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HAL Authorization

1 **Title:**

2 Gas-phase rate coefficient of OH + 1,2-epoxybutane determined between 220 and 950 K

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14 **Keywords:**

15 Epoxide, hydroxyl, kinetics, atmospheric chemistry, non-Arrhenius

16

17 **Abstract:**

18 Epoxides have many primary and secondary atmospheric sources. As with other oxygenates,
19 they exhibit a complex temperature-dependent reaction with OH, whose full description is
20 necessary in order to understand their interactions in atmospheric and combustion
21 environments. We measured the kinetics of the title reaction using two complementary
22 absolute methods: pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF) and a
23 discharge-flow mass spectrometric system (DF-MS), both monitoring temporal decays in OH.
24 In addition, two relative methods employing the DF-MS as a function of temperature, as well
25 as several simulation chamber experiments at room temperature were performed. A very weak
26 negative temperature dependence was observed at $T \leq 285$ K, and only through the
27 combination of precise data and a large temperature range were we able to discern the
28 transition towards positive temperature dependence found at $T \geq 295$ K. The non-Arrhenius
29 temperature dependence of OH + 1,2-epoxybutane implies the agency of pre-reactive
30 complexes in this reaction mechanism, albeit with a smaller effect than with its acyclic ether
31 analogues. This will have implications for understanding the chemical fate of epoxides within
32 oxidizing environments.

33 **1. Introduction:**

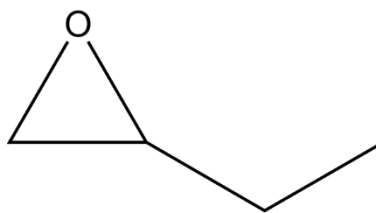
34 Many epoxide-forming reaction channels have so far been identified. Within the atmosphere,
35 these may include simple association reactions with oxidants such as $O(^3P) +$ alkenes,¹ $NO_3 +$
36 alkenes,² $O_3 +$ conjugated dialkenes,^{3–5} and $O_3 +$ halogenated/ sterically hindered alkenes.⁶
37 Potentially more important are the unimolecular processes such as ring-closure reactions that
38 occur for hydroperoxyalkyl radicals,^{7,8} and unsaturated hydroperoxides.⁹ These have been
39 implicated in the formation of highly functionalized oxidation products of biogenic volatile
40 organic compounds such as isoprene epoxydiols (IEPOX), key gas-phase oxidation products
41 of isoprene.

42 There are several primary emissions of epoxides relating to industrial production, e.g.
43 alkoxylation reactions for polymer synthesis,¹⁰ as well as natural emissions such as floral
44 perfumes and other semiochemicals.¹¹

45 Once epoxides enter the atmosphere, they will engage in subsequent reactions. Notable among
46 these are acid-catalyzed ring-opening processes, which lead to highly functionalized polyol
47 species. These products have a greatly reduced volatility compared with the epoxide starting

48 material, and are thought to contribute significantly to secondary organic aerosol production.^{12–}
49 ¹⁴ However, these multiphase processes occur in competition with gas-phase oxidation
50 reactions in the atmosphere, the most important of which is expected to be hydrogen abstraction
51 reactions with the OH radical. By querying a recently compiled near-comprehensive database
52 of gas-phase atmospheric reactions of organic compounds,¹⁵ it can be concluded that as few as
53 two epoxides have been studied as a function of temperature: ethylene oxide and 1,2-propylene
54 oxide.^{16,17}

55 With such limited knowledge of the OH kinetics, the overall atmospheric fate of epoxides
56 therefore remains highly uncertain. We address this by taking a relatively simple epoxide, 1,2-
57 epoxybutane (EPB), and subjecting it to a set of precise and accurate kinetic measurements,
58 such that we can better understand the effects of the epoxide functionality on chemical
59 reactivity throughout the tropospheric temperature range and higher, which may be of
60 importance to combustion chemistry.



61

62 Structure of 1,2-epoxybutane (EPB)

63 **2. Experimental methods:**

64 **2.1. Absolute measurements:**

65 Two absolute techniques were employed in this study to measure the temperature-dependent
66 rate coefficient of Reaction 1:



68 Notably, the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF) technique, and the
69 discharge-flow mass spectrometry method (DF-MS), which are described in the following
70 subsections.

71 **2.1.1. Pulsed-Laser Photolysis–Laser-induced by fluorescence measurements:**

72 The PLP–LIF system has been described in detail elsewhere,¹⁷ and will be described only
73 briefly here. This system consists of a 5-way cross Pyrex reaction cell (volume = 200 cm³), the

74 gaseous contents of which were temperature-regulated by circulating heated or cooled fluid
75 through an outer jacket. Measurements were conducted over the temperature range 220–373 K
76 and ~100 Torr of bath gas (He), and were performed under pseudo-first-order conditions, where
77 [EPB] \gg [OH]. OH radicals were produced in Reactions 2 or 3 from OH precursors (H₂O₂ or
78 HNO₃) that were photolyzed at 10 Hz at a wavelength of 248 nm by a KrF excimer laser pulse.



