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Gas-Phase Rate Coefficients for the Reaction of 3-hydroxy-2-butanone and 4-hydroxy-2-butanone with OH and Cl

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ABSTRACT

The reactions of the OH radicals and the Cl atoms with 3-hydroxy 2-butanone (3H2B) and 4-hydroxy 2-butanone (4H2B) were investigated in the gas-phase using relative rate method. The kinetic study on the OH-reactions was carried out using a Pyrex atmospheric chamber at 600-760 Torr of purified air. The temperature ranges were 298-338 K for 3H2B and 278-333 K for 4H2B. A slight negative dependence of the rate coefficients behavior was observed and the Arrhenius expressions obtained are (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{3\text{H2B}(\text{OH})} = (1.25 \pm 0.20) \times 10^{-12} \exp(612 \pm 50/T)$ and $k_{4\text{HB}(\text{OH})} = (7.50 \pm 2.0) \times 10^{-12} \exp(196 \pm 20/T)$. Rate coefficients for the gas-phase reactions of Cl atoms with 3H2B and 4H2B were measured using an atmospheric simulation chamber made of Teflon at 298 ± 3 K and 760 Torr. The obtained rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were $(4.90 \pm 0.45) \times 10^{-11}$ and $(1.45 \pm 0.15) \times 10^{-10}$ for 3H2B and 4H2B, respectively. The obtained data are presented, compared to those reported in the literature and the reactivity trends discussed. The estimated tropospheric lifetimes obtained in this work suggest that once emitted into the atmosphere, 3H2B and 4H2B will be oxidized near the emission sources.

Keywords

OH radicals, Cl atoms, kinetics, hydroxyketones, Arrhenius expression, Atmospheric lifetimes

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35

36 **1. Introduction**

37 Hydroxycarbonyls, a variety of multi-functional Volatile Organic Compounds (VOCs),
38 are used in a number of industrial sectors namely in food (Rivas et al., 2003), chemicals and
39 pharmaceuticals synthesis (Ichikawa et al., 2005). Furthermore, they are formed in situ in the
40 atmosphere through the oxidation of anthropogenically and naturally emitted VOCs such as
41 alkanes, alkenes, alkynes, oxygenated and carbonyl compounds. For example, the photo-
42 oxidation of diols and branched alcohols leads to the formation of 2-hydroxybutanone and
43 hydroxycarbonyls at 60% and 20% yields, respectively (Bethel et al., 2001; Bethel et al.,
44 2003). β -hydroxycarbonyls are mainly produced from the OH-initiated oxidation of alkenes
45 (Atkinson, 1997a) and 1,4-hydroxycarbonyls can be formed during the oxidation of alkanes
46 (Aschmann et al., 2000; Atkinson et al., 2008).

47 The release of these compounds in the atmosphere may contribute to the formation of
48 other secondary pollutants such as tropospheric ozone and photochemical smog precursors. In
49 common with other carbonyl compounds, the most important atmospheric sinks of
50 hydroxycarbonyls not containing C=C bonds are by daytime reaction with OH and/or by
51 photolysis. The oxidation of these compounds can affect the atmospheric chemistry of
52 radicals and the oxidizing capacity of the atmosphere.

53 Despite the importance of hydroxyketones in atmospheric chemistry and their effect on
54 the production of atmospheric free radicals and photooxidants, very little information exists
55 about the atmospheric fate of longer chain C₄-hydroxyketones (Aschmann et al., 2000; Baker
56 et al., 2004; El Dib et al., 2013; Messaadia et al., 2012). The atmospheric degradation of C₄-
57 hydroxyketones by reactions with oxidants has been studied by Aschmann et al. (2000a),
58 Baker et al. (2004) and El Dib et al. (2013). In the first two studies, the gas phase kinetics of
59 a series of C₄ - hydroxyketones was investigated at room temperature and atmospheric
60 pressure using a relative technique. Aschmann et al. (2000a) have studied the reaction of a
61 series of hydroxyketones including four C₄-hydroxyketones, with OH, NO₃ and O₃. The
62 obtained results indicated that the gas-phase reaction with the OH radical dominates over
63 reactions with NO₃ and that no reactions were observed with O₃. In the study carried out by
64 Baker et al. (2004) two C₄ - hydroxyketones (1-hydroxy 2-butanone and 4-hydroxy 2-
65 butanone) have been identified as products of the reactions of hydroxyaldehydes with OH.
66 The rate coefficient of the reaction of these hydroxyketones with OH has been measured as
67 well. The obtained rate coefficients for 1-hydroxy 2-butanone was found to be in good

