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Gas-phase rate coefficient of OH + cyclohexene oxide measured from 251–373 K

Author list:

Hajar El Othmani,[1,2] Yangang Ren,[1] Abdelwahid Mellouki,[1] Véronique Daële,[1] Max R. McGillen[1]*

[1] Institut de Combustion Aérothermique Réactivité et Environnement/OSUC−CNRS, 45071 Orléans, Cedex 2, France

[2] Faculty of Science, Mohammed V University in Rabat, 10100 Rabat, Morocco

* corresponding author, email: max.mcgillen@cnrs-orleans.fr

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Abstract:

Absolute measurements of the rate coefficient of the title reaction are reported from 251–373 K using the laser-induced fluorescence–pulsed-laser photolysis technique, together with room-temperature relative rate determinations using a simulation chamber. These are the first reported values of this rate coefficient, which demonstrates a predominantly negative temperature dependence that is more pronounced than with other epoxides, suggesting that pre-reactive complexes contribute to the overall reactivity, and that these complexes are comparatively stable for OH + cyclohexene oxide, which may result from its bicyclic structure. This work provides new insights into the lesser-studied reactivity of the epoxide functionality.

Keywords: epoxide, oxirane, hydroxyl, atmospheric chemistry, kinetics, rate constant

1. Introduction

There are many sources of epoxides in Earth's atmosphere, both natural and anthropogenic. Epoxides can be formed in the troposphere, mainly through the oxidation of alkenes. Some epoxides are generated directly, from the reactions of alkenes with O_3 [1], NO_3 [2] and $O(^3P)$ [3]. Whereas others can arise from the ring closure reactions of secondary radical species formed from alkenes, such as the atmospherically important isoprene epoxydiols [4].

Epoxides may also be emitted directly to the atmosphere from floral scents [5], as well as emissions being inferred from their various industrial applications [6].

Given the large global emission of olefinic precursor molecules, and the variety of these unsaturated species, it is logical to expect that a large and diverse flux of epoxides enters the atmosphere each year, and that knowledge of the atmospheric chemistry of epoxides is required to understanding the total life-cycle of an alkene emission. Another potential source of epoxides comes from the low-temperature combustion of hydrocarbons, which is known to generate a variety of oxirane species [7].

Once they are released or formed in the troposphere, epoxides are expected to react with radical species in the gas phase to form more oxidized species, or engage in acid-catalyzed ring-opening reactions in the heterogeneous phase, forming low-volatility polyols [8]. The competition between these processes will be defined by their respective reaction rates. At the time of writing very few kinetic measurements are available for the oxidation of reactions of epoxides with atmospheric oxidants such as OH or Cl [9], which limits our understanding of the overall environmental fate of compounds possessing the epoxide functionality.

In this study, we report the rate coefficient of the following reaction over the temperature range 251–373 K:

$$\text{OH + cyclohexene oxide} \rightarrow \text{products} \qquad (1)$$

Cyclohexene oxide (1,2-epoxycyclohexane) is larger than those epoxides studied previously [10–13], and, by virtue of the fact that it contains more C–H bonds than other epoxides found in the kinetic database [9], is expected to react comparatively rapidly with OH and be lost primarily through Reaction (1) under atmospheric conditions. The bicyclic structure of cyclohexene oxide also contrasts with previously studied epoxides, and may influence its reaction with OH. We will therefore discuss the reactivity of this molecule within the context of other epoxides that have been studied so far.

2. Experimental methods

Two complementary methods were used in this work to determine the kinetics of Reaction (1). First, an absolute measurement, employing the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF) technique to measure the rate coefficient as a function of temperature. Second, a relative rate chamber method was used to measure the rate coefficient

at room temperature. The details of these measurements are described in the following subsections.

