\times10^{-12(d)}$		
	$6.60\times10^{-12(e)}$		
1,2-epoxybutane	$1.81\times10^{-12(a)}$	$(1.98\pm0.39)\times10^{-12}$	This work
	$1.65\times10^{-12(b)}$	$(1.90\pm0.67)\times10^{-12}$	(Wallington et al., 1988a)
	$1.83\times10^{-12(c)}$	$(2.20\pm0.02)\times10^{-12}$	(El Othmani et al., 2021b)
	$1.45\times10^{-12(d)}$		
	$3.69\times10^{-12(e)}$		
trans-2,3-epoxybutane	$0.92\times10^{-12(a)}$	$(1.81\pm0.42)\times10^{-12}$	This work
	$0.73\times10^{-12(b)}$		
	$0.99\times10^{-12(c)}$		
	$0.49\times10^{-12(d)}$		
	$1.61\times10^{-12(e)}$		
cis-2,3-epoxybutane	$0.92\times10^{-12(a)}$	$(1.50\pm0.26)\times10^{-12}$	This work
	$0.73\times10^{-12(b)}$		
	$0.99\times10^{-12(c)}$		
	$0.49\times10^{-12(d)}$		
	$1.61\times10^{-12(e)}$		

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).

Table 4. Reactivity trends of epoxy compounds towards OH radicals compared with their homologous alkanes, cycloalkanes and ethers.

Epoxide	$k_{OH}\times10^{12}$ †	Alkane/cycloalkane	$k_{OH}\times10^{12}$ †	Cyclic ethers	$k_{OH}\times10^{12}$ †	Acyclic ethers	$k_{OH}\times10^{12}$ †
CHO	5.93	methylcyclohexane	9.26[1]	oxane	12.0[2]	di-*n*-propyl ether	20.0[2]
						di-isopropyl ether	10.0[2]
				oxolane	17.0[2]		
EHX	5.77	heptane	6.23[1]				
				oxetane	10.3[2]		
12EB	1.98						
		2-methylbutane	3.74[2]				
*t*EB	1.81	pentane	3.76[1]			diethylether	12.7[1]
		2,3-dimethylbutane	5,86[1]				
*c*EB	1.50						

† units: cm³molecule⁻¹s⁻¹
[1](McGillen et al., 2020); [2](Calvert et al., 2015) (Recomended values of the most recent revision of database for the kinetics of the gas-phase atmospheric reactions of organic compounds).

From Table 4 we can assess the influence of the ring size. In this way, epoxides are less reactive than their counterparts with larger rings. (Tamres et al., 1954) stated that the electron ability in hydrogen bonding can act as a measure of the relative electron density. 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) is 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

305 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 sp³like 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 (Tovar et al.,

310 2021). 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).

315 We can also evaluate the influence of the ring strain over the epoxides examined in the present study. As it is shown in Table 4, epoxides are less reactive towards OH radicals than the analogous alkanes. Besides, the rate coefficients for cycloalkanes are higher than for cyclohexene oxide. 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

320 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. As we discussed in Tovar et al. (2021), for the series of epoxides in the gas phase, the pseudo ethylenic character in the epoxy ring could explain the reactivity favouring the abstraction of H in β position. The aforementioned factors can provide a possible explanation about the bad correlation between the different SAR estimations. The presented SAR estimations assume a factor for ether and

325 another for ring strain. However, for a more accurate evaluation of the reactivity of epoxides, the structural properties and the unsaturated character of the ring should be considered. This could only be properly evaluated by means of theoretical calculations.

When comparing the reactivity of the 1,2-epoxyhexane with its corresponding aliphatic alkane, the presence of a 3-membered ring and oxygen in the molecule affect in a more subtle way the reactivity towards OH radicals. Moreover, when epoxides of

330 four carbon atoms are compared with their corresponding aliphatic alkane, the presence of a 3-membered ring decreases the reactivity independently of the position of the substituents in the aliphatic chain. This can be seen by comparing the behaviour between *cis/trans* epoxy butane and 1,2-epoxy butane.

Finally, from Table 3 it can be observed that the consecutive addition of a CH_2 group into the aliphatic chain increases the reactivity of the epoxides toward OH radicals.

335 This effect is summarised in Figure 3 where the rate constants for the reactions of the OH radical with the studied epoxides have been plotted as a function of the number of carbon atoms. Since SAR estimations do not match very well the experimental

rate coefficients, the reactivity trends for the series of these compounds could add valuable information regarding the reactivity of epoxides. From Figure 3 it can be estimated that the rate coefficients for the reaction of epoxy pentanes with OH radicals should be in the range of $(2.0\pm5.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

340   The comparison of the rate coefficients for the reaction of chlorine atoms with epoxides Tovar et al. (2021) with those obtained in this study for the reaction with OH radicals would show similar reactivity trends. A ratio of 1:3 between the rate coefficients for the reaction with OH radicals of C4-epoxides (EHX, *t*EB and *c*EB) and C6-epoxides (CHO and EHX) has been observed. This ratio has been also found by Tovar et al.(2021) for the epoxides series in the reaction with chlorine atoms. In this study, an experimental and theoretical structural analysis has been proposed considering the geometry of the molecule, in order to

345   explain the reactivity of a series of epoxides.