68 agreement with the previous study carried out by Aschmann et al. (2000a). However, the rate
69 coefficient obtained by these authors for 4-hydroxy 2-butanone was 42 % higher than that
70 obtained by Aschmann et al. (2000a). In the study carried out by El Dib et al. (2013), the
71 reaction of 4-hydroxy 2-butanone with OH radicals was investigated using the pulsed laser
72 photolysis - laser induced fluorescence technique at room temperature and over the pressure
73 range of 10 to 330 Torr in He and air as diluents gases. An absolute rate coefficient of $(4.8 \pm$
74 $1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined which is lower than those measured by
75 Aschmann et al. (2000a) and Baker et al. (2004) by factors of 40 % and 65%, respectively.

76 The study of the gas-phase atmospheric chemistry of 3H2B is presently limited to only
77 one investigation carried out by Aschmann et al. (2000a) at $294 \pm 2 \text{ K}$ and 740 Torr total
78 pressure of purified air using a relative rate technique.

79 Upper limits of the UV photolysis rates of a series of hydroxyketones have been
80 calculated by Messaadia et al. (2012) using a quantum yield of unity assuming that photolysis
81 might be a loss process for these species. These previous studies showed that the UV
82 photolysis and the gas-phase reaction with the OH radicals are expected to be the dominant
83 tropospheric chemical loss processes for these species. To our knowledge, no data on the
84 reaction of these species with Cl atoms exist in the literature. Thus, to enrich kinetic databases
85 regarding these compounds, we have undertaken the present kinetic study.

86 The purpose of this work is to study the kinetics of two C_4 - hydroxyketones with OH
87 radicals as a function of temperature and with Cl atoms at room temperature. The studied
88 compounds were: 3-hydroxy 2-butanone $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$ (3H2B) where the OH group
89 is in the α position, 4-hydroxy 2-butanone $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$ (4H2B), where the OH group
90 is in the β position.

91 The experiments were conducted using two different experimental systems. The reactions
92 with OH were investigated at GSMA-Reims over the pressure range of 600 to 760 Torr and
93 the temperature ranges of 298-338 K and 278-333 K for 3H2B and 4H2B, respectively. The
94 reactions with Cl atoms were conducted at ICARE-Orléans at $298 \pm 3 \text{ K}$ and 760 Torr of
95 purified air.

96 This work provides the first kinetic data for the reactions of 3H2B and 4H2B with OH as a
97 function of temperature and the first data for the reaction of these species with Cl atoms. The
98 data obtained in this work were used to estimate the effective lifetimes in the troposphere of
99 the studied compounds. The obtained data are presented and compared to those reported in the

100 literature for the studied species and for other hydroxyketones. In addition, the results are
101 discussed in terms of the temperature and the hydroxyl group position effects.

102

103

104 **2. Experimental section**

105 *2.1. Reactions with OH radicals*

106 The reactions of 3H2B and 4H2B with OH radicals were studied using a simulation
107 chamber coupled to a FTIR spectrometer at GSMA-Reims. The set up used is shown in Fig.1.
108 The reactor is a triple-jacket Pyrex cell (length 2m, internal diameter 20 cm) equipped with a
109 multiple reflection system. The first two outer layers delimit a vacuum envelope by using a
110 pump in order to isolate the whole system from its surroundings. The temperature regulation
111 is provided by a fluid (water or ethanol) circulating between the inner wall and the second
112 jacket using a thermostat (Julabo FPW 90). The working temperature range of the thermostat
113 was –between -40 and +100 °C. Platinum resistance temperature sensors were used to provide
114 continuous and simultaneous temperature readings. Meanwhile, the pressure inside the cell
115 was measured by (0 – 1000) Torr MKS Baratron capacitance manometers.

