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1 **Reactivity of 3-hydroxy-3-methyl-2-butanone: Photolysis**
2 **and OH reaction kinetics**

3
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Abstract

Hydroxycarbonyl compounds are important secondary reaction products in the oxidation of Volatile Organic Compounds (VOCs) in the atmosphere. The atmospheric fate of these oxygenated VOCs is however poorly understood, especially the relevance of the photolytic pathway. In this work, a combined investigation of the photolysis and temperature-dependent OH radical reaction of 3-hydroxy-3-methyl-2-butanone (3H3M2B) is presented. A photolysis lifetime of about 4-5 days was estimated with a global quantum yield of 0.10. The OH reaction rate coefficient follows the Arrhenius trend (298 – 356 K) and could be modelled through the following expression: $k_{3H3M2B}(T) = (5.12 \pm 0.07) \times 10^{-12} \exp(-563 \pm 119/T)$ in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. A 3H3M2B atmospheric lifetime of 15 days towards the OH radical was evaluated. Our results showed that the photolysis pathway is the major degradation channel for 3H3M2B. Photolysis products were identified and quantified in the present work with a carbon balance of around 80% enabling a reaction mechanism to be proposed. The present work underlines the need for further studies on the atmospheric chemistry of oxygenated VOCs.

Keywords: 3-hydroxy-3-methyl-2-butanone, photolysis, kinetics, OH radicals, tropospheric lifetimes

56 1. Introduction

57 Oxygenated Volatile Organic Compounds (OVOCs) are critical components in
58 the chemistry of the troposphere. These species constitute a large family of Volatile
59 Organic Compounds (VOCs) (Atkinson et al., 2003) emitted from various
60 anthropogenic and biogenic sources. More importantly, they are formed *in situ* as
61 intermediates of photooxidation of several VOCs. Though scarce measurement data
62 exist on the concentrations of multi oxygenated VOCs (e.g. (Matsunaga et al., 2000;
63 Destailats et al., 2002; Spaulding et al., 2002)), evidence has been gained in the last
64 decade for a significant role played by such compounds in atmospheric chemistry
65 (Singh et al., 2001).

66 Chemical mechanism modelling studies indicate that more and more oxidized
67 species are formed in the course of VOC oxidation, especially compounds bearing
68 hydroxyl and carbonyl functions (Aumont et al., 2005; Madronich, 2006; Goldstein et
69 al., 2007). Thus, β -hydroxycarbonyls can be formed from the OH^\bullet radical initiated
70 reactions of diols with molar formation yields between 50% and 90% (Bethel et al.,
71 2003), as well as from alcohols and alkenes (Tuazon et al., 1998; Reisen et al.,
72 2003). In the atmosphere, OVOCs are supposed to react mainly with OH^\bullet radicals,
73 although reactions with NO_3^\bullet , Cl and ozone cannot be excluded for some of the
74 species in specific environments (Mellouki et al., 2003). The photolysis channel could
75 be significant for carbonyl species (Moortgat, 2001; Bouzidi et al., 2014) and yet, its
76 importance in the case of hydroxycarbonyl VOCs is almost unknown, while recent
77 studies suggest that photolysis could be significant (Henry et al., 2012; Messaadia et
78 al., 2012). Atmospheric chemistry of hydroxyacetone, the smallest hydroxyketone
79 compound, is reasonably well understood (Orlando et al., 1999; Dillon et al., 2006).
80 For larger hydroxycarbonyls ($\geq \text{C}_4$), degradation pathways have not been well
81 characterized. The few available studies indicate that saturated hydroxyketones are
82 mainly removed by OH^\bullet radicals (Aschmann et al., 2000; Magneron et al., 2003;
83 Messaadia et al., 2012; El Dib et al., 2013; Messaadia et al., 2013; Sleiman et al.,
84 2013). Reactivity with O_3 and NO_3^\bullet radicals is expected to be not important in the
85 atmosphere (Calvert et al., 2011). Hydroxyketone lifetimes with respect to OH^\bullet
86 radicals are in the range of about 1 day (e.g. for 4-hydroxy-2-butanone) to several
87 days (e.g. 14 days for 3-hydroxy-3-methyl-2-butanone) (Aschmann et al., 2000;
88 Calvert et al., 2011), thus showing large variability in the reactivity that can be
89 attributed to the structure of the molecule. Recently, the determination of the
90 absorption cross-sections for four hydroxycarbonyl ($\geq \text{C}_4$) compounds by (Messaadia
91 et al., 2012) showed that all obtained spectra of these compounds were similar in
92 shape with two absorption bands, the first one below 220 nm and the second one
93 between 230 and 340 nm with a maximum in the wavelength range 265-290 nm. The
94 tropospheric lifetime of 3H3M2B due to photolysis was estimated by Messaadia et al.
95 (2012) to be at least 0.4 day using an upper limit of the photolysis rate assuming a
96 quantum yield of unity. Therefore, atmospheric fate of these compounds may also be
97 significantly affected by photolytic loss processes. As a consequence, a more
98 detailed characterization of the photochemical fate of hydroxyketone compounds is
99 clearly needed to make further progress in our understanding of the implication of
100 these species in tropospheric chemistry and allow further extension of atmospheric
101 chemistry models (especially for hydrocarbons) for improvement of air quality
102 predictions.