2.1 Absolute measurements using the PLP–LIF

The PLP–LIF apparatus used in this work has been used in several previous studies, and will be described only briefly here, for more details, please see these earlier publications [14,15]. The LIF reactor is a jacketed 200 cm^3 Pyrex cell, with 4 quartz windows orthogonal to each other. Heated/ cooled thermal transfer fluid (water or ethanol) was circulated through the outer jacket in order to control the temperature of the gases inside the cell between 251 and 373 K. Bath gas (He) pressures of ~100 Torr were used in all measurements, and were performed under pseudo-first-order conditions such that [cyclohexene oxide] >> [OH]. OH radicals were generated from the photolysis of precursor molecules using a 248 nm excimer laser operated at 10 Hz. To check for possible secondary interferences on OH decay profiles, two OH precursors were used, H_2O_2 and HNO_3, which form OH through the following reactions:

$$H_2O_2 + h\nu \rightarrow 2OH \quad (2)$$

$$HNO_3 + h\nu \rightarrow OH + NO_2 \quad (3)$$

Both of these precursors were introduced by sweeping over the headspace/ bubbling of liquid samples with carrier gas (He). Given that both of these precursors have poor transmission through mass flow controllers (MFCs), the flow of these precursors was controlled upstream of the sample using an MFC. This leads to an uncertainty in the exact OH precursor concentration, which we estimate instead, similar to previous work [16], using the following equation:

$$[\text{OH precursor}] = k_d/k(T)_{OH}$$

where k_d represents the decay of OH in the absence of the cyclohexene oxide co-reactant, and $k(T)_{OH}$ is the temperature-dependent reaction rate of OH with the OH precursor molecule in question.

OH radicals were probed at 10 Hz using a frequency-doubled Nd:YAG pumped dye laser tuned to the $A^2\Sigma^+$ (v = 1) ← $X^2\Pi$ (v = 0) transition near 282 nm. The resultant 308 nm fluorescence was detected with a photomultiplier tube equipped with a bandpass filter centered around 310 nm.

OH temporal decays were generated by varying the delay time between the photolysis and probe pulses, thus changing the reaction time between OH and cyclohexene oxide. These

decays were found to abide by pseudo-first-order kinetics in each case, as described in the following equation:

$$\ln\left(\frac{[\mathrm{OH}]_t}{[\mathrm{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k[\text{cyclohexene oxide}] + k_d)t = -k't$$

where the concentrations of OH, [OH], are proportional to fluorescence signal, S, at times 0 and t, respectively; and k' and k_d are first-order decay rates in the presence of and absence of co-reactant cyclohexene oxide. k_d represents the decay of OH as a consequence of reactions with OH precursors and diffusion out of the reaction volume, and was found to be exponential over typical reaction times of 10,000 μs, and ranged from ~70–500 s^{-1} in our experiments. k' ranged from ~3000–50,000 s^{-1}, and was likewise found to be exponential under the experimental conditions of this study. Rate coefficients, k, were determined from a weighted linear least-squares fit to k' against [cyclohexene oxide].

To minimize experiment errors associated with co-reactant concentration, [cyclohexene oxide] was monitored on-line using a multipass FTIR spectrometer, that was positioned directly downstream of the LIF reactor. To be quantitative, the integrated band intensity was determined as part of this work, and the band located between 2800 and 3100 cm^{-1} with an integrated band intensity of 3.66×10^{-17} cm $molecule^{-1}$ was used in our analyses (see Figures S1 and S2 for further details).

2.2 Relative measurements using a chamber apparatus

To complement the absolute measurements, a simulation chamber was used as an independent determination of the rate coefficient of Reaction (1). This system consists of a large PTFE Teflon chamber equipped with *in situ* multipass FTIR and high-resolution time-of-flight proton-transfer reaction mass spectrometry (PTR-ToF-MS) measurements. This apparatus has been employed recently to measure the reaction rates of compounds of low volatility [17], and is therefore considered to be a good additional test of kinetic determinations for potentially surface-active chemicals such as an epoxide, that may be affected by the higher surface area:volume ratios – as well as higher reactant and OH precursor concentrations – encountered in the LIF reactor and its accompanying FTIR cell.