116 The multiple reflection system in the inner chamber is a White cell equipped with three
117 gold mirrors located at both ends of the cell. These mirrors were used to regulate the path
118 length of the probe beam by controlling the number of reflections as detailed below. 24 UV
119 lamps providing radiation of wavelength varying between 300 and 400 nm are symmetrically
120 placed around the reactor to yield a homogeneous photolysis of the reactants. An Equinox 55
121 FT-IR spectrometer provided by Bruker was used to monitor the concentration of the
122 reactants and reference compounds. The spectral resolution was in the range of 2 - 0.5 cm^{-1} in
123 the spectral range 600–4000 cm^{-1} .

124 OH radicals were generated by the photolysis of nitrous acid which was produced in a
125 drop-wise by the addition of 10 % of sulphuric acid to a solution of 0.2 M of sodium nitrite. A
126 small flow of nitrogen gas was used to carry the generated nitrous acid into the reactor. For
127 these experiments, benzaldehyde was used as reference compound.

128 The experimental conditions are summarized in Table 1 used during these measurements.
129 The kinetic studies were performed at different temperatures depending on the vapor
130 pressures of the studied compounds (less than 0.1 Torr for 3H2B as measured during our
131 experiments and in the range of 0.38-11.3 Torr for 4H2B in the temperature range 278-333 K
132 as reported by El Dib et al. (2013)).

133 2.2. *Reactions with Cl atoms*

134 The reactions of 3H2B and 4H2B with Cl atoms were studied using a simulation chamber
135 coupled to a GC-FID at ICARE–Orléans. The experimental procedure has been presented in
136 details by Thevenet et al. (2000), therefore, it will be only described briefly here. Experiments
137 were carried out in a 120 to 180 L Teflon bag at room temperature and atmospheric pressure.
138 The Teflon bag was surrounded by fluorescent black lamps, providing suitable UV radiation
139 with a maximum around 360 nm and positioned in a wooden box with the internal faces
140 covered with aluminum foil. Measured amounts of reagents were flushed from calibrated
141 bulbs into the Teflon bag through a stream of ultra pure air. The reactor was then filled to its
142 full capacity at atmospheric pressure with ultra pure air. Photolysis of Cl₂ at 300-400 nm was
143 used as the source of Cl atoms. A gas chromatograph equipped with flame ionization detector
144 (GC-FID, CP-3800 Varian) was used for the quantitative analysis of the reactants.
145 Chromatographic separation was achieved by using a DB-1 capillary column (J&W
146 Scientific. 30 m. 0.25 mm id. 5 μm Film). The column was operated between 333 and 353 K
147 and helium was used as carrier gas. The kinetics started with the lighting of the lamps. The
148 experimental conditions were varied in order to validate our measurements. In fact, the
149 number of lamps was varied from 2 to 6 depending of the reactivity of the studied compound.
150 The concentrations of the studied hydroxyketone and the reference compounds were chosen
151 according to the ratio of their reactivities with chlorine atoms. The introduced reagent
152 quantities (in molecule cm⁻³) and the experimental conditions are summarized in Table 2.
153 Four different reference compounds were used: ethane C₂H₆, cyclohexane C₆H₁₂, dioxolane
154 C₃H₆O₂ and ethyl formate C₃H₆O₂.

155 It is to be noted that the reference compounds were chosen in such a way that their rate
156 coefficients are well defined in the literature. In addition to these constraints, the reference
157 compound should have a FTIR spectrum and a retention time (for FTIR and GC FID,
158 respectively) sufficiently different from that of the investigated hydroxyketones.

159 Before starting the kinetic study with OH and Cl, two tests were carried out to check:

160 • that in the absence of the radical precursor, the studied hydroxyketones are not
161 photolysed in the spectral range used to generate OH (Cl). The tests showed that the variation
162 of the concentrations of the studied compounds was lower than 2 %.

163 • the stability of the gas mixture concentrations in the absence of irradiation. This test
164 showed a good stability and a negligible effect of the losses on the walls for measurements
165 above 298 K as discussed in Section “Results”.

