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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 $cm^3$ $molecule^{-1}$ $s^{-1}$): $k_{3H2B(OH)} = (1.25\pm0.20)\times 10^{-12}\exp(612\pm50/T)$ and $k_{4HB\,(OH)} = (7.50\pm 2.0)\times10^{-12}\exp(196\pm20/T)$. 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 $cm^3$ $molecule^{-1}$ $s^{-1}$) were $(4.90\pm 0.45)\times10^{-11}$ and $(1.45\pm 0.15)\times10^{-10}$ 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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## 1. Introduction

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

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

Despite the importance of hydroxyketones in atmospheric chemistry and their effect on the production of atmospheric free radicals and photooxidants, very little information exists about the atmospheric fate of longer chain $C_4$-hydroxyketones (Aschmann et al., 2000; Baker et al., 2004; El Dib et al., 2013; Messaadia et al., 2012). The atmospheric degradation of $C_4$-hydroxyketones by reactions with oxidants has been studied by Aschmann et al. (2000a), Baker et al. (2004) and El Dib et al.( 2013). In the first two studies, the gas phase kinetics of a series of $C_4$ - hydroxyketones was investigated at room temperature and atmospheric pressure using a relative technique. Aschmann et al. (2000a) have studied the reaction of a series of hydroxyketones including four $C_4$-hydroxyketones, with OH, $NO_3$ and $O_3$. The obtained results indicated that the gas-phase reaction with the OH radical dominates over reactions with $NO_3$ and that no reactions were observed with $O_3$. In the study carried out by Baker et al. (2004) two $C_4$ - hydroxyketones (1-hydroxy 2-butanone and 4-hydroxy 2-butanone) have been identified as products of the reactions of hydroxyaldehydes with OH. The rate coefficient of the reaction of these hydroxyketones with OH has been measured as well. The obtained rate coefficients for 1-hydroxy 2-butanone was found to be in good

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

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

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

The purpose of this work is to study the kinetics of two $C_4$ - hydroxyketones with OH radicals as a function of temperature and with Cl atoms at room temperature. The studied compounds were: 3-hydroxy 2-butanone $CH_3C(O)CH(OH)CH_3$ (3H2B) where the OH group is in the $\alpha$ position, 4-hydroxy 2-butanone $CH_3C(O)CH_2CH_2OH$ (4H2B), where the OH group is in the $\beta$ position.

The experiments were conducted using two different experimental systems. The reactions with OH were investigated at GSMA-Reims over the pressure range of 600 to 760 Torr and the temperature ranges of 298-338 K and 278-333 K for 3H2B and 4H2B, respectively. The reactions with Cl atoms were conducted at ICARE-Orléans at 298±3K and 760 Torr of purified air.

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

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

## 2. Experimental section

*2.1. Reactions with OH radicals*

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

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

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

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

*2.2. Reactions with Cl atoms*

The reactions of 3H2B and 4H2B with Cl atoms were studied using a simulation chamber coupled to a GC-FID at ICARE–Orléans. The experimental procedure has been presented in details by Thevenet et al. (2000), therefore, it will be only described briefly here. Experiments were carried out in a 120 to 180 L Teflon bag at room temperature and atmospheric pressure. The Teflon bag was surrounded by fluorescent black lamps, providing suitable UV radiation with a maximum around 360 nm and positioned in a wooden box with the internal faces covered with aluminum foil. Measured amounts of reagents were flushed from calibrated bulbs into the Teflon bag through a stream of ultra pure air. The reactor was then filled to its full capacity at atmospheric pressure with ultra pure air. Photolysis of $Cl_2$ at 300-400 nm was used as the source of Cl atoms. A gas chromatograph equipped with flame ionization detector (GC-FID, CP-3800 Varian) was used for the quantitative analysis of the reactants. Chromatographic separation was achieved by using a DB-1 capillary column (J&W Scientific. 30 m. 0.25 nm id. 5 μm Film). The column was operated between 333 and 353 K and helium was used as carrier gas. The kinetics started with the lighting of the lamps. The experimental conditions were varied in order to validate our measurements. In fact, the number of lamps was varied from 2 to 6 depending of the reactivity of the studied compound. The concentrations of the studied hydroxyketone and the reference compounds were chosen according to the ratio of their reactivities with chlorine atoms. The introduced reagent quantities (in molecule $cm^{-3}$) and the experimental conditions are summarized in Table 2. Four different reference compounds were used: ethane $C_2H_6$, cyclohexane $C_6H_{12}$, dioxolane $C_3H_6O_2$ and ethyl formate $C_3H_6O_2$..