Measurements were conducted at 295±2 K, in an atmosphere of purified air in a 7.3 m^3 cuboidal chamber constructed of Teflon foil, described in detail elsewhere [18]. OH radicals were generated from methylnitrite, photolyzed at 365 nm using 24 × UV-A T-40 L Viber-Lourmat lamps in the following sequence of reactions:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (4)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (5)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (6)$$

A relative method was employed to determine the rate coefficient, by measuring the decay rate of [cyclohexene oxide] relative to that of a reference compound (1-propanol) with a known OH rate coefficient, $k_{\text{reference}}$. Comparison of these decays, taking into account dilution rate and wall-losses, k_d, yields the rate coefficient, k, through the following equation:

$$\ln\left(\frac{[\text{cyclohexene oxide}]_0}{[\text{cyclohexene oxide}]_t}\right) - k_d t = \frac{k_{\text{cyclohexene oxide}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) - k_d t$$

2.3 Materials

Cyclohexene oxide (>98%, Aldrich) was passed through several freeze-pump-thaw cycles prior to use. Helium carrier gas (Alphagaz 2, Air Liquide, 99.999%) was used as supplied in the PLP-LIF experiments. H_2O_2 (50 wt%, Alrich) was purified over the course of weeks with a slow flow of purified air. Gas-phase HNO_3 was taken from the headspace of a sample of 70% redistilled HNO_3, dehydrated by the dropwise addition of pure H_2SO_4 in a HNO_3:H_2SO_4 ratio of 1:2 by volume, and maintained at 0°C in an ice bath. Methylnitrite was synthesized by dropwise addition of 50% H_2SO_4 in water into a stirred saturated solution of $NaNO_2$ in methanol, maintained at 0°C, the gaseous methylnitrite was then carried through a water bubbler and a u-tube containing P_2O_5 using a slow flow of nitrogen, and cold trapped at -196°C. 1- propanol (>99%, Aldrich) was used as supplied.

3. Results and discussion

Absolute measurements of the rate coefficient of Reaction (1) were measured using the PLP–LIF apparatus between 251 and 373 K in 100 Torr (He). Second-order plots of k' against [cyclohexene oxide] were of good quality in each case, with 2σ statistical errors between 2 and 7%. An example of one of these plots is shown in Figure 1, and a summary of rate coefficient measurements together with experimental conditions is provided in Table S1. Total combined estimated uncertainties including cyclohexene oxide concentration (5%), pressure (2%) and temperature (2%) varied from 7–15%.