166 The measurements were performed in purified air provided by Air Liquide (> 99.9999%).
 167 The used reagents were obtained from the following sources: C₂H₆ (99.999%) and Cl₂
 168 (99.5%) provided by Air Liquide, C₆H₅CHO (99.5%), cyclohexane (99.5%), dioxolane (99%)
 169 and ethyl formate (97%), 3-hydroxy 2-butanone (99%), 4-hydroxy 2-butanone (95%)
 170 provided from Aldrich. They were further purified by repeated freeze-pump-thaw cycles
 171 before use.

172

173 3. Results

174 The rate coefficients of the following reactions have been measured:



179 The rate coefficients of the reactions with the reference compounds used in this study are
 180 (in cm³molecule⁻¹s⁻¹): k_(benzaldehyde+OH) = (5.33×10⁻¹² exp((2020±710)/RT) (Semadeni et al.,
 181 1994); k_(ethane+Cl) = (4.80 ± 1) ×10⁻¹¹ (Anderson et al., 2007); k_(cyclohexane+Cl) = (3.83 ± 0.12) ×
 182 10⁻¹⁰ (Anderson et al., 2007); k_(dioxolane+Cl) = (1.67 ± 0.09) ×10⁻¹⁰ (Sauer et al., 1999);
 183 k_(ethyl-formate+Cl) = (1.34 ± 0.15)×10⁻¹¹ (Notario et al., 1998).

184 In relative kinetic experiments the following reactions take place:



187 As mentioned above, no loss on the wall or by photolysis was observed during the tests prior
 188 to the measurements at temperatures above 298 K. Therefore, the reaction with the oxidant
 189 (OH or Cl) is the only sink for the hydroxyketone and the reference compounds. Hence, it can
 190 be shown that:

191
$$\ln \frac{[\text{hydroxyketone}]_0}{[\text{hydroxyketone}]_t} = \frac{k_{\text{hydroxyketone}}}{k_{\text{ref}}} \times \frac{[\text{ref}]_0}{[\text{ref}]_t} \quad (\text{I})$$

192 where [hydroxyketone]₀, [hydroxyketone]_t, [ref]₀ and [ref]_t are the concentrations of the
 193 reagents before irradiation and at time t respectively and k_{hydroxyketone} is the rate coefficient of
 194 the reaction of the studied reagents with the oxidant (OH or Cl), k_{ref} is the rate coefficient of
 195 the reference compounds with the oxidant (OH or Cl).

196 The plot of $\ln \frac{[\text{hydroxyketone}]_0}{[\text{hydroxyketone}]_t}$ vs. $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t}$ should be a straight line that pass through
 197 the origin with a slope equal to $\frac{k_{\text{hydroxyketone}}}{k_{\text{ref}}}$.

198 The obtained data are presented in the form $\ln \frac{[\text{hydroxyketone}]_0}{[\text{hydroxyketone}]_t}$ vs. $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t}$ as can be
 199 seen in Fig. 2a - 2b and Fig. 3a - 3b for the reactions with OH and Cl of 3H2B and 4H2B,
 200 respectively.

201 A slight decrease in the 4H2B concentration was observed however at 278 K in absence of
 202 the oxidant indicating a loss on the chamber wall which might be due to the low vapor
 203 pressure of 4H2B (≈ 0.4 Torr at 278 K, (El Dib et al., 2013)). Therefore, the rate coefficient of
 204 the reaction of 4H2B with OH at 278 K was extracted using the following relation:

$$205 \quad \frac{1}{(t-t_0)} \ln \frac{[4H2B]_{t_0}}{[4H2B]_t} = \frac{k_{4H2B(OH)}}{k_{ref}} \cdot \frac{1}{(t-t_0)} \ln \frac{[Ref]_{t_0}}{[Ref]_t} + (k' - \frac{k_{4H2B(OH)}}{k_{ref}} k'_{ref}) \quad (II)$$