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

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

- that in the absence of the radical precursor, the studied hydroxyketones are not photolysed in the spectral range used to generate OH (Cl). The tests showed that the variation of the concentrations of the studied compounds was lower than 2 %.
- the stability of the gas mixture concentrations in the absence of irradiation. This test showed a good stability and a negligible effect of the losses on the walls for measurements above 298 K as discussed in Section “Results”.

The measurements were performed in purified air provided by Air Liquide (> 99.9999%). The used reagents were obtained from the following sources: $C_2H_6$ (99.999%) and $Cl_2$ (99.5%) provided by Air Liquide, $C_6H_5CHO$ (99.5%), cyclohexane (99.5%), dioxolane (99%) and ethyl formate (97%), 3-hydroxy 2-butanone (99%), 4-hydroxy 2-butanone (95%) provided from Aldrich. They were further purified by repeated freeze-pump-thaw cycles before use.

## 3. Results

The rate coefficients of the following reactions have been measured:

| | | |
|---|---|---|
| OH + 3H2B → products | (1) | $k_{3H2B\ (OH)}$ at (298-338 K) |
| OH + 4H2B → products | (2) | $k_{4H2B\ (OH)}$ at (278-333 K) |
| Cl + 3H2B → products | (3) | $k_{3H2B\ (Cl)}$ at (298 K) |
| Cl + 4H2B → products | (4) | $k_{4H2B\ (Cl)}$ at (298K) |

The rate coefficients of the reactions with the reference compounds used in this study are (in $cm^3molecule^{-1}s^{-1}$): $k_{(benzaldehyde+OH))}$ = $(5.33\times10^{-12}\exp((2020\pm710)/RT)$ (Semadeni et al., 1994); $k_{(ethane+Cl)}$ = $(4.80 \pm 1) \times10^{-11}$ (Anderson et al., 2007); $k_{(cyclohexane+Cl)}$ = $(3.83 \pm 0.12) \times 10^{-10}$ (Anderson et al., 2007) ; $k_{(dioxolane+Cl)}$ = $(1.67 \pm 0.09) \times10^{-10}$ (Sauer et al., 1999) ; $k_{(ethyl\text{-}formate+Cl)}$ = $(1.34 \pm 0.15)\times10^{-11}$ (Notario et al., 1998).

In relative kinetic experiments the following reactions take place:

| | |
|---|---|
| Oxidant (OH or Cl) + hydroxyketone → products | $k_{hydroxyketone}$ |
| Oxidant (OH or Cl)+ reference → products | $k_{ref}$ |

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

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

where $[hydroxyketone]_0$, $[hydroxyketone]_t$, $[ref]_0$ and $[ref]t$ are the concentrations of the reagents before irradiation and at time t respectively and $k_{hydroxyketone}$ is the rate coefficient of the reaction of the studied reagents with the oxidant (OH or Cl), $k_{ref}$ is the rate coefficient of the reference compounds with the oxidant (OH or Cl).

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

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

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

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

where $[4H2B]_0$ and $[Ref]_0$ are the initial concentrations of 4H2B and the reference compound at time $t_0$, respectively; $[4H2B]_t$ and $[ref]_t$ are the concentrations of 4H2B and the reference compound at time t. $k_{4H2B\,(OH)}$ and $k_{ref}$ are the rate coefficients of the reactions of OH with 4H2B and the reference compound. k' and $k'_{ref}$ represent the pseudo-first order rate coefficients of the secondary reactions of both compounds, such as wall losses. Fig. 2c represents the plots of $\ln([4H2B_{t0}/[4H2B]_t)/(t-t_0)$ vs $\ln([Ref]_{t0}/[Ref]_t)/(t-t_0)$ where the consumption of 4H2B due to the loss on the wall is taken into account.

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

$$k_{3H2B\,(OH)} = (1.25\pm 0.20)\times10^{-12}\exp(612\pm50/T)$$

$$k_{4H2B\,(OH)} = (7.5\pm 2.0)\times10^{-12}\exp(196\pm20/T)$$

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

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

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

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

## 4. Discussion

*4.1. Error analysis*

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

$$\Delta k_{hydroxykeone} = k_{hydroxykeone} \times \left[ \left( \frac{\Delta k_{ref}}{k_{ref}} \right)^2 + \left[ \frac{\Delta \left( \frac{k_{hydroxykeone}}{k_{ref}} \right)}{\frac{k_{hydroxykeone}}{k_{ref}}} \right]^2 \right]^{1/2} \qquad \text{(III)}$$