103 The objective of the present work was to evaluate the importance of the
104 photolysis and the OH -initiated reaction in the case of 3-hydroxy-3-methyl-2-
105 butanone (3H3M2B), $((\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O})\text{CH}_3)$. This oxygenated VOC is an oxidation

106 product of the OH-initiated reaction of 2-methyl-2-butene (Tuazon et al., 1998). It has
107 been observed in a measurement campaign carried out at San Francisco (Destailats
108 et al., 2002). In the atmosphere, like other carbonyl compounds, 3H3M2B is
109 expected to be removed by chemical reactions with the atmospheric photooxidants
110 and by photolysis. The atmospheric degradation of this species is not well known
111 however. In fact, only one kinetic study on the gas phase reaction of 3H3M2B is
112 found in the literature (Aschmann et al., 2000a). In this study, the degradation of
113 3H3M2B due to its reaction with OH, NO₃ and O₃ was only investigated at room
114 temperature and atmospheric pressure using a relative rate technique.

115 In order to elucidate the atmospheric fate of 3H3M2B, photolysis and kinetic
116 studies as a function of temperature are necessary. In this work, photolysis of this
117 species was studied from 270 to 390 nm and major products were analysed.
118 Moreover, the OH-initiated reaction of 3H3M2B was studied and rate constants were
119 determined as a function of temperature.

120

121 **2. Experimental section**

122 Experiments have been carried out using two different experimental set-ups, a
123 simulation chamber made of Teflon film, located at the SAGE department of Mines
124 Douai, and a temperature controlled Pyrex simulation chamber, located at University
125 of Reims.

126 **2.1 Photolysis study (Mines Douai)**

127 **2.1.1 Simulation chamber description and experimental conditions**

128 The experimental procedure and equipments used for the photolysis
129 experiments performed are briefly described in the following. More details on the
130 experimental setup can be found in previous publications (Turpin et al., 2006; Szabo
131 et al., 2009; Szabo et al., 2011). Experiments were carried out in a ~ 300 L FEP
132 Teflon film chamber in an air-conditioned laboratory (296 K) and at 1 atm.
133 Fluorescent tubes emitting in the 270-390 nm region with an energy peak at 312 nm
134 were used for irradiation. In a typical experiment, a known amount of 3H3M2B was
135 introduced in the chamber through a stream of purified air and the reaction mixture is
136 allowed to stand for about 1 h in the dark. Three samples were then analysed to
137 determine the initial concentration of the reactant. After the third sampling, the lamps
138 are switched on and about 10 samples are taken along the photolysis experiments
139 (lasting 6-8h) to monitor the concentrations of 3H3M2B and end-products over the
140 time. 3H3M2B initial concentration was in the range of 9 to 50 ppm. Some
141 experiments were conducted in the presence of excess cyclohexane (151-227 ppm),
142 cyclopentane (280 ppm), m-xylene (33-280 ppm) or carbon monoxide (1330-3750
143 ppm) in order to scavenge any OH radicals formed in the reaction mechanism.

144 **2.1.2 Test experiments**

145 Test experiments were performed to investigate possible losses of 3H3M2B
146 and products in the dark and during the photolysis experiments. First, deposition
147 rates on the chamber walls were tested for by running experiments in the dark.
148 Results showed that such losses were negligible for 3H3M2B, CH₂O, acetone,
149 biacetyl, and methanol (rates < 1% per hour). In addition, tests for possible losses of
150 products through photolysis were carried out. Results indicated that photolysis could
151 be significant in the case of CH₂O, acetone and biacetyl with loss rates of 31%, 7%
152 and 4% per hour, respectively. In the following, all the reported concentrations of
153 CH₂O, acetone and biacetyl have been corrected for wall deposition and photolysis
154 according to the rates determined in the test experiments. Formaldehyde was also
155 corrected for production from acetone photolysis.