207 where $[4H2B]_0$ and $[Ref]_0$ are the initial concentrations of 4H2B and the reference compound
 208 at time t_0 , respectively; $[4H2B]_t$ and $[ref]_t$ are the concentrations of 4H2B and the reference
 209 compound at time t . $k_{4H2B(OH)}$ and k_{ref} are the rate coefficients of the reactions of OH with
 210 4H2B and the reference compound. k' and k'_{ref} represent the pseudo-first order rate
 211 coefficients of the secondary reactions of both compounds, such as wall losses. Fig. 2c
 212 represents the plots of $\ln([4H2B]_{t_0}/[4H2B]_t)/(t-t_0)$ vs $\ln([Ref]_{t_0}/[Ref]_t)/(t-t_0)$ where the
 213 consumption of 4H2B due to the loss on the wall is taken into account.

214 In all figures, good linearity is observed with a correlation coefficient greater than 92%.
 215 The rate coefficients obtained are summarized in Table 3. The Arrhenius equations for the
 216 reactions with OH and the average rate coefficients for the reactions with Cl atoms were as
 217 follows (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$218 \quad k_{3H2B(OH)} = (1.25 \pm 0.20) \times 10^{-12} \exp(612 \pm 50/T)$$

$$219 \quad k_{4H2B(OH)} = (7.5 \pm 2.0) \times 10^{-12} \exp(196 \pm 20/T)$$

$$220 \quad k_{3H2B(Cl)} = (4.90 \pm 0.45) \times 10^{-11}$$

$$221 \quad k_{4H2B(Cl)} = (1.45 \pm 0.15) \times 10^{-10}$$

222 The results given above are derived from the average of 3 to 6 independent measurements.
 223 For each point in Fig.2-3, the error bar indicates the systematic errors due to uncertainties on
 224 the experimental conditions as described in section "Error analysis". The overall uncertainties

225 on the rate coefficient values incorporate both statistical errors due to the fit and systematic
226 errors due to experimental conditions. This point will be discussed in the following section.

227

228 4. Discussion

229 4.1. Error analysis

230 The overall error in the rate coefficient values reported in this work arises from two different
231 types of error: (i) Random errors are caused by unknown and unpredictable changes in the
232 experiment that mainly occur in the measuring instruments. These errors are reduced by
233 averaging multiple experiments and their contribution is smaller than that of systematic errors.
234 (ii) Systematic errors are due to methodological, instrumental and personal mistakes. In this
235 work, the errors on the measured rate coefficients errors are determined using the error
236 propagation method according to equation III:

$$237 \quad \Delta k_{hydroxyketone} = k_{hydroxyketone} \times \left[\left(\frac{\Delta k_{ref}}{k_{ref}} \right)^2 + \left[\frac{\Delta \left(\frac{k_{hydroxyketone}}{k_{ref}} \right)}{\frac{k_{hydroxyketone}}{k_{ref}}} \right]^2 \right]^{1/2} \quad (III)$$

238 Where $\left(\frac{\Delta k_{ref}}{k_{ref}} \right)$ and $\left(\Delta \left(\frac{k_{hydroxyketone}}{k_{ref}} \right) / \left(\frac{k_{hydroxyketone}}{k_{ref}} \right) \right)$ are the relative errors on k_{ref} and

239 $\frac{k_{hydroxyketone}}{k_{ref}}$, respectively.

240 the errors sources mainly come from:

241 • the determination of k_{ref} : This error found in the literature, varies from 3 to
242 20% according to the used reference compound.

243 • the determination of the ratio $\frac{k_{hydroxyketone}}{k_{ref}}$. This parameter represents the slope of

244 the plot of $\ln \frac{[Hydroxyketone]_0}{[Hydroxyketone]_t}$ vs. $\ln \frac{[ref]_0}{[ref]_t}$.

245 This slope is determined directly from experimental data points. The error of this parameter is
246 mainly influenced by the analytical technique used to monitor the reagents' concentrations. In
247 fact, for the reaction with OH radicals, the uncertainty on the slope $k_{hydroxyketone}/k_{ref}$ depends
248 mainly on the errors related to the measurements of the areas of spectroscopic peaks,
249 corresponding to both the analyte and the reference compound. In order to minimize this error

250 a large number of spectra (30 to 70) were collected at different time intervals for each
251 experiment. For the reaction with Cl atoms, the uncertainty on the slope is related to the areas
252 of the chromatograms peaks corresponding to the reagents. In order to minimize this
253 uncertainty, several preliminary tests were carried out. This enabled us to optimize the
254 experimental conditions such as the column temperature and the selection of the reference
255 compound and to have relatively intense chromatograms peaks. Moreover, for each
256 experiment, a large number of samples (20-40) were analyzed in order to minimize the error
257 on the determination of the slope.