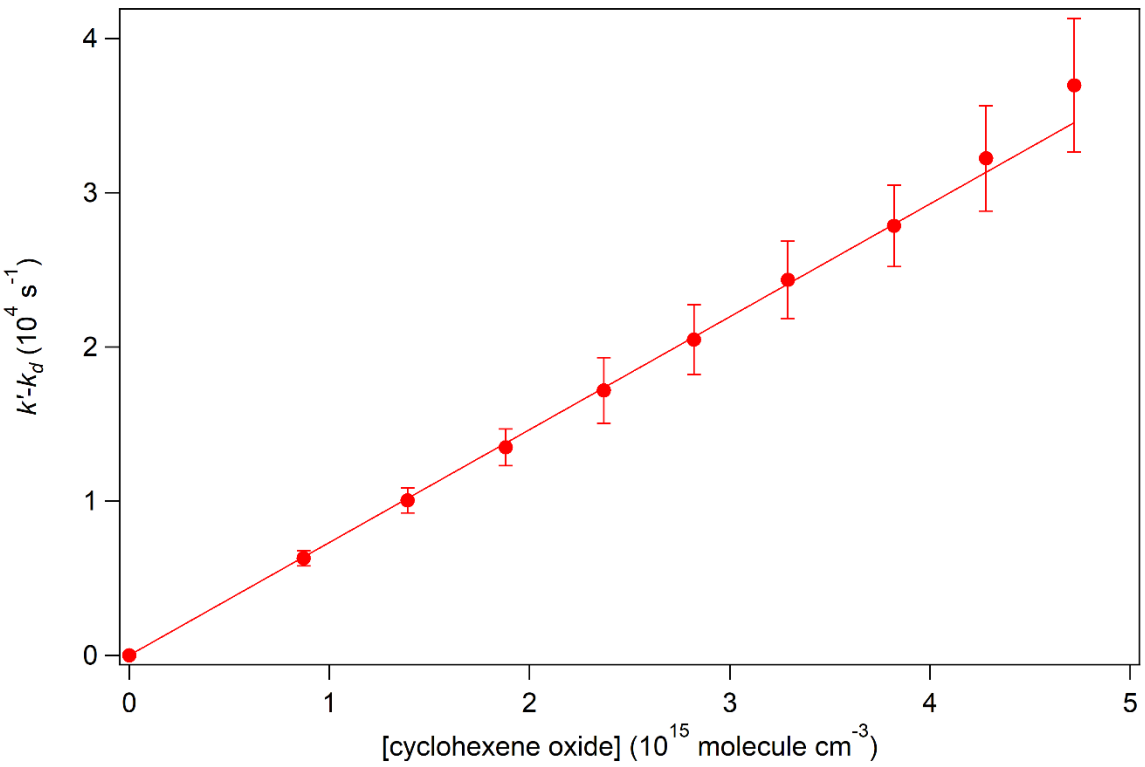

Figure 1: An example of a second-order plot measured at 274 K and 100 Torr (He). Bimolecular rate coefficients are obtained from the slopes of error-weighted linear least-squares fits to data such as these.

The relative rate measurements at 295 K in an atmosphere of purified air using 1-propanol as a reference generated relative rate plots of high linearity and negligible intercept as shown in Figure 2. We made two separate determinations in this way, which were found to be self-consistent and also in excellent agreement with our absolute measurements. The consistency between the chamber and PLP–LIF measurements suggests that there is no strong pressure or bath gas dependence under our experimental conditions. Relative rate coefficient determinations are tabulated in Table S2. Total combined uncertainties for relative measurements were dominated by the absolute uncertainties in the 1-propanol reference rate coefficient, which is 5.86×10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature, with estimated uncertainties of 10% [9].