156 **2.1.3 Sampling and analytical techniques**

157 3H3M2B and photolysis product analysis were performed either by a
158 ThermoDesorption-Gas phase Chromatograph (TD-GC) coupled with Fourier
159 Transform Infrared (FTIR) spectroscopy and Flame Ionization Detection (FID) or by
160 direct FTIR spectrometry using a White cell. The FTIR-White cell analytical system
161 was similar to that used in the study carried out by (Bouzidi et al., 2014). The IR
162 spectra typically result from the co-addition of 100 interferograms with a resolution of
163 2 cm^{-1} representing a measurement time of about 4 min. In the case of the TD-GC-
164 FTIR-FID, gas samples of 100 cm^3 volume were collected every 45 min on Tenax
165 adsorbent microtrap cooled down to -30°C . Injection was achieved by rapid heating
166 of the microtrap to 300°C . Both analytical systems were connected to the chamber
167 through a Teflon line heated to $\sim 338\text{ K}$. Some samples were also collected onto
168 Tenax solid adsorbent and analysed by TD-GC-FID-Mass Spectrometry. Reactant
169 and product concentrations were monitored using classical calibration procedures.
170 Carbonyl products were analyzed following the same procedure as that described by
171 (Bouzidi et al., 2014) using 2,4-dinitrophenylhydrazine (DNPH) derivatization followed
172 by HPLC-UV analysis.

173 **2.1.4 Actinometry**

174 Acetone and acetaldehyde were used as actinometers in order to estimate the
175 tropospheric photolysis lifetime and the effective quantum yields, as they have
176 relatively similar UV absorption spectra compared to 3H3M2B (Messaadia et al.,
177 2012). The photolysis frequencies of acetone and acetaldehyde in the simulation
178 chamber in the presence of cyclopentane were $(0.070 \pm 0.01)\text{ h}^{-1}$ and (0.22 ± 0.02)
179 h^{-1} , respectively. Acetone photolysis frequency calculated from the recommended
180 values of cross-sections and quantum yields with a solar zenith angle of 20° within
181 the lower troposphere for a cloudless day is about 0.00216 h^{-1} (Calvert et al., 2011).
182 For acetaldehyde, a photolysis frequency of 0.0104 h^{-1} was measured at the Euphore
183 chamber for a solar zenith angle of 20° (Calvert et al., 2011).

184 **2.1.5 Chemicals**

185 3H3M2B ($> 95\%$), 2,3-butanedione ($> 97\%$), cyclopentane ($> 99\%$),
186 cyclohexane ($> 99\%$), m-xylène ($> 99\%$) and acetone ($> 99\%$) were purchased from
187 Sigma-Aldrich, acetic acid ($> 99\%$) from Acros Organics and methanol from Fluka ($>$
188 99%). Dry air was produced by a zero air generator (Claind AZ 2020). Carbon
189 monoxide (4939 ppmv in N_2) was obtained from Praxair.

190 **2.2 Oxidation by OH-radicals (GSMA-Reims)**

191 **2.2.1 Experimental set-up**

192 The kinetics of the reaction of 3H3M2B with OH radicals was studied using a
193 photo-chemical reactor coupled to a FTIR spectrometer. The set-up has been
194 presented in details in a previous publication (Messaadia et al., 2013). Therefore, it
195 will be described only briefly herein. The chamber is composed of a triple-jacket
196 Pyrex cell (length of 2 m, internal diameter of 20 cm and total volume of 63 L). Multi-
197 reflection was achieved through the use of gold-plated mirrors suitable for working
198 with IR radiation, and was used to vary the path-length between 4 and 80 m. A
199 primary pump was used to suck up the chamber to 10^{-3} mbar . The temperature in the
200 chamber was regulated through the circulation of a thermostatic fluid (water or
201 ethanol) between the inner and middle jackets. The fluid temperature and circulation
202 were commanded by a Julabo FPW 90 thermostat. The working temperature range
203 was from 298 K to 356 K. The temperature and the pressure in the chamber were
204 respectively measured by a thermocouple and a MKS Baratron manometer with 0-
205 1000 Torr full scale. 24 UV lamps emitting in the range of 300 to 400 nm were

206 symmetrically disposed around the chamber in order to ensure homogeneous
 207 photolysis and to generate OH-radicals from nitrous acid. The extremities of the
 208 chamber were sealed by inox plates which hold two optical windows made of ZnSe
 209 as well as the ports used for the introduction of the reacting species into the reaction
 210 medium.