258

259 *4.2. Comparison with previous studies*

260 The study of the gas-phase atmospheric chemistry of 3H2B with OH radicals is
261 presently limited to only one investigation carried out by Aschmann et al. (2000a) at 294 ± 2
262 K and 740 Torr total pressure of purified air using a relative rate method. The rate coefficient
263 obtained by these authors $(1.03 \pm 0.22) \times 10^{-11}$ in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined by using
264 n-octane as reference compound. Our value is in good agreement with this determination with
265 a difference less than 5%.

266 The room temperature rate coefficient for the reaction of 4H2B with OH radicals has been
267 reported in three previous studies (Aschmann et al., 2000a; Baker et al., 2004; El Dib et al.,
268 2013). Aschmann et al. (2000a) measured a rate coefficient of $(8.1 \pm 1.8) \times 10^{-12} \text{ cm}^3$
269 $\text{ molecule}^{-1} \text{ s}^{-1}$ whereas Baker et al. (2004) obtained a larger rate coefficient of (13.9 ± 2.8)
270 $\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Both studies have been conducted at 740 Torr and 296 K in purified
271 air using a relative method. The rate coefficient obtained in the present work is found to be
272 very close to that reported by Baker et al. (2004) ($\approx 7\%$) and larger than that measured by
273 Aschmann et al. (2000a) by a factor of 38%.

274 In the study carried out by El Dib et al. (2013) using an absolute method, a rate
275 coefficient of $(4.8 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is reported. This value is lower than our
276 value by a factor of 63 %. The accuracy of the results obtained in absolute methods might be
277 limited by the concentration measurement. In fact, a potential source of discrepancy could be
278 an overestimation of the 4H2B concentration in the experiment carried out by El Dib et al.
279 (2013) which would result in an underestimation of the rate coefficient. However, as stated by
280 the authors, no loss of 4H2B has been observed during its introduction into the main reactor
281 due either to possible loss to the wall or to the photodissociation. In addition, the kinetics of
282 4-hydroxy 4-methyl 2-pentanone (4H4M2P) with OH has been carried out recently by these
283 authors at 298K in the gas phase using the same technique as that used for 4H2B. 4H4M2P

284 has a vapor pressure very close to that of 4H2B. The obtained value was found to be in good
285 agreement with the three values reported in the literature and determined by using a relative
286 method. In light of the above explanation, at this time, we cannot identify any potential
287 systematic error that might be the source of this discrepancy with the absolute value reported
288 by El Dib et al. (2013).

289 Until now, no kinetic data are reported in the literature for the reaction of 3H2B and 4H2B
290 with OH radicals as a function of temperature.

291 Our experimental values were compared to calculated values obtained by using
292 (AOPWIN,2000) v.1.92 based on SAR calculations. A rate coefficient of $5.9 \times 10^{-12} \text{ cm}^3$
293 $\text{molecule}^{-1} \text{ s}^{-1}$ was obtained for the reaction of 3H2B with OH. This value is lower than our
294 experimental value by a factor of 44%. The calculated rate coefficient ($1.39 \times 10^{-11} \text{ cm}^3$
295 $\text{molecule}^{-1} \text{ s}^{-1}$) for the reaction of 4H2B with OH was however in very good agreement with
296 our measurement.