81 OH radicals were detected following excitation from a probe laser pulse, tuned to excite the
82 $\text{A}^2\Sigma^+(\nu = 1) \leftarrow \text{X}^2\Pi(\nu = 0)$ transition near 282 nm using a frequency-doubled Nd:YAG
83 pumped dye laser. The resulting fluorescence was detected using a photomultiplier tube fitted
84 with a 308 nm bandpass filter. The photomultiplier signal was collected using a boxcar
85 integrator and recorded on a data acquisition card (see Figure S1, Supporting Information SI).
86 Temporal profiles of integrated OH signal were collected by changing the delay time between
87 the photolysis and probe lasers, which, under pseudo-first-order conditions obey the following
88 relationship:

89 $\ln\left(\frac{[\text{OH}]_t}{[\text{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k[1,2\text{-epoxybutane}] + k_d)t = -k't$ Equation 1

90 where t is the delay time between laser pulses, S is the OH fluorescence signal, integrated over
91 the box-car sampling window, and k' and k_d represent the pseudo-first-order decay rate of OH
92 in the presence or absence of EPB respectively. Values of k_d were typically 30–150 s⁻¹ and were
93 a consequence of the reaction of OH with the OH precursor (H₂O₂ or HNO₃) and diffusion of
94 OH out of the reaction volume. We expect that this diffusion term is not truly first-order in
95 nature, and besides, given that signal:noise is reduced at long delay times, in order to ensure
96 high-quality first-order fits in each case, we limited our temporal profiles to include only the
97 first three decades of integrated OH fluorescence signal. Values for k' were obtained through
98 an error-weighted least-squares fit of S_t vs t . Following this, an error-weighted least-squares fit
99 of k' against [EPB] yielded a slope equal to the bimolecular rate coefficient, k . This procedure
100 was conducted at each temperature of the dataset.

101 As with similar studies,^{20,21} in order to reduce systematic uncertainties in this relationship, EPB
102 concentrations were quantified on-line using a multipass Fourier transform infrared
103 spectrometer (pathlength = 1000 cm). For this purpose, the infrared band intensity of EPB was
104 determined. This was achieved by introducing known concentrations of EPB from a
105 manometrically prepared sample bulb (He bath gas) into the multipass cell, and the absorbance
106 was quantified over a range of concentrations. Absorbance was found to obey the Beer-Lambert

107 law over the concentration range of our measurement. During experiments, [EPB] was
108 monitored on-line, whereby the FTIR absorption cell was situated directly downstream from
109 the LIF reactor. Figure S2 shows a plot of the integrated band intensity determination.

110

111 **2.1.2. Discharge-flow mass spectrometry measurements:**

112 Complementary measurements were performed using a fast-flow reactor coupled with a
113 molecular beam sampling electron impact ionization quadrupole mass spectrometer.^{22,23} These
114 measurements were performed over a pressure range of 2–9 Torr (He), and were conducted in
115 one of two reactors, either for low- or high-temperature measurements. The low-temperature
116 flow reactor covered the temperature range 240–340 K, and consisted of a Pyrex tube (45 cm
117 in length, 2.4 cm i.d.) with an outer jacket through which a temperature-regulated fluid was
118 circulated (see Figure S3). To minimize wall-loss of OH, the inner surface of the reactor, as
119 well as the movable injector, were coated with halocarbon wax. The high-temperature flow
120 reactor was employed over the temperature range 360–950 K, a quartz tube (45 cm in length,
121 2.5 cm i.d.), where the temperature was controlled with electrical heating elements (see Figure
122 S4).

123 OH was produced by passing H₂ in a bath gas (He) through a microwave discharge, yielding H
124 atoms, which subsequently react with NO₂ in Reaction 4, to produce OH:



126 OH radicals were detected indirectly by scavenging with Br₂, yielding HOBr (see Reaction 5),
127 and detected at m/z 96/98 (HOBr⁺):



129 The excess concentrations of Br₂ employed ($3\text{--}5 \times 10^{13}$ molecule cm⁻³) combined with the
130 rapidity of Reaction 4, leads to efficient scavenging under our experimental conditions. This
131 reaction was also used to determine absolute concentrations of OH through their chemical
132 conversion to HOBr in an excess of Br₂, whereby $[\text{OH}] = [\text{HOBr}] = \Delta[\text{Br}_2]$, i.e. the
133 concentration of OH (HOBr) was determined from the consumed fraction of [Br₂]. A detailed
134 discussion on the possible influence of secondary chemistry on this method of OH detection
135 and determination of the absolute concentrations of the radicals is presented elsewhere.²⁴

136 EPB was delivered to the reactor by passing carrier gas (He) over a liquid sample of pure EPB,
137 and was detected by mass spectrometry at its parent ion of $m/z = 72$ (C₄H₈O⁺). The absolute

138 calibration of the mass spectrometer for EPB was performed by two methods. Firstly, absolute
139 concentrations of EPB (as well as of other stable species, NO₂, Br₂ and *n*-butane) were
140 calculated from the flow rates obtained from the measurements of the pressure drop of the
141 manometrically prepared mixtures in He stored in calibrated volume flasks. Secondly, a known
142 volume (generally, 0.6 μl) of sample was injected into a helium flow in the reactor under the
143 experimental conditions of the kinetic measurements (pressure, temperature, total flow of bath
144 gas) and the mass peak at $m/z = 72$ was recorded. The integrated area of the mass spectrometric
145 signal, corresponding to the total number of EPB molecules injected into the reactor, allowed
146 the determination of the calibration factor. These two methods were found to agree within 10%.

147 **2.2. Relative rate measurements:**

148 In addition to the absolute measurements of Section 2.1., two relative rate techniques were used
149 to determine the rate coefficient of Reaction 1, notably, the same DF-MS described earlier to
150 make temperature-dependent measurements, but operated in a different mode; and a 7.3 m³
151 Teflon atmospheric simulation chamber, used to make room-temperature measurements. These
152 are described in the following subsections.