211 An Equinox 55 FT-IR spectrometer provided by Bruker was used to monitor
 212 the concentration of the reactants and reference compounds inside the reaction
 213 medium. This FTIR spectrometer is equipped with a Globar IR source, a KBr beam-
 214 splitter, and two detectors (DTGS and MCT). Its operating spectral range varies
 215 between 600 and 4000 cm^{-1} , with a spectral resolution of 2 to 0.5 cm^{-1} . MCT was
 216 used as a detector in this study. The alignment of the IR beam inside the chamber
 217 was accomplished by using a He-Ne laser beam by adjusting the positions of the
 218 gold mirrors.

219 2.2.2 Experimental conditions

220 All experiments were performed in purified air. The OH reaction of 3H3M2B
 221 was studied relatively to tert-butyl alcohol (tert-C₄H₉OH) as a reference compound
 222 whose homogeneous reactivity towards OH-radicals is known. The OH radicals were
 223 generated by the photolysis of nitrous acid at 300-400 nm. Nitrous acid (HONO) was
 224 produced via the drop-wise addition of a 10 % sulphuric acid solution to a 0.2 M
 225 sodium nitrite solution. A flow of nitrogen gas was used to sweep along the
 226 generated acid into the chamber in the vapour phase. The used reagents were
 227 obtained from the following sources: Purified Air (99.999%) provided by Air Liquide,
 228 3H3M2B (95%) provided by Sigma-Aldrich and tert-butyl alcohol (> 99.7%) provided
 229 by Fluka. They were further purified by repeated freeze-pump-thaw cycles before
 230 use.

231 Before starting the kinetic measurements, two tests were carried out: the first
 232 one aimed at evaluating the loss of 3H3M2B and the reference compound by
 233 photolysis in the absence of HONO. The second one consisted on monitoring the
 234 concentration of 3H3M2B and tert-C₄H₉OH in the absence of irradiations and in the
 235 presence of HONO to check for the stability of the reagents. These tests showed that
 236 photolysis and wall losses were negligible for both compounds. At each temperature,
 237 2 to 3 independent experiments were carried out. Table 1 summarizes the
 238 experimental conditions.

239 The reference was chosen in such a way that at least one absorption band of
 240 the 3H3M2B does not exhibit any interference with those of the reference compound
 241 and vice versa, and that the OH-degradation rate constants of both, 3H3M2B and
 242 reference, are of the same order of magnitude. The rate constant of the reaction of
 243 tert-C₄H₉OH with OH used in this work is that reported by (Téton et al., 1996):

$$244 k_{\text{ref}} = (2.66 \pm 0.48) \times 10^{-12} \exp((-2240 \pm 1080)/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{I})$$

245

246 3. Results and discussion

247 3.1 Photolysis

248 3.1.1 Photolysis rate constants

249 The photolysis of 3H3M2B was carried out either in the absence or in the
 250 presence of excess of OH[•] radical scavenger. The photolysis rate constants $J_{3\text{H}3\text{M}2\text{B}}$
 251 were determined by plotting the natural logarithm of the ratio $[3\text{H}3\text{M}2\text{B}]_0/[3\text{H}3\text{M}2\text{B}]_t$
 252 versus time:

$$253 \ln \frac{[3\text{H}3\text{M}2\text{B}]_0}{[3\text{H}3\text{M}2\text{B}]_t} = J_{3\text{H}3\text{M}2\text{B}} \times t \quad (\text{II})$$

254 where $[3\text{H3M2B}]_0$ and $[3\text{H3M2B}]_t$ indicate the 3H3M2B concentrations at the initial
 255 and time t , respectively.

256 The 3H3M2B concentration data were well fitted to a straight line using a
 257 linear least-square procedure (Figure 1) and the slope of the linear regression
 258 (weighted by 1σ) represents $J_{3\text{H3M2B}}$. The experimental conditions and the photolysis
 259 frequencies obtained for 3H3M2B in the presence and absence of OH^\bullet scavenger
 260 are summarized in Table 2.