297 Up to now, there is no published study on the reaction of chlorine atoms with 3H2B and
298 4H2B.

299

300 4.3. Temperature effect

301 In the temperature range explored in this work, a slight variation of the rate coefficient
302 with the temperature was observed for the reactions of OH with 3H2B and 4H2B. With non-
303 linear least-squares fitting routine, the following Arrhenius expression is obtained (cm^3
304 $\text{molécule}^{-1} \text{ s}^{-1}$):

$$305 \quad k_{3\text{H2B}(\text{OH})} = (1.25 \pm 0.20) \times 10^{-12} \exp(612 \pm 50/T)$$

$$306 \quad k_{4\text{H2B}(\text{OH})} = (7.5 \pm 2.0) \times 10^{-12} \exp(196 \pm 20/T)$$

307 For both reactions, the rate coefficient shows negative temperature dependence. This indicates
308 that the reaction is carried out initially without activation energy barrier. This trend shows that
309 the processes involved in this reaction are a succession of elementary steps involving unstable
310 intermediate complexes.

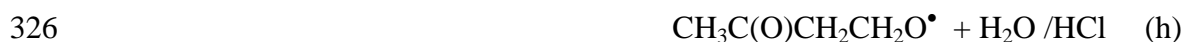
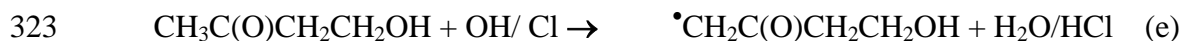
311 4.4. Mechanism and Effect of the structure on the reactivity

312 As for other aliphatic ketones or alcohols, the reaction of 3H2B and 4H2B with OH
313 radicals and Cl atoms are expected to proceed mainly by H-abstraction process from different
314 sites as follows:





319 SAR calculations based on the structure / reactivity relationship using AOPWIN model,
 320 (AOPWIN, 2000) were done for the reaction of 3H2B with OH. The results estimate that the
 321 contribution of each reaction pathway (a), (b), (c) and (d) are respectively 0.5%, 2.5%, 94%
 322 and 3%.



327 SAR calculations showed that the contribution of each reaction pathway (e), (f), (g) and
 328 (h) for the reaction of 4H2B with OH are respectively: 0.8%, 1.2%, 92% and 6% showing that
 329 the reaction of 4H2B with OH radicals proceeds mainly by H-abstraction from the C-H bonds
 330 in the β position to carbonyl group.

331 The dominant pathways (c and g) may lead to the formation of dicarbonyl products such
 332 as 2,3-butanedione from the oxidation of 3H2B with OH and 3-oxobutanal from the oxidation
 333 of 4H2B with OH. For the reaction with Cl atoms, chlorine atoms are less selective than OH
 334 radicals and the contribution of H-atom abstraction in Cl atoms would be more spread out
 335 than that for OH. Therefore, a mechanistic study would be of great interest in order to
 336 facilitate the comprehension of these results.

337 The Cl reactivity of the hydroxyketones investigated here is lower by a factor of 1.5
 338 and 3 than that of the corresponding alcohols showing the deactivating effect of the carbonyl
 339 group (Table 4). However, no significant effect of the carbonyl group on the reactivity with
 340 OH was observed in comparison between the studied hydroxyketones to the corresponding
 341 alcohols (Table 4). Additionally, as for other C₄-hydroxyketones studied by Aschmann et al.
 342 (2000a), the rate coefficients obtained in this work at 298 K for reactions with OH are lower
 343 than those for C₅-C₈ hydroxyketones (except for 1-hydroxy 4-heptanone). As expected, the
 344 comparison shows that the reactivity of these species with OH increases with the chain length.
 345 Until now, there is no study concerning the Cl reactivity with $\geq\text{C}_4$ -hydroxyketones. Our
 346 values are therefore compared to the rate coefficient of the reaction of hydroxyacetone with
 347 Cl (5.6 ± 0.7) $\times 10^{-11}$ cm³ molécul⁻¹ s⁻¹ reported by Orlando et al. (1999). This comparison
 348 shows an increasing of the reactivity with the carbon chain length.

349 The rate coefficients for 3H2B and 4H2B obtained in this work compared to that of 2-
350 butanone ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$) suggests that the reactions with OH proceed via H-abstraction
351 of the weakest C–H bond on the $-\text{CH}_2\text{OH}$ group activated by the presence of the $-\text{OH}$
352 substituent group. Further, the position of the hydroxyl group relative to the carbonyl group
353 was found to affect the kinetics of the studied reactions. Indeed, the rate coefficients of the
354 oxidation of 4H2B by OH are higher than those for 3H2B. This shows that the carbonyl group
355 deactivate the H-abstraction from the C-H bond located in the α position and activate that
356 located in the β position.