Where $\left( \frac{\Delta k_{ref}}{k_{ref}} \right)$ and $\left( \Delta \left( \frac{k_{hydroxykeone}}{k_{ref}} \right) / \left( \frac{k_{hydroxykeone}}{k_{ref}} \right) \right)$ are the relative errors on $k_{ref}$ and $\frac{k_{hydroxykeone}}{k_{ref}}$, respectively.

the errors sources mainly come from:

- the determination of $k_{ref}$: This error found in the literature, varies from 3 to 20% according to the used reference compound.
- the determination of the ratio $\frac{k_{hydroxykeone}}{k_{ref}}$. This parameter represents the slope of the plot of $\ln \frac{[Hydroxyketone]_0}{[Hydroxyketone]_t}$ vs. $\ln \frac{[ref]_0}{[ref]_t}$.

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

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

*4.2. Comparison with previous studies*

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

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

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

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

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

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

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

*4.3. Temperature effect*

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

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

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

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

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

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

$$CH_3C(O)CH(OH)CH_3 + OH / Cl \rightarrow \quad {}^{\bullet}CH_2C(O)CH(OH)CH_3 + H_2O / HCl \qquad (a)$$

$CH_3C(O)CH(O^{\bullet})CH_3 + H_2O$ /HCl (b)

$CH_3C(O)C^{\bullet}(OH)CH_3 + H_2O$/ HCl (c)

$CH_3C(O)CH(OH)CH_2^{\bullet} + H_2O$ / HCl (d)

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

$CH_3C(O)CH_2CH_2OH$ + OH/ Cl → $^{\bullet}CH_2C(O)CH_2CH_2OH + H_2O$/HCl (e)

$CH_3C(O)CH^{\bullet}CH_2OH + H_2O$/HCl (f)

$CH_3C(O)CH_2CH^{\bullet}OH + H_2O$/HCl (g)

$CH_3C(O)CH_2CH_2O^{\bullet} + H_2O$ /HCl (h)

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

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

The Cl reactivity of the hydroxyketones investigated here is lower by a factor of 1.5 and 3 than that of the corresponding alcohols showing the deactivating effect of the carbonyl group (Table 4). However, no significant effect of the carbonyl group on the reactivity with OH was observed in comparison between the studied hydoxyketones to the corresponding alcohols (Table 4). Additionally, as for other $C_4$-hydroxyketones studied by Aschmann et al. (2000a), the rate coefficients obtained in this work at 298 K for reactions with OH are lower than those for $C_5$-$C_8$ hydroxyketones (except for 1-hydroxy 4-heptanone). As expected, the comparison shows that the reactivity of these species with OH increases with the chain length. Until now, there is no study concerning the Cl reactivity with $\geq C_4$-hydroxyketones. Our values are therefore compared to the rate coefficient of the reaction of hydroxyacetone with Cl $(5.6 \pm 0.7)\times10^{-11}$ $cm^3$ $molécule^{-1}$ $s^{-1}$ reported by Orlando et al. (1999). This comparison shows an increasing of the reactivity with the carbon chain length.

The rate coefficients for 3H2B and 4H2B obtained in this work compared to that of 2-butanone ($CH_3C(O)CH_2CH_3$) suggests that the reactions with OH proceed via H-abstraction of the weakest C–H bond on the -$CH_2OH$ group activated by the presence of the -OH substituent group. Further, the position of the hydroxyl group relative to the carbonyl group was found to affect the kinetics of the studied reactions. Indeed, the rate coefficients of the oxidation of 4H2B by OH are higher than those for 3H2B. This shows that the carbonyl group deactivate the H-abstraction from the C-H bond located in the α position and activate that located in the β position.

## 5. Atmospheric implication

The tropospheric lifetimes due to reactions with OH and Cl were estimated according to the equation $\tau = 1/k[X]$ where [*X*] represents the average concentration of the oxidant and *k* the rate coefficient for the reaction of the studied compounds with the oxidant. The rate coefficients obtained in this work were combined with the average tropospheric concentration of OH radicals and Cl atoms to assess the major atmospheric loss process of 3H2B and 4H2B and their atmospheric lifetimes. The lifetimes were calculated by using 24 hours daytime average global tropospheric concentration of $1\times10^6$ molecule $cm^{-3}$ (Atkinson et al., 1997b) and $1\times10^3$ molecule $cm^{-3}$ (Singh et al., 1996) for OH radicals and Cl atoms respectively.

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

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

than the degradation by chemical reactions. However, the reactions with Cl atoms could be an important loss process for these species in coastal areas where the concentration of Cl atoms reaches $1\times10^{5}$ molecule $cm^{-3}$ (Spicer et al., 1998).

## 6. Conclusion

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

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

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

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