153 **2.2.1. Discharge-flow mass spectrometry:**

154 The DF-MS was used to determine the decay rate of EPB in the presence of a reference
155 compound (Reaction 6), whose rate coefficient is already known:



157 Comparing these decay rates, the rate coefficient is determined from the following equation:

158
$$\ln \left(\frac{[1,2\text{-epoxybutane}]_0}{[1,2\text{-epoxybutane}]_t} \right) = \frac{k_{1,2\text{-epoxybutane}}}{k_{\text{reference}}} \ln \left(\frac{[\text{reference}]_0}{[\text{reference}]_t} \right)$$
 Equation 2

159 where subscripts 0 and t refer to initial species concentrations at time 0 and time t respectively.
160 In this case, the reference compound was *n*-butane, which has a well characterized temperature
161 dependence over a large temperature range (231–1236 K).¹⁵

162
$$k(T) = 2.09 \times 10^{-12} \exp\left(\frac{42}{T}\right) \left(\frac{T}{300}\right)^{1.82}$$
 Equation 3

163 Initial concentrations of EPB and *n*-butane were in the range 1.8–3.6 and $0.9\text{--}2.0 \times 10^{12}$
164 molecule cm⁻³, respectively. OH radicals were produced by Reaction (3) with [NO₂] ≈ 5×10^{13}
165 molecule cm⁻³. EPB and *n*-butane were monitored by mass spectrometry at their parent peaks

166 at $m/z = 72$ and 58, respectively. A small contribution (3–4%) of EPB at $m/z = 58$ was observed
167 and was subtracted from the *n*-butane signal. In addition, an appearance of a small signal at m/z
168 = 72 (probably, as a result of *n*-butane secondary chemistry) was observed upon consumption
169 of *n*-butane in its reaction with OH. The corresponding corrections applied to the EPB signal at
170 $m/z = 72$ depended on the consumed fraction of *n*-butane and were $\leq 20\%$. Although the possible
171 impact of secondary reactions of EPB and *n*-butane with organic radicals produced in Reactions
172 (1) and OH + *n*-butane was not verified, it is expected to be insignificant, considering the
173 relatively low initial concentrations of EPB and *n*-butane used in the experiments. The observed
174 independence of the experimental results of the reaction time, which was varied from 0.02 to
175 0.04 s, and their good agreement (within the region of overlap) with the data obtained for the
176 other methods of this study supports this assumption. Another possible secondary loss of EPB/
177 *n*-butane may be initiated by oxygen atoms formed in the self-reaction of OH radicals (see
178 Reaction 7):



180 whose rate coefficient is as follows:

181 $k_7 = 2.68 \times 10^{-14} \times (T/300)^{2.75} \exp(1165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($T=220\text{--}2384 \text{ K}$),²⁵ Equation 4

182 but this has a negligible effect on the concentrations of EPB and *n*-butane, because O-atoms are
183 mainly consumed in the rapid reactions with OH radicals and NO₂ present in high
184 concentrations in the reactor:



186 $k_8 = 6.1 \times 10^{-12} \exp(155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($T = 220\text{--}950 \text{ K}$),²⁶ Equation 5



188 $k_9 = 1.8 \times 10^{-11} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($T = 136\text{--}515 \text{ K}$),²⁷ Equation 6

189 Examples of the observed plots of $\ln([\text{EPB}]_0/[\text{EPB}]_t)$ against $\ln([n\text{-butane}]_0/[n\text{-butane}]_t)$ are
190 presented in Figure 3.

191 Relative rate measurements were also performed using Br₂ (Reaction 5) as a reference,
192 conducted at a total pressure of 2–9 Torr and relied on determining the HOBr yield as a function
193 of the [EPB]/[Br₂] ratio upon OH consumption in reaction with a mixture of Br₂ and EPB.

194 The fraction of the initial concentration of OH radicals, $[\text{OH}]_0$, transformed to HOBr in
195 Reaction 5, is:

$$196 \quad [\text{HOBr}] = \frac{k_5[\text{Br}_2]}{k_5[\text{Br}_2] + k_1[\text{EPB}] + k_w} \times [\text{OH}]_0 \quad \text{Equation 7}$$

197 After rearrangement of this expression we obtain:

$$198 \quad \frac{[\text{OH}]_0}{[\text{HOBr}]} - 1 = \frac{k_1[\text{EPB}]}{k_5[\text{Br}_2]} + \frac{k_w}{k_5[\text{Br}_2]} \quad \text{Equation 8}$$

199 At a constant concentration of Br_2 , the second term in Equation 8 is constant and k_1/k_5 can be
200 determined as the slope of the linear dependence of $([\text{OH}]_0/[\text{HOBr}] - 1)$ with $[\text{EPB}]/[\text{Br}_2]$. In
201 these experiments, HOBr was monitored in both EPB-free system, corresponding to $[\text{OH}]_0$, and
202 in the Br_2 - and EPB-containing systems, corresponding to the fraction of $[\text{OH}]_0$ reacted with
203 Br_2 . Reaction time was 0.03–0.07 s, $[\text{OH}]_0 = 2.5\text{--}6.0 \times 10^{11}$ molecule cm^{-3} , concentrations of
204 EPB and Br_2 are shown in (Table S3, SI).

205 **2.2.2. Atmospheric simulation chamber**

206 Relative rate measurements were also performed in the ICARE-CNRS chamber in 760 Torr of
207 zero air bath gas at a temperature of 291 ± 2 K. This chamber is 7.3 m^3 in volume and has been
208 described in detail in an earlier work,²⁸ and has been employed in several recent studies from
209 our group.^{29,30} The walls of the chamber are constructed of FEP Teflon foil and contains two
210 Teflon fans to ensure that the chamber contents are well mixed. In these experiments, the
211 chamber was illuminated at 365 nm using an array of $24 \times \text{UV-A T-40 L}$, Viber-Lourmat lamps,
212 to generate OH through the following sequence of reactions:



216 In order to prevent the ingress of atmospheric contamination into the chamber through the
217 permeability of the Teflon foil and any small leaks, experiments were performed at a slight
218 overpressure using a continuous flow of zero air. As a consequence, chamber contents were
219 gradually diluted over time. This was accounted for by monitoring an inert tracer (SF_6), whose
220 concentration was determined at regular intervals, using a multipass in-situ Fourier transform
221 infrared spectrometer. Samples of reactants were introduced into the chamber through the

222 injection of known volumes of liquid samples introduced into a stream of zero air flowing
223 through a Pyrex impinger.