261 3H3M2B photolysis frequencies were found to be $(0.24 \pm 0.02) \text{ h}^{-1}$ and $(0.33 \pm$
 262 $0.02) \text{ h}^{-1}$ in the presence and absence of OH^\bullet scavenger, respectively. The reported
 263 uncertainties represent one standard deviation of the slope of the regression line. In
 264 the absence of OH^\bullet scavenger, an increase of around 40% in $J_{3\text{H3M2B}}$ is noted. Using
 265 the average OH-radical rate constant obtained in the present work, $k_{\text{OH}^\bullet+3\text{H3M2B}} =$
 266 $7.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see below) enables to estimate an OH^\bullet photostationary
 267 concentration of around $3 \times 10^7 \text{ radical cm}^{-3}$ from the observed difference in the
 268 photolysis frequencies. This suggests that OH^\bullet radicals were produced in the
 269 chemical mechanism, which is confirmed by the observation of cyclopentanol and
 270 cyclopentanone ($\text{OH}^\bullet + \text{cyclopentane}$ reaction products) in the presence of excess
 271 cyclopentane, or cyclohexanol and cyclohexanone ($\text{OH}^\bullet + \text{cyclohexane}$ reaction
 272 products) in the presence of cyclohexane.

273 3.1.2 Effective quantum yields

274 From the obtained photolysis frequencies, the effective quantum yield of the
 275 3H3M2B photolysis can be calculated using acetone and acetaldehyde actinometry
 276 experiments according to the following equation (Bacher et al., 2001; Bouzidi et al.,
 277 2014):

$$278 \Phi_{3\text{H3M2B}} = \frac{J_{3\text{H3M2B}}/J_{\text{actin}}}{J_{3\text{H3M2B}}^{\text{calc}}/J_{\text{actin}}^{\text{calc}}} \quad (\text{III})$$

279 $J_{3\text{H3M2B}}^{\text{calc}}$ and $J_{\text{actin}}^{\text{calc}}$ are the 3H3M2B and actinometer (acetone or acetaldehyde)
 280 photolysis frequencies, respectively, calculated using:

$$281 J_{3\text{H3M2B}}^{\text{calc}} = \int_{\lambda} \Phi_{3\text{H3M2B}}(\lambda) \times \sigma_{3\text{H3M2B}}(\lambda) \times F(\lambda) d\lambda \quad (\text{IV})$$

$$282 \text{ and } J_{\text{actin}}^{\text{calc}} = \int_{\lambda} \Phi_{\text{actin}}(\lambda) \times \sigma_{\text{actin}}(\lambda) \times F(\lambda) d\lambda \quad (\text{V})$$

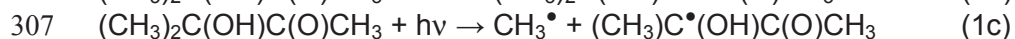
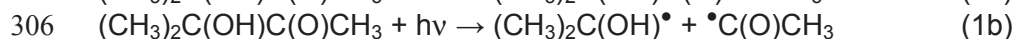
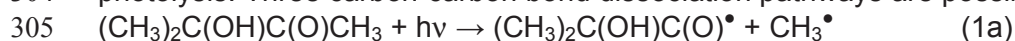
283 where $\Phi_{3\text{H3M2B}}(\lambda)$ and $\Phi_{\text{actin}}(\lambda)$ represent the 3H3M2B and actinometer wavelength-
 284 dependent quantum yields, respectively. $\sigma_{3\text{H3M2B}}(\lambda)$ and $\sigma_{\text{actin}}(\lambda)$ are the 3H3M2B and
 285 actinometer absorption cross-sections, respectively and $F(\lambda)$ the relative actinic flux
 286 intensity. For 3H3M2B, cross-sections were from (Messaadia et al., 2013) and
 287 quantum yields in Equation (IV) were set to unity. $\sigma_{\text{acetone}}(\lambda)$, $\Phi_{\text{acetone}}(\lambda)$, $\sigma_{\text{acetaldehyde}}(\lambda)$
 288 and $\Phi_{\text{acetaldehyde}}(\lambda)$ were all from the last evaluation from IUPAC (IUPAC, 2013). Using
 289 Equation (III), the 3H3M2B effective quantum yields are: $\Phi_{3\text{H3M2B}} = 0.85 \pm 0.30$ with
 290 acetone as actinometer and $\Phi_{3\text{H3M2B}} = 0.76 \pm 0.20$ with acetaldehyde as actinometer.
 291 An average quantum yield of $\Phi_{3\text{H3M2B}} = 0.81 \pm 0.30$ is thus recommended over the
 292 wavelength range 270-390 nm.

293 The main sources of uncertainties are the 3H3M2B and actinometer
 294 absorption cross-sections, the acetone and acetaldehyde quantum yields and the
 295 measured 3H3M2B, acetone and acetaldehyde photolysis frequencies. Using the
 296 propagation of errors yields an overall uncertainty of 35% and 28% on the 3H3M2B
 297 quantum yields with acetone and acetaldehyde, respectively. The fairly large
 298 effective 3H3M2B quantum yields are comparable to those obtained for
 299 hydroxyacetone (Orlando et al., 1999): $\Phi_{\text{hydroxyacetone}} = 0.65 \pm 0.25$ for 240-420 nm

300 and $\Phi_{\text{hydroxyacetone}} < 0.6$ for $\lambda > 290$ nm. Note that these quantum yields values are the
 301 only data for hydroxyketone species known in the literature.