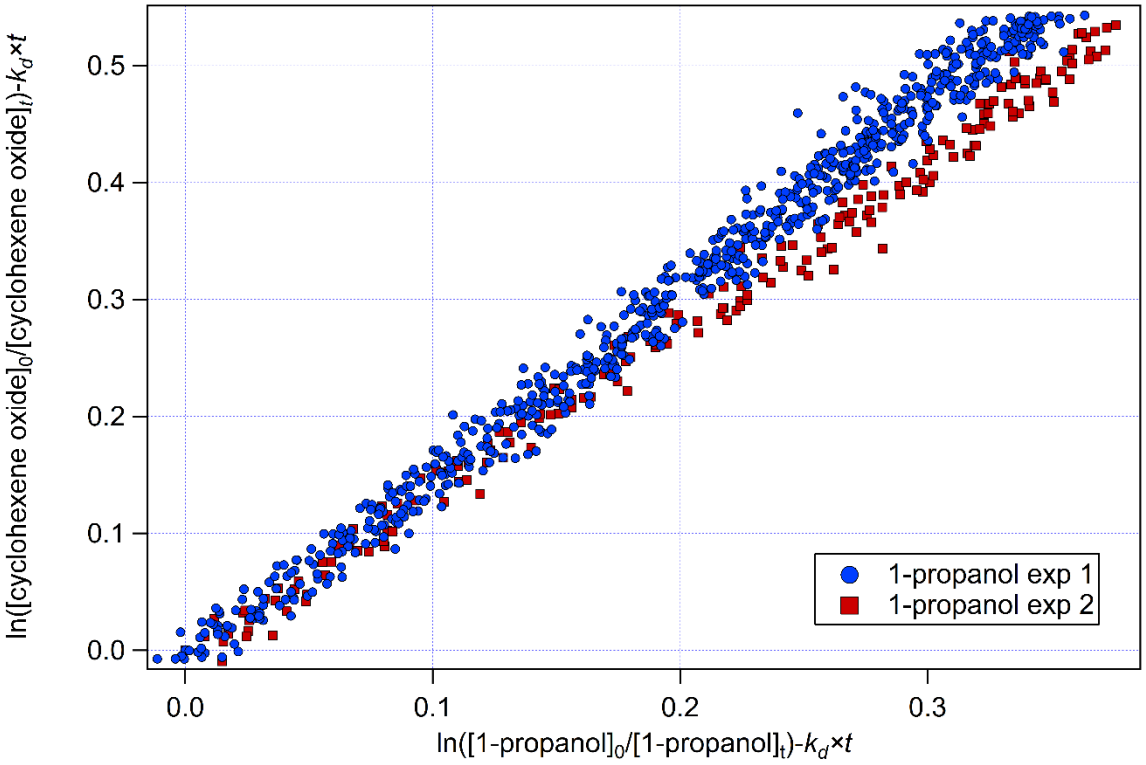

Figure 2: Relative rate experiments performed in a 7.3 m^3 chamber, in which the decay of cyclohexene oxide is monitored using a PTR-ToF-MS alongside the reference compound, 1-propanol. Experiments 1 and 2 correspond to rate coefficient determinations of 7.01±0.70 and 6.79±0.70 cm^3 $molecule^{-1}$ s^{-1} respectively.

There are no measurements available in the literature with which we can compare our current data, and the only gas-phase rate coefficient data for cyclohexene oxide known to this study is the reaction with atomic chlorine [19].

An Arrhenius diagram showing the dependence of the rate coefficient of Reaction (1) upon temperature is shown in Figure 3. A negative temperature dependence is observed, with some minor curvature towards the higher temperatures of this study.