224 In these experiments, the relative rate was determined using the following equation:

$$225 \ln \left(\frac{[1,2\text{-epoxybutane}]_0}{[1,2\text{-epoxybutane}]_t} \right) - k_d t = \frac{k_{1,2\text{-epoxybutane}}}{k_{\text{reference}}} \ln \left(\frac{[\text{reference}]_0}{[\text{reference}]_t} \right) - k_d t \quad \text{Equation 9}$$

226 which is similar to Equation 2, except that additional loss processes besides the reaction with
227 OH (e.g. dilution, wall-loss and decomposition) are taken into account using the first-order term
228 k_d . Two reference compounds were selected for these experiments: 2-propanol and ethanol, and
229 these, together with the EPB were monitored continuously using a PTR-ToF-MS 8000 (Ionicon
230 Analytik) operated in NH_4^+ ,³¹ and H_3O^+ modes. Both 2-propanol and ethanol have well-defined
231 OH rate coefficients at 291 K, 5.32 and $3.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.¹⁵

232 **2.3 Materials:**

233 For DF-MS experiments: the purities of the gases used were as follows: He (>99.9995%,
234 Alphagaz), passed through a liquid nitrogen trap; H_2 (>99.998%, Alphagaz); Br_2 (>99.99%,
235 Aldrich); NO_2 (>99%, Alphagaz), EPB (>98%, Aldrich), *n*-butane (>99.5%, Air Liquide). For
236 PLP-LIF experiments: He carrier gas (Alphagaz, 99.999%) was taken directly from the cylinder
237 without further purification. Hydrogen peroxide, H_2O_2 , (50 wt%, Aldrich) was purified over
238 the course of several days by bubbling with zero air. Gas-phase nitric acid was taken from the
239 headspace of a sample of 70% redistilled nitric acid, which had been dehydrated through the
240 dropwise addition of pure H_2SO_4 added in a 1:2 ratio. Methyl nitrite was synthesized through
241 the dropwise addition of 50% H_2SO_4 into a continuously stirred saturated solution of NaNO_2 in
242 methanol maintained at 0°C, the effluent of which was swept through a water bubbler and a u-
243 tube containing P_2O_5 using a slow flow of pure nitrogen, and trapped in a liquid nitrogen cold
244 trap. For the atmospheric simulation chamber, ethanol (>99%, Aldrich) and 2-propanol (>99%,
245 Aldrich) were used as references.

246 **3. Results:**

247 **3.1. Absolute measurements:**

248 **3.1.1. PLP-LIF measurements:**

249 Absolute overall rate coefficients were determined at temperatures between 243 and 371 K and
250 at pressures of ~100 Torr (He). Concentrations of EPB ranged from 0.33 to $16.6 \times 10^{15} \text{ molecule}$
251 cm^{-3} . Initial OH concentrations, $[\text{OH}]_0$, varied from 2 to $50 \times 10^{10} \text{ molecule cm}^{-3}$. A summary

252 of results together with experimental conditions are given in Table S1. Typical examples of
253 second-order plots of k' vs [EPB] are shown in Figure 1. Under the pseudo-first-order conditions
254 of our study, single exponential decays of OH were observed in all cases, with low scatter
255 indicating no apparent complications of secondary chemistry or OH recycling. Second-order
256 plots displayed good linearity in all cases, indicating that [EPB] was determined precisely and
257 that no apparent heterogeneous or dimerization processes were perturbing the mixing ratio or
258 reactivity of the reaction mixture.

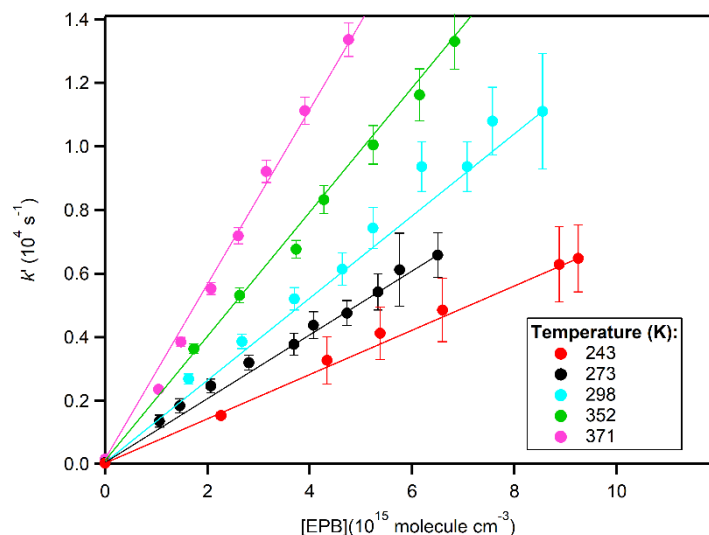
259 Combined uncertainties of rate coefficients were estimated to be <10%, accounting for
260 statistical error in k' (~3%), EPB infrared cross section (5%), pressure (2%), temperature (2%).

261 3.1.2. DF-MS measurements:

262 Absolute rate coefficients were measured over a temperature range of 298–720 K at pressures
263 between 2.0 and 2.2 Torr (He). [EPB] was varied between 0.5 and 20×10^{13} molecule cm^{-3} .
264 $[\text{OH}]_0$ ranged from $2\text{--}4 \times 10^{11}$ molecule cm^{-3} . As with the PLP–LIF measurements, high quality
265 single exponential decays were observed in all cases, examples of which are shown in Figure
266 S5. All the pseudo-first order rate constants were corrected for axial and radial diffusion of OH
267 radicals³² with the diffusion coefficient of OH in He calculated as $D_0 = 660 \times (T/298)^{1.85}$ Torr
268 $\text{cm}^{-2} \text{ s}^{-1}$,³³ which accounted for <11% of the observed k' values. These data are tabulated in
269 Table S2.