357

358 **5. Atmospheric implication**

359 The tropospheric lifetimes due to reactions with OH and Cl were estimated according to
360 the equation $\tau = 1/k[X]$ where $[X]$ represents the average concentration of the oxidant and k the
361 rate coefficient for the reaction of the studied compounds with the oxidant. The rate
362 coefficients obtained in this work were combined with the average tropospheric concentration
363 of OH radicals and Cl atoms to assess the major atmospheric loss process of 3H2B and 4H2B
364 and their atmospheric lifetimes. The lifetimes were calculated by using 24 hours daytime
365 average global tropospheric concentration of 1×10^6 molecule cm^{-3} (Atkinson et al., 1997b) and
366 1×10^3 molecule cm^{-3} (Singh et al., 1996) for OH radicals and Cl atoms respectively.

367 In the atmosphere, another removal source of the studied compounds can be
368 photodissociation due to sun light. The absorption cross sections of these species have been
369 measured by Messaadia et al. (2012) and their upper limits of photodissociation rate
370 coefficients (J_p) have been calculated using their cross section measurements and assuming a
371 quantum yield of unity. Therefore, the calculated lifetimes (see Table 5) have to be considered
372 as lower limits since the photolysis quantum yields could be much lower than unity. The
373 reactivity of 3H2B and 4H2B towards NO_3 radicals and O_3 has been investigated by
374 Aschmann et al. (2000a), by using a relative technique. A lower limit of 150 days for the
375 tropospheric lifetime of these species due to their reaction with O_3 is reported. This shows
376 that the contribution of the reaction with O_3 in the atmospheric fate of the studied compounds
377 is negligible. In Table 5, the lifetimes of 3H2B and 4H2B due to OH and Cl calculated in this
378 work are compared to those due to NO_3 and O_3 and photolysis.

379 The obtained lifetimes of 3H2B and 4H2B due to reactions with OH (~ 1 day) indicate
380 that the gas-phase reaction with the OH will dominate over the other chemical processes.
381 Photolysis seems to be an important loss process for 3H2B and 4H2B provided that the
382 assumption with respect to the quantum yield is correct, and then it could be more important

383 than the degradation by chemical reactions. However, the reactions with Cl atoms could be an
384 important loss process for these species in coastal areas where the concentration of Cl atoms
385 reaches 1×10^5 molecule cm^{-3} (Spicer et al., 1998).

386

387 **6. Conclusion**

388 The kinetics of the reaction of 3-hydroxy-2-butanone and 4-hydroxy-2-butanone with
389 respect to reaction with OH radicals and Cl atoms was investigated using relative method. The
390 obtained data showed that the reaction of the studied compounds with Cl atoms proceeds
391 more rapidly than that with OH radicals. The reactivity of these species was found to be
392 sensitive to the structure of hydroxyketones and to be activated by the presence of the
393 hydroxyl group. Slight negative temperature dependence was observed for the reactions of
394 3H2B and 4H2B with OH showing that the processes involved in these reactions are a
395 succession of elementary steps involving unstable intermediate complexes.

396 The atmospheric lifetimes of the studied compounds were calculated with respect to OH
397 and Cl using rate coefficients at room temperature obtained in this work. The calculated
398 tropospheric lifetime suggests that once emitted into the atmosphere, 3H2B and 4H2B can be
399 degraded quite rapidly (~ 1 day) and thus contribute to the photochemical pollution in a local
400 or regional scale.

401 This work represents the first reported kinetic study of the reaction of OH radicals with
402 hydroxyketones as a function of temperature and the first kinetic study of the reaction of Cl
403 with these species ever obtained. However, a detailed mechanistic study of the reaction with
404 OH radicals and Cl atoms is required to provide a much improved understanding of the
405 mechanism of the reaction of OH and Cl with hydroxyketones and the temperature
406 dependence.

407

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