302 3.1.3 Photolysis products

303 Product analysis was carried out to unravel the mechanism of 3H3M2B
 304 photolysis. Three carbon-carbon bond dissociation pathways are possible:



308 In addition, the direct OH^\bullet release from the carbon – hydroxy group dissociation is
 309 also possible:

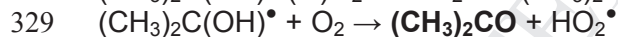
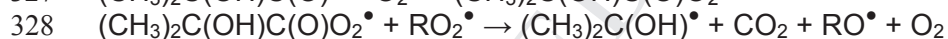
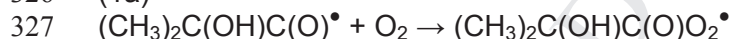


311 Five major reaction products – acetone, acetic acid, formaldehyde, CO and
 312 methanol – were observed. Figure 2 shows reactant and product time profiles
 313 obtained in the presence of m-xylene as OH-scavenger. The shape of the profiles for
 314 acetone, formaldehyde and methanol displays non-zero derivative at the origin,
 315 indicating that these compounds are primary products. On the contrary, carbon
 316 monoxide and acetic acid present secondary product profiles with a delay time before
 317 their concentrations increase.

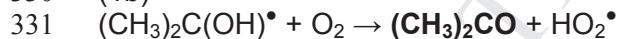
318 Yield plots in the form of [products] vs. $[\text{3H3M2B}]_{\text{reacted}}$ are shown in Figure 3
 319 for the primary products: linear profiles were obtained for acetone and formaldehyde
 320 while a slightly increasing curved profile was obtained for methanol. Table 2
 321 summarizes the corresponding corrected yields obtained in the photolysis of
 322 3H3M2B with and without OH^\bullet scavenger.

323 Acetone $(\text{CH}_3)_2\text{CO}$ is expected to originate from channels (1a), (1b) and/or
 324 (1d) through the following reaction sequences (where RO_2^\bullet represents a peroxy
 325 radical):

326 (1a)



330 (1b)



332 (1d)



335 As an acetone yield of nearly 1 is obtained, it is concluded that the branching
 336 to channel (1c) (which is not supposed to yield acetone) is rather low (< 2%).

337 Formaldehyde arises from the radical recombination of $\text{CH}_3\text{O}_2^\bullet$: for example,
 338 the $\text{CH}_3\text{O}_2^\bullet$ self reaction leads to CH_2O :



341 with a branching ratio $k_{2b}/k_2 = 0.63$ recommended by (Sander et al., 2011).

342 The CH_2O yield of 23% (corrected for wall loss, photolysis and production from
 343 acetone photolysis) - well below 100% - indicates that a fraction of the $\text{CH}_3\text{O}_2^\bullet$
 344 radicals will react with HO_2^\bullet in a terminating channel to form essentially methyl-
 345 hydroperoxide (Orlando et al., 2012) and that some of the $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet$ radicals will
 346 be lost through the $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet + \text{HO}_2^\bullet$ reaction which gives only 0.44 $\text{CH}_3\text{O}_2^\bullet$
 347 (Dillon et al., 2008). Note that this last reaction is known to produce OH radicals with
 348 branching ratios between 0.4 and 0.6 (Gross et al., 2014) and may represent the sole
 349 source of OH radicals in the 3H3M2B photolysis. Noteworthy the CH_2O yield

350 decreases from the conditions with OH-scavenger (23%) to the conditions without
 351 OH-scavenger (16%) probably due to the $\text{OH}^\bullet + \text{CH}_2\text{O}$ reaction.

352 Methanol mostly originates from the molecular channel of $\text{CH}_3\text{O}_2^\bullet$ peroxy
 353 radical reactions:

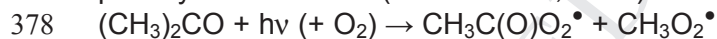


355 Results from experiments with m-xylene and CO as OH^\bullet scavenger showed a higher
 356 methanol yield with m-xylene (11%) than with CO (6%), revealing that the additional
 357 RO_2^\bullet radicals from m-xylene + OH^\bullet convert more $\text{CH}_3\text{O}_2^\bullet$ into CH_3OH (as $\text{CO} + \text{OH}^\bullet$
 358 leads to $\text{HO}_2^\bullet + \text{CO}_2$ and no RO_2^\bullet).