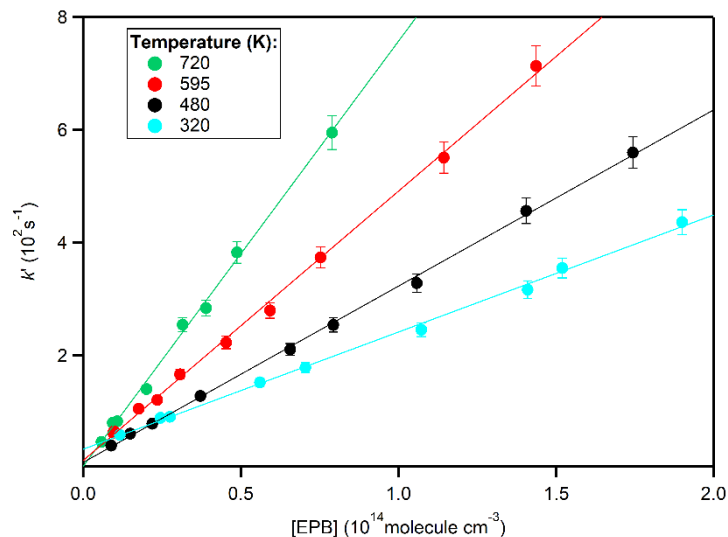
270 Second-order plots obtained using the DF-MS method are shown in Figure 2. The y-intercepts
271 in Figure 2 arise from wall-loss processes, k_w , are $10 \pm 5 \text{ s}^{-1}$ over the temperature range 480 to
272 720 K. At 320 K, this value rises to $34 \pm 4 \text{ s}^{-1}$, which we attribute to surface contamination with
273 EPB or its oxidation products. Enhanced wall-losses were observed for both halocarbon wax-
274 coated ($T < 298 \text{ K}$) and uncoated quartz reactors ($T < 430 \text{ K}$), and for this reason, these
275 temperatures were used as lower temperature limits for these respective reactors in the absolute
276 measurements of k_1 . Conversely, at temperatures $>720 \text{ K}$, some evidence of thermal
277 decomposition of EPB is observed in the appearance of signals at $m/z = 94/96$ and $108/110$
278 which can be assigned to CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, or fragments of potentially higher-mass products,
279 and which could affect the absolute kinetic determinations, and was therefore considered to be
280 an upper temperature limit for the absolute measurements of this study.

281 Combined uncertainties of rate coefficient determinations were estimated to be <15%,
282 accounting for statistical error ($\leq 5\%$), determination of [EPB] ($\sim 10\%$), mass flow (3%),
283 pressure (2%) and temperature (1%).



284

285 **Figure 1.** Dependence of the pseudo-first-order rate constant (k') on [1,2-epoxybutane] at
286 different temperatures obtained in PLP-LIF system. Error bars represent 2σ statistical
287 uncertainties.



288

289 **Figure 2.** Pseudo-first-order rate constant (k_1') as a function of [1,2-epoxybutane] at different
290 temperatures obtained in the DF-MS system. Partially shown error bars represent typical
291 uncertainties ($\leq 5\%$) on the determination of k_1' .

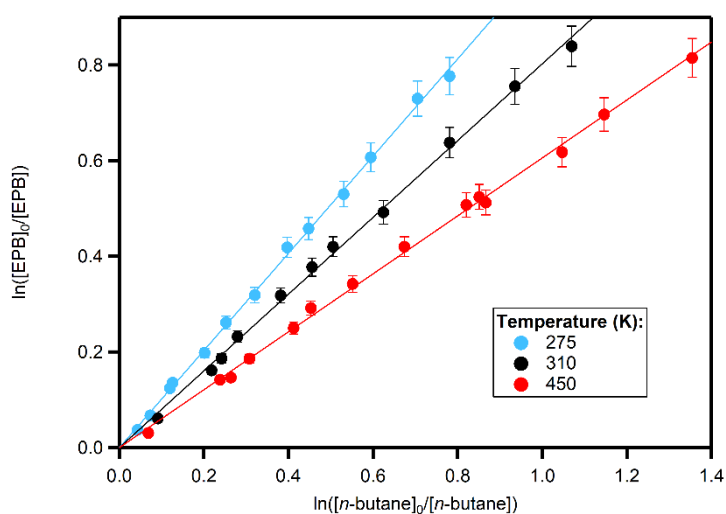
292 3.2. Relative rate measurements:

293 3.2.1. DF-MS measurements:

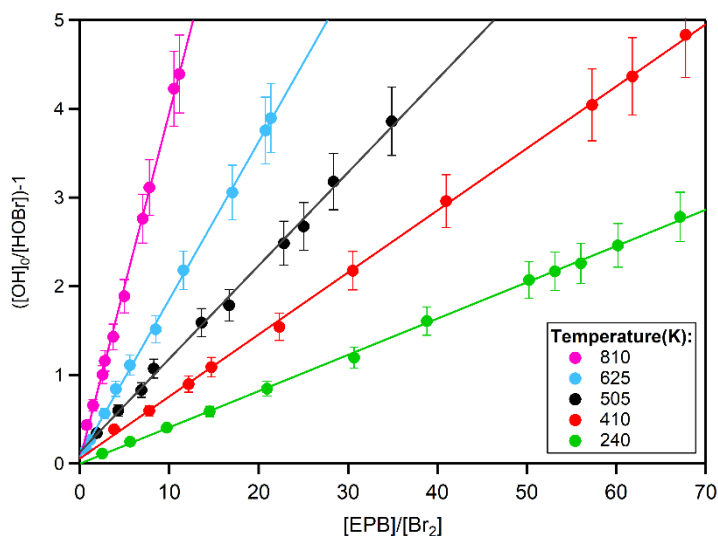
294 In order to extend the temperature range of the measurements of k_1 , we used the DF-MS
295 apparatus to make relative rate measurements, using both *n*-butane and Br₂ as reference
296 compounds. Total pressures in the flow-tube ranged from 2–9 Torr (He). In the case of *n*-butane,
297 rate coefficients were determined at temperatures between 275 and 950 K, and for Br₂, between
298 240 and 810 K. Linear relative rate plots were observed in each case, some examples of which
299 are shown in Figures 3 and 4.