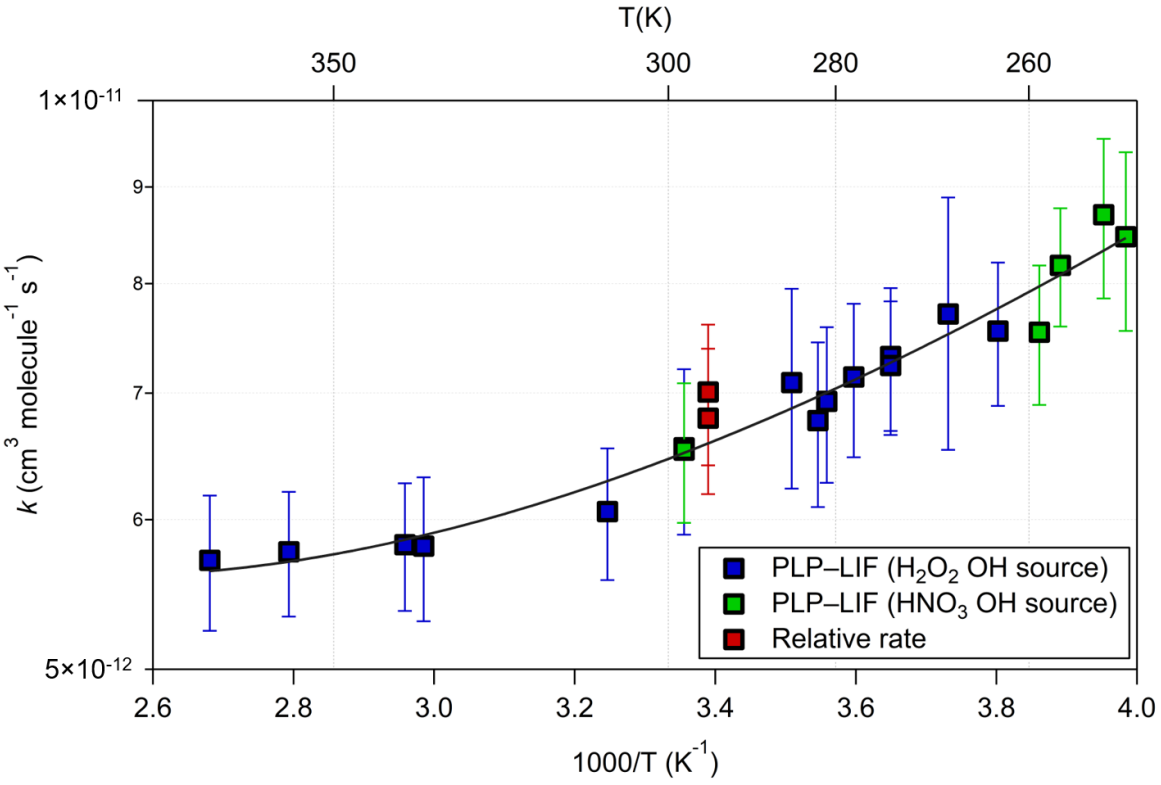

Figure 3: Arrhenius diagram showing the temperature dependence of the rate coefficient of OH + cyclohexene oxide. Error bars represent the total combined uncertainties. The black line represents a modified Arrhenius fit to the data.

A modified Arrhenius expression was found to fit the data adequately over the temperature range of 251–373 K:

$$k_1 = 7.20 \times 10^{-14} \exp\left(\frac{1349}{T}\right)\left(\frac{T}{300}\right)^{3.4}$$

These results are qualitatively consistent with the reactions of OH with other epoxides as well as with other oxygenates, which tend to exhibit curvature and/ or negative temperature dependence below room temperature. This suggests, as discussed in case of 1,2-epoxybutane, that pre-reactive complexes may be facilitating these reactions at low temperatures [13]. What remains uncertain is to what extent these complexes enhance the overall rate coefficient when compared with the direct hydrogen abstraction mechanisms that are available to these molecules. To guide this discussion, we present the temperature dependence of a variety of epoxides together with their alkane analogs in Figure 4. From this diagram, it is apparent that for much of the atmospheric temperature range, epoxides tend to be less reactive than their corresponding alkane structure. As discussed by El Othmani et al. (2021) [13], this reduction

in reactivity is likely to relate to the increased bond dissociation energy of C–H bonds adjacent to the epoxide moiety. However, at lower temperatures, the OH rate coefficient of an epoxide can be larger than that of its alkane analog. This phenomenon can be explained by the increased stability of hydrogen-bonded van der Waals (vdW) complexes, which in turn increases the probability of quantum tunnelling in these reactions, as has been observed for other oxygenated molecules [20]. Besides this, there are other possibilities, such as the existence of a submerged barrier, a low barrier, or a barrierless reaction towards products. In such circumstances, quantum tunnelling may not contribute to the overall rate coefficient. Submerged and low barriers are encountered frequently under atmospheric conditions such as the electrophilic addition of OH to alkenes [21]. Low barriers are also observed in certain hydrogen abstraction reactions, especially where weak C–H bonds are present, as is the case of the reaction of OH + formaldehyde [22]. However, given that this is considered to be a hydrogen abstraction mechanism, and accounting for the fact that the presence of the oxirane functionality is calculated to increase bond strength in neighbouring C–H bonds [23], we favour the hypothesis that vdW complexes are enhancing the overall rate coefficient at low temperatures through quantum tunnelling.