359 In addition to the three major primary products, carbon monoxide and acetic
 360 acid (AA) were also observed in the present study. The plots $[\text{CO}]$ and $[\text{AA}]$ vs.
 361 $[\text{3H3M2B}]_{\text{reacted}}$ are not linear but follow roughly a second order polynomial with a
 362 zero derivative at the origin, indicating the occurrence of only secondary sources
 363 both in presence and in absence of OH^\bullet scavenger (Figure 4). Direct formation of CO
 364 from 3H3M2B photolysis through $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O})\text{CH}_3 + h\nu \rightarrow (\text{CH}_3)_2\text{C}(\text{OH})^\bullet + \text{CO}$
 365 + CH_3^\bullet is thus excluded. It should be stressed that a larger amount of CO is
 366 quantified in the absence of OH^\bullet scavenger. The secondary formation of CO may
 367 thus be attributed essentially to formaldehyde photolysis and reaction with OH^\bullet .

368 Similarly, the absence of acetic acid formation at the beginning of the reaction
 369 (Figure 4) suggests a unique secondary origin for this product. As AA is produced
 370 through $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet + \text{HO}_2^\bullet/\text{RO}_2^\bullet$ reactions (Tomas et al., 2001; Sander et al., 2011),
 371 we conclude that the photodissociation channels (1b) and (1d) (both producing
 372 $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet$) are minor channels. Assuming that AA only comes through the
 373 $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet + \text{HO}_2^\bullet$ reaction with a branching ratio of 0.2 (Tomas et al., 2001) and
 374 using an AA detection limit of 50 ppb enable a rough estimation of the maximum
 375 branching ratio for the (1b) + (1d) channels of 5% to be calculated.

376 The secondary formation of acetic acid can be primarily attributed to the
 377 photolysis of acetone (Calvert et al., 2011):



379 followed by peroxy radical reactions of $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet$ (Tomas et al., 2001). The
 380 heterogeneous formation of acetic acid in the $\text{OH}^\bullet + \text{acetone}$ reaction reported by
 381 (Turpin et al., 2006) is probably not significant in the present conditions, as more AA
 382 is observed when OH radicals are scavenged. We also suspect the $\text{OH}^\bullet + \text{m-xylene}$
 383 reaction that produces methylglyoxal with yields of about 40% (Calvert et al., 2002).
 384 Methylglyoxal can readily be photolysed into $\text{CH}_3\text{CO}^\bullet + \text{HCO}^\bullet$, giving $\text{CH}_3\text{C}(\text{O})\text{O}_2^\bullet$,
 385 HO_2^\bullet and CO. This source could explain the large difference in the AA formed with
 386 m-xylene as OH-scavenger compared to that formed in the absence of OH-
 387 scavenger (see Figure 4). This result underlines the role that can be played by a
 388 scavenger in modifying the type and amount of peroxy radicals in the investigated
 389 chemical system, and thus the products observed.

390 Minor products were also identified: 2,3-butanedione (or biacetyl,
 391 $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3$), hydroxyacetone and methylglyoxal. Biacetyl yields of 1.4% and
 392 0.4% have been quantified in the absence and presence of OH scavengers. This α -
 393 diketone is expected to originate from the photolysis channel (1c). The increase in
 394 the biacetyl yields between OH^\bullet and no OH^\bullet conditions may be attributed to a weak
 395 biacetyl formation through $\text{OH}^\bullet + \text{3H3M2B}$. Finally, hydroxyacetone and
 396 methylglyoxal were also tentatively identified and quantified with very low yields (<
 397 0.5%).

398 Overall, the carbon balance obtained in the present work represents nearly
 399 80%. The lacking products are assumed to be mainly peroxides formed by $\text{RO}_2^\bullet +$
 400 HO_2^\bullet reactions (Orlando et al., 2012).

401 3.1.4 Mechanism interpretation

402 Based on the reaction product observations, it is possible to propose a
 403 simplified photolysis mechanism of 3H3M2B as shown in the scheme displayed in
 404 Figure 5. The high yields of acetone (98%) coupled with negligible amounts of CO
 405 and acetic acid at the beginning of the experiments in the presence of OH^\bullet
 406 scavenger indicates that the photolysis of 3H3M2B proceeds mainly through the
 407 rupture of the C1-C2 bond of the molecule (channel (1a)). Photolysis channels (1b)
 408 and (1d), both producing acetic acid, and channel (1c) leading to 2,3-butanedione,
 409 respectively, are of minor importance.