300 Final values of k_1 , calculated using experimentally determined k_1/k_{ref} ratios. See Table S3 for
301 tabulated data of measurements with the Br₂ reference and Table S4 for the *n*-butane reference.

302 The temperature dependence of OH + *n*-butane and OH + Br₂ are both well-established over
303 the temperature range of these measurements.^{15,22} Therefore, we estimate ~15% combined
304 uncertainty in the DF-MS relative rate measurements, accounting for ~10% uncertainty in the
305 reference rate coefficients, combined with uncertainties in temperature (1%) and statistical
306 uncertainty in the relative rate, EPB/reference decomposition and heterogeneous loss (<5%).



307
308 **Figure 3.** Relative rate plot showing the linear dependence of $\ln([EPB]_0/[EPB])$ with $\ln(n$ -
309 butane)₀/ $[n$ -butane]) observed at T = 275, 310 and 450 K. Error bars represent the statistical
310 errors (<5%) in the relative rate.



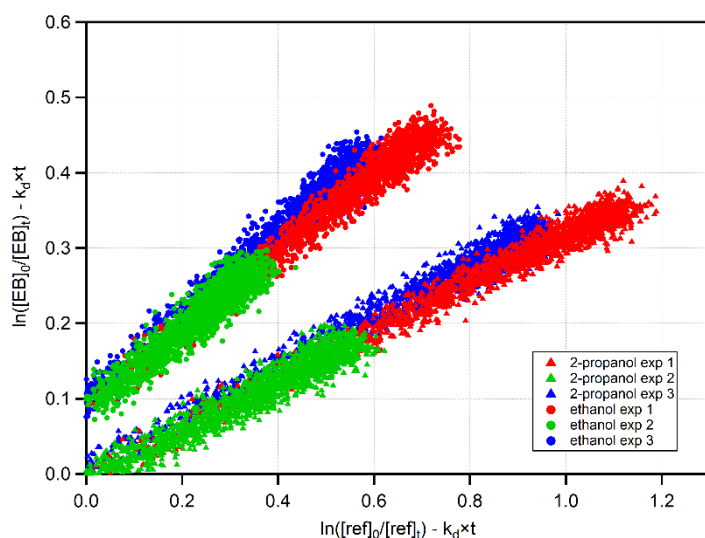
311

312 **Figure 4.** An alternative relative rate approach, monitoring the yield of HOBr from OH-radical
 313 titration with Br₂ + 1,2-epoxybutane mixtures at different temperatures. Error bars represent
 314 typical uncertainties of the measurements (<10%).

315 3.2.2. Atmospheric simulation chamber measurements:

316 As a further test, and to reduce the potential effects of wall interactions, a series of experiments
 317 was conducted in a 7.3 m³ simulation chamber at 760 Torr of zero air and a temperature of
 318 291±2K. Relative rate plots were found to be linear, with intercepts close to the origin in all
 319 cases (see Figure 5). Relative rates measured with both 2-propanol and ethanol as reference
 320 compounds were found to be in excellent agreement (1.70±0.14) and (1.71±0.11) ×10⁻¹² cm³
 321 molecule⁻¹ s⁻¹, respectively, leading to a weighted-average value of (1.70±0.12) ×10⁻¹² cm³
 322 molecule⁻¹ s⁻¹. These data are tabulated in Table S5.

323



324

325 **Figure 5.** Plots of relative kinetic data obtained from the reaction of 1,2-epoxybutane + OH
 326 using ethanol and 2-propanol as the reference compounds. For clarity, ethanol experiments
 327 have been offset by 0.1.

328 4. Discussion:

329 All the kinetic measurements of this study are shown in Figure 6, together with the sole
 330 literature room-temperature measurement of which we are aware.³⁴ All measurements of this
 331 study – within their respective overlap regions – were found to be in close agreement, and were
 332 also found to agree with the literature relative rate determination. The curvature observed in the
 333 data was fitted using the following modified Arrhenius expression, and is valid over the
 334 temperature range 220–950 K:

335

$$336 \quad k_1 = 1.72 \times 10^{-14} \times \exp(1407/T)(T/300)^{4.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{Equation 10}$$

337

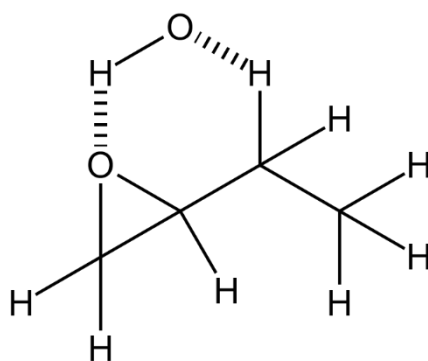
338 From Figure 6, it is apparent that the reaction of OH with EPB demonstrates clear non-
 339 Arrhenius behaviour. Indeed, this appears to be a general rule for oxygenates, wherever precise
 340 kinetic information is available over an extensive temperature range.³⁵ The main explanation
 341 for this phenomenon is the formation of cyclic hydrogen-bonded van der Waals (vdW)
 342 complexes, otherwise referred to as pre-reactive complexes. These structures can be stabilized
 343 into potential energy wells of ~5–33 kJ mol⁻¹ for alcohols, ethers, aldehydes, ketones, esters
 344 and carboxylic acids.^{36,37} The general mechanism by which vdW complexes increase the rate
 345 coefficient can be rationalized by the prolonged contact time between OH and the oxygenated
 346 co-reactant, which is afforded by stabilization into the pre-reactive complex energy well, and