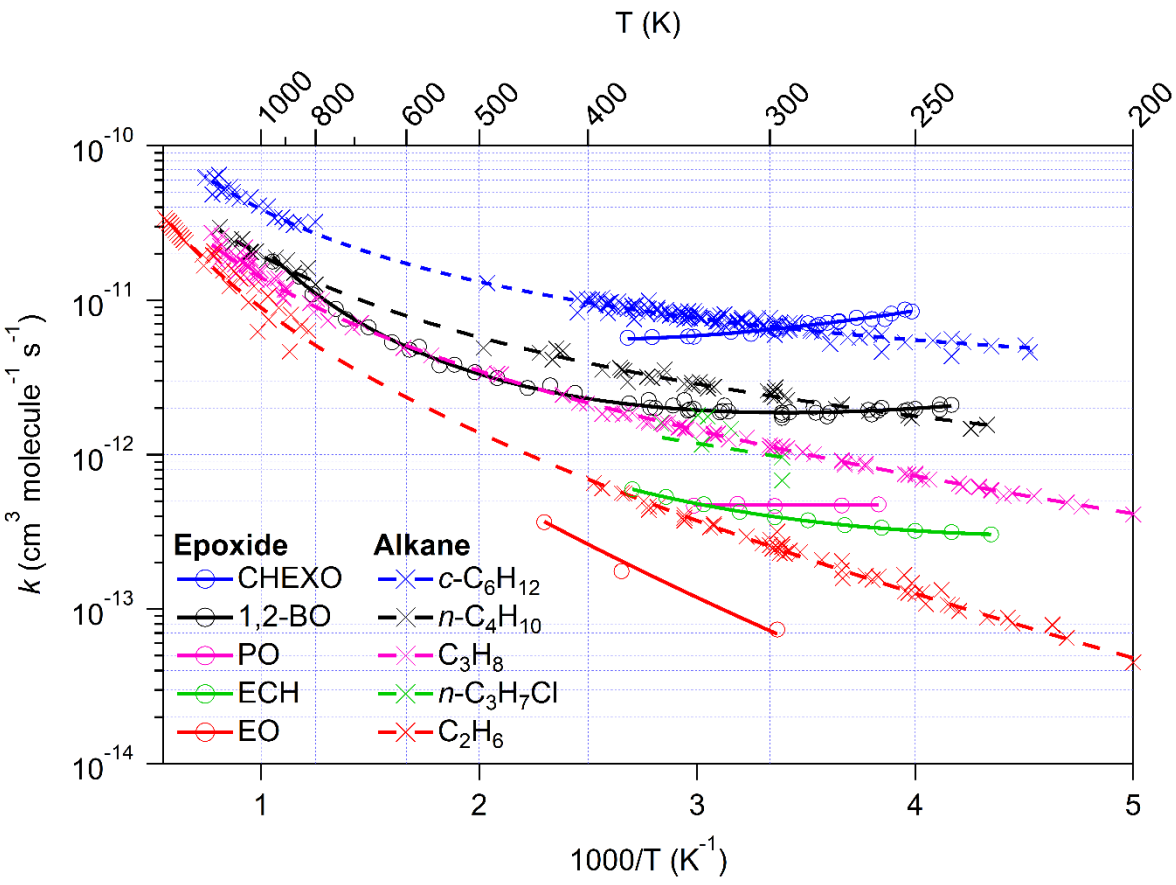

Figure 4: A comparison between the temperature dependences of epoxides and their alkane analogs. Epoxides are abbreviated as follows: CHEXO (cyclohexene oxide), 1,2-BO (1,2-butylene oxide), PO (propylene oxide), ECH (epichlorohydrin), EO (ethylene oxide). All kinetic data are taken from the database of McGillen et al. (2020) [9], except for the recent data of El Othmani et al. [13].