   Systematic theoretical data compilations could constitute a valuable tool in the development, evaluation, and validation of the SARs and kinetics models (Vereecken et al., 2018). As is shown in present work, although epoxides are rather simple structurally, there are still several discrepancies using different SARs estimation approaches for these species.

   To improve the accuracy of SARs predictions, temperature-dependent data is also important, with special attention to the

350   effects of functional groups (Vereecken et al., 2018). 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

355   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.

Figure 3. Trends of the rate coefficients for the reaction of OH radicals with epoxides: effect of CH$_2$ addition to the aliphatic chain.

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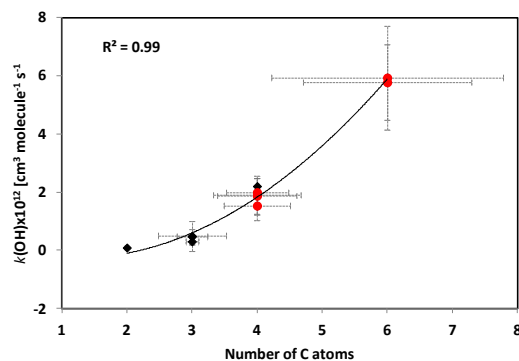
4 Atmospheric implications

Using the kinetic data obtained in the present work, in combination with daytime average radical concentrations, the estimation of the tropospheric lifetimes of the investigated compounds can be calculated using the expression:

$$\tau_{OH/Cl} = 1/k_{OH/Cl}[OH/Cl]$$

365   Therefore, for a globally averaged [OH] of 1×10^6 radicals cm^{-3} (Prinn et al., 1995), the atmospheric lifetimes for cyclohexene oxide, 1,2-epoxyhexane, 1,2-epoxybutane, *trans*-2,3-epoxybutane and *cis*-2,3-epoxybutane are estimated between 2 to 8 days, as shown in Table 5.

According to the rate coefficients presented in Tovar et al. (2021) and considering an estimated atmospheric concentration [Cl] of 3×10^3 atoms cm^{-3} (Singh et al., 1996; Rudolph et al., 1996; Wingenter et al., 1996), an atmospheric lifetime between 16 and

370   56 days has been calculated for the epoxides. Accordingly, the reaction with OH radicals is the primary sink for epoxides in the atmosphere under these conditions.

However, in highly polluted areas or coastal locations where [Cl] can be up to 5×10^4 atoms cm^{-3} (Hossaini et al., 2016; Spicer et al., 1998), Cl chemistry could contribute significantly to the removal of epoxides.

375   **Table 5.** Comparison of the atmospheric lifetimes of epoxides towards OH radicals and chlorine atoms.

Epoxides	τ_{OH} (days)	τ_{Cl} (days)
cyclohexene oxide	1.9	16.1*
1,2-epoxyhexane	2.0	21.8*
1,2- epoxybutane	5.8	45.8*
trans-2,3-epoxybutane	6.4	55.2*
cis-2,3-epoxybutane	7.7	55.8*

* Calculated values using the rate coefficients of epoxides towards Cl atoms (**Tovar et al., 2021**).

With the reported lifetimes, the epoxides studied in the present work will contribute mainly to local air pollution. In laboratory

380   and ambient SOA, epoxides are considered as potential precursors for sulphate esters, polyols, hydroxy nitrates and halides. Aerosol epoxide concentrations will be limited by the rates of the corresponding uptake process from the gas phase, which will be largely determined by the gas phase epoxide concentrations (Minerath and Elrod, 2009; Minerath et al., 2009). A study by (Lal et al., 2012) suggests that the 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

385   epoxides. Besides, in urban environments particle acidity can be significantly high, with a 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 SOA particles and to the possible modification of their physical and chemical properties (Zhang et al., 2007). Monitoring and evaluating the emissions of these compounds under different ambient conditions, as pH and different regimens of NO_x, is recommended in rural and urban locations.

390   **Conclusions**

The rate coefficients for the reaction of OH radicals with three different epoxides have been determined for the first time in this study. The rate coefficient for 1,2-epoxy butane and cyclohexene oxide are in very good agreement with previous studies (Wallington et al., 1988a; El Othmani et al., 2021b, a). A comparison of the reactivity trends from the gas-phase reaction of the epoxides obtained in this study showed a very good correlation with the reactivity trends of epoxides with chlorine atoms.

395   Differences have been observed between the experimental OH rate coefficients and those obtained from SAR estimations. However, the values determined by the SAR method show some discrepancies dependent on the substituent factors, which were considered for the calculations. Such discrepancies could be explained by taking into consideration the structural effect of the ring acting in conjunction with the oxygen atom and the unsaturated character of the epoxy ring. From the atmospheric chemistry viewpoint, the rate coefficient from the present study would help to extend the database for the reaction of cyclic

400   ethers under atmospheric conditions. Parallel to the present work, product studies of the reactions presented here have been undertaken, to delve a little deeper into the reaction mechanisms of these reactions.

Data availability.   Data can be provided upon request to the corresponding author Carmen Maria Tovar carmen.tovar_ramos@uni-wuppertal.de

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Author contributions. CMT conducted the experiments and processed the data. CMT performed the data analysis. IB, IGB, and PW made revisions at different stages of the study. CMT prepared the paper with contributions from all co-authors.

Competing interests. The contact author has declared that neither they nor their co-authors have any competing interests.

410

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640