347 which therefore provides a greater probability for quantum tunnelling processes to occur. There
348 are several factors that determine the magnitude of this effect as a function of temperature. This
349 relates to the binding energy of the vdW complex, which limits the lifetime of a complex at a
350 given temperature. For strongly bound vdW complexes such as those between OH and
351 carboxylic acids,³⁷ a dominantly negative temperature dependence can be observed even at 575
352 K for the reaction of OH with acetic acid.³⁸ In contrast, for weakly bound vdW complexes, such
353 as those between OH and ketones, the onset at which a negative temperature dependence is
354 observed in the Arrhenius diagram can be at much lower temperatures. Another aspect that can
355 affect the tunnelling process is the entropic cost of forming the vdW. It has been observed, for
356 example, that several vdW complexes can form for the reactions of larger species such as *n*-
357 butanol + OH, and where it can be seen that even though the geometry may be favourable for
358 larger cyclic vdW structures, the entropic cost of shutting down more free rotors within a
359 molecule will reduce the overall favourability of forming the vdW complex. This results in the
360 C–H bonds that are directly adjacent to the alcohol substitution being more reactive despite
361 possessing a larger ring-strain associated with the 5-membered ring structure,³⁹ an observation
362 that has been borne out by experimental kinetic²⁰ and product studies.⁴⁰ A further factor
363 affecting the importance of vdW complexes is the width of the barrier going towards products,
364 whereby quantum tunnelling becomes less probable in the case of broader barriers. This has
365 been demonstrated experimentally by the pronounced preference of hydrogen abstraction from
366 the O–H bond in methanol at very low temperatures, which involves traversing a high (yet
367 narrow) barrier towards forming the methoxy radical + H₂O.⁴¹ On a related theme, the overall
368 bond-strength of a given reactive site may also play a role in the reactivity of a given C–H bond.
369 In the case of 2-butanol, for example, the alpha tertiary hydrogen atom is especially weak (92.9
370 kcal/mol),^{42,43} which is estimated to account for 63% of the overall reactivity of the molecule
371 at room temperature.²⁰ In contrast, the reactivity of the two alpha secondary hydrogen atoms in
372 *n*-butanol are slightly stronger (93.2 kcal/mol),^{42,43} and only account for 28% of the total room
373 temperature rate coefficient on a per hydrogen basis.²⁰

374 However, it is acknowledged that negative temperature dependence has been observed
375 experimentally in several other metathesis reactions, notably those of alkyl radicals with
376 hydrogen halides.⁴⁴ Subsequently, this temperature-dependent behaviour was rationalized
377 through a modified transition state theory (MTST), which, when applied to systems with
378 negative apparent activation energies, can explain negative temperature dependence without
379 invoking statistical intermediate complexes.⁴⁵ Furthermore MTST predicts the transition from

380 negative to positive temperature dependence in several reactions, similar to that observed in our
381 case for OH + EPB.^{45,46}

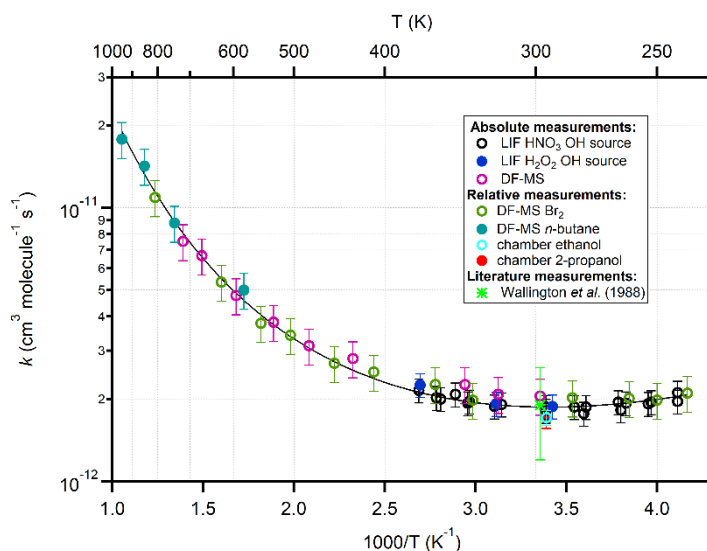
382 The EPB measurements of this study represent the first measurements of the reaction of an
383 epoxide with OH over an extended temperature range. To provide a context for what we
384 observe, we show in Figure 7 an Arrhenius diagram of several other molecules, each of which
385 have been measured over an extended temperature range, and like EPB, possess 8 C–H bonds.¹⁵
386 When the temperature dependence is compared with that of what we could take to be a base
387 case alkane-like reactivity of OH + propane, it becomes apparent that the epoxide functionality
388 does not impart a strong increase in the overall reactivity of this molecule. This contrasts
389 markedly with acyclic ethers such as methyl ethyl ether, which is significantly more reactive
390 than propane across the entire temperature range. An even more potent effect is observed for
391 the reaction of *n*-butanal, which can at least in part be explained by the relative weakness of the
392 aldehydic C–H bond. Conversely, the temperature dependence of EPB appears to be somewhere
393 intermediate between the alcohols and alkanes. As explained above, there are several potential
394 reasons for this. We note that the C–H bonds are relatively strong directly adjacent to the
395 epoxide ring: 102 and 103 kcal/mol for the tertiary and secondary sites respectively, and the
396 most favourable reaction site is probably the remaining secondary C–H bonds, which possess
397 a BDE of 95.9 kcal/mol.^{42,43} Assuming this to be the case and that the curvature that is observed
398 is indeed associated with the formation of a vdW complex, we can hypothesize that such a
399 configuration would lead to a bicyclic structure such as this:



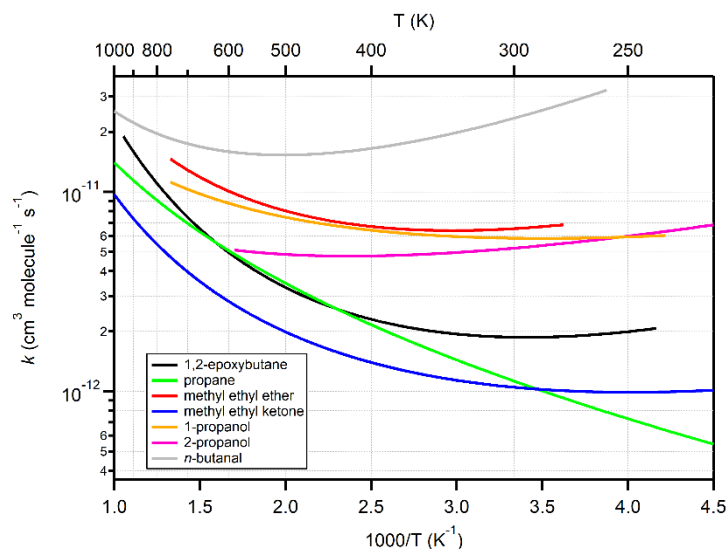
400
401 which would restrict the rotation of the epoxide group, the formation of which is entropically
402 costly and becomes favourable only at low temperatures. We expect that detailed theoretical
403 calculations would be useful in constraining this mechanism further; however, this is outside
404 the scope of the present study. In addition, it would be valuable to obtain quantitative product
405 yield data, especially as a function of temperature, since it has been demonstrated in some
406 oxygenated systems such as *i*-butanol, that a relatively temperature independent region of the

407 Arrhenius diagram can be underlain by several more temperature-dependent reaction channels
408 offsetting each other.⁴⁷

409 With regards to the atmospheric implications of epoxide chemistry, based on the EPB + OH
410 kinetics, it would appear that the epoxide functionality does not enhance reactivity strongly in
411 the tropospheric temperature range, and simple epoxides such as this may react at similar rates
412 to alkanes. For more functionalized epoxides such as the IEPOX derivatives, larger rate
413 coefficients are observed, which is likely to relate to the enhanced reactivity of the functional
414 groups to which the epoxide moiety is attached.^{48,49} It is therefore probable that for simple
415 epoxides and those epoxides that possess deactivating functional groups such as ketones, that
416 acid-catalyzed ring-opening becomes highly competitive with oxidative loss under tropospheric
417 conditions. Conversely, for more functionalized epoxides, reaction with OH may represent an
418 important sink.



419
420 **Figure 6.** Summary of the OH + 1,2-epoxybutane rate coefficients obtained in this work,
421 together with the sole room-temperature literature determination. The line represents an error-
422 weighted fit to all data (see Equation 10). Error bars represent the total combined uncertainties
423 for each determination (see Results section).



424
 425 **Figure 7.** Arrhenius diagram comparing the temperature dependence of the OH + 1,2-
 426 epoxybutane rate coefficient with analogous molecules possessing 8 C–H bonds taken from a
 427 recently compile kinetic database.¹⁵

428 5. Conclusions:

429 Absolute and relative measurements of the rate coefficient of 1,2-epoxybutane + OH have been
 430 determined over a temperature range between 220 and 950 K. Excellent agreement between
 431 these measurements and techniques was observed in their respective regions of overlap. The
 432 high precision of the measurements combined with the large temperature range allows us to
 433 observe the non-Arrhenius behaviour of this rate coefficient. This represents the first epoxide
 434 whose rate coefficient has been measured over an extended temperature range, which provides
 435 new insights into the reactivity of the epoxide functional group. Curvature is observed at the
 436 lower temperatures of this study, which suggests that van der Waals complexes are playing a
 437 role in the reaction mechanism within the tropospheric temperature range. The data obtained
 438 for this simple epoxide suggests that the epoxide moiety itself is not especially reactive, and
 439 that the fate of more functionalized epoxides with respect to bimolecular processes in the
 440 atmosphere is likely to be governed by the reactivity of functional groups to which the epoxide
 441 is attached. Detailed theoretical calculations and quantitative product yield studies would be
 442 useful in understanding the reaction mechanism further.

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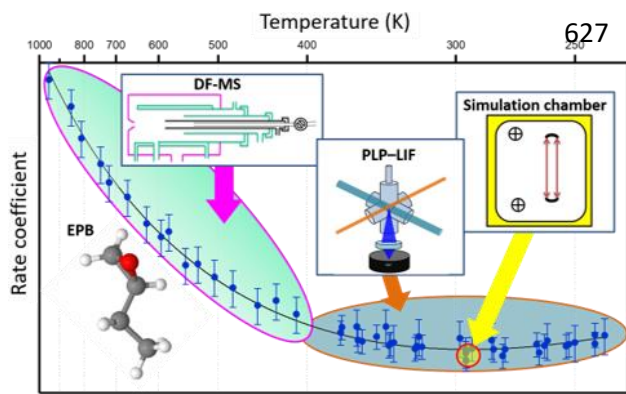
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