The temperature at which the rate coefficient of the epoxide overtakes its alkane counterpart – after some necessary extrapolation – appears to follow the order cyclohexene oxide > 1,2-epoxybutane > propylene oxide > epichlorohydrin > ethylene oxide. This also follows the order of decrease in the number of C–H bonds contained within each of these pairs. Simultaneously, it can be seen that the proportion by which the rate coefficient is decreased becomes less as the number of C–H bonds increases. This is intuitive, since the fraction of C–H bonds adjacent to the epoxide (i.e. the least reactive sites) decreases as the total number of C–H bonds grows, with the corollary being that, for larger epoxides, the reactivity would tend towards that of the alkane analog.

Assuming that our hypothesis is valid, and that the overall rate coefficient is affected by quantum tunnelling effects brought about by vdW complexes, the lifetime of the vdW complex will affect the extent to which the rate coefficient is enhanced by tunnelling processes. This lifetime increases as temperature (and kinetic energy) decreases. However, there are several other factors that can influence this phenomenon. One example is the binding energy of the complex, which will be largely dictated by the facility with which a molecule forms hydrogen bonds with the OH radical co-reactant. Carboxylic acids, for example, form particularly stable complexes, which reside in a potential energy well of ~33 kJ mol^{-1} [24], and as a result, their OH rate coefficients tend to be large, with a pronounced negative temperature dependence even at high temperatures [25]. A second factor is the entropic cost of forming the vdW complexes. These tend to have a cyclic structure, and as a consequence, have the capacity to shut down free rotors within molecules, which has been calculated to affect the phenomenological rate coefficient under some conditions [26]. Cyclohexene oxide is an interesting counterexample, in that it is purely cyclic to begin with, which should make the formation of the vdW complex more favourable energetically, a second factor contributing to this phenomenon is that the oxirane cycle is expected to be out-of-plane of the C_6 cycle, which may facilitate the participation of the neighbouring CH_2 group in a vdW complex. Both of which represent potential reasons why the onset of negative temperature dependence occurs at a higher temperature for Reaction (1) than with other epoxides. A further effect may

come from an increase in the rate of vibrational relaxion that is afforded to molecules of a larger size, which would explain why the reaction of OH with ethylene oxide shows no negative temperature dependence within the temperature range that it has been studied so far [10].

Other interpretations of the overall u-shaped Arrhenius profiles of the epoxides are possible, for example, this would be anticipated from modified transition state theory in systems with negative activation energies [27]. However, in the absence of high-level calculations, we cannot assess whether or not this is a better explanation of our kinetic results compared with the statistical complexes mentioned above.

4. Conclusions

We present the first reported absolute kinetic measurements of the gas-phase reaction of OH + cyclohexene oxide as a function of temperature between 251 and 373 K. This work serves to extend the overall knowledge on the reactivity of epoxides towards the OH radical. Our results indicate that the presence of the epoxide moiety in cyclohexene oxide leads to an enhancement of the rate coefficient compared with its alkane analog, cyclohexane. This suggests that the dominant loss process for this epoxide will be with atmospheric oxidants such as the OH radical, and that acid-catalyzed ring-opening reactions for larger, more reactive epoxides such as this may be of less importance. Assuming a representative tropospheric OH concentration of 2×10^{6} molecule cm^{-3}, and a room temperature rate coefficient for Reaction (1) of 6.51×10^{-12} cm^{3} $molecule^{-1}$ s^{-1}, we estimate from the following equation:

$$\tau = \frac{1}{k[\mathrm{OH}]}$$

that the tropospheric lifetime, τ, of cyclohexene oxide is approximately 1 day. As it becomes oxidized, this bicyclic molecule is expected (by analogy to the atmospheric fate of cyclohexyl peroxy/ cyclohexyl alkoxy radicals) to lead to ring-opened products [28]. These have an increased capacity for forming multifunctional oxygenated species, which we expect can contribute to secondary organic aerosol formation.

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