410 3.2 OH reaction kinetics

411 The kinetics of the reaction of OH radicals with 3H3M2B was determined
 412 relatively to that of a reference compound using the following equation:

$$413 \ln\left(\frac{[\text{3H3M2B}]_{t_0}}{[\text{3H3M2B}]_t}\right) = R \times \ln\left(\frac{[\text{ref}]_{t_0}}{[\text{ref}]_t}\right) \quad (\text{VI})$$

414 where $[\text{3H3M2B}]_{t_0}$ and $[\text{ref}]_{t_0}$ are the initial concentrations of 3H3M2B and tert-butyl
 415 alcohol at time t_0 , respectively; $[\text{3H3M2B}]_t$ and $[\text{ref}]_t$ are the concentrations of
 416 3H3M2B and tert-butyl alcohol at time t , respectively and R is the ratio of rate
 417 constants ($R = k_{\text{3H3M2B}}/k_{\text{ref}}$) where k_{ref} is the rate constant of the reference reaction. A
 418 plot of $\ln([\text{3H3M2B}]_{t_0}/[\text{3H3M2B}]_t)$ as a function of $\ln([\text{ref}]_{t_0}/[\text{ref}]_t)$ results in a straight
 419 line with the slope equal to R . Knowing k_{ref} , it is possible to determine k_{3H3M2B} , the
 420 rate constant of the reaction of OH-radicals with 3H3M2B. During an experiment, IR
 421 spectra were recorded every 5 minutes. Each spectrum constitutes the average of 20
 422 accumulated acquisitions leading to a signal to noise ratio of ~ 15 . The obtained data
 423 are presented in the form of $\ln([\text{3H3M2B}]_{t_0}/[\text{3H3M2B}]_t)$ vs. $\ln([\text{ref}]_{t_0}/[\text{ref}]_t)$. As can be
 424 seen on Figure 6, good linearity is observed with correlation coefficients greater than
 425 0.91. The rate constants obtained in the present study are reported in Table 3. The
 426 given rates are derived from the average of 2 to 4 independent measurements. At
 427 298 K, the average rate constant for the reaction of 3H3M2B with OH radicals is:
 428 $k_{\text{3H3M2B}} = (7.6 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

429 For each experiment, the overall error in the rate constant values reported in
 430 this work is calculated using propagation of error according to the following relation:

$$431 \Delta k_{\text{3H3M2B}} = k_{\text{3H3M2B}} \sqrt{(\Delta k_{\text{ref}}/k_{\text{ref}})^2 + (\Delta R/R)^2} \quad (\text{VII})$$

432 where k_{ref} , Δk_{ref} are the rate constant of the reference reaction and the uncertainty on
 433 this parameter, respectively and $R = k_{\text{3H3M2B}}/k_{\text{ref}}$ is the slope of the plot according to
 434 Equation (VI) with ΔR the uncertainty on this value. Errors originate mainly from:

- 435 (i) the determination of k_{ref} : this error varies from 10% to 20% according
 436 to the temperature (Téton et al., 1996);
 437 (ii) the determination of the slope R : this parameter is determined
 438 directly from the experimental data. The uncertainty on this
 439 parameter is related to the areas corresponding to the absorption
 440 bands of 3H3M2B and the reference compound. The standard
 441 deviation in R values obtained for each set of experiments varies
 442 between 10% and 25% (Table 3), which indicates that the
 443 experiments are fairly reproducible.

444 The Arrhenius plot derived from the experimental rate constants (Table 3) is
 445 presented in Figure 7 and shows a good linearity. The corresponding Arrhenius
 446 equation is:

$$447 \quad k_{3\text{H3M2B}}(T) = (5.12 \pm 0.07) \times 10^{-12} \exp(-563 \pm 119/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

448 In contrast to other hydroxyketones studied in our laboratory (Messaadia et al.,
 449 2013), the rate constant $k_{3\text{H3M2B}}$ exhibits a slight positive temperature dependence.
 450 However, this temperature coefficient remains relatively weak (E/R around 600 K).
 451 This indicates that this reaction may proceed initially via the reversible formation of
 452 unstable intermediate complexes.

453 Until now, no kinetic data were reported in the literature for the reaction of
 454 3H3M2B with OH radicals as a function of temperature. Only one study regarding the
 455 kinetics of OH-oxidation of 3H3M2B exists but only at room temperature (Aschmann
 456 et al., 2000). Our value of $(7.6 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in good agreement
 457 with this determination (of $(9.4 \pm 3.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with a difference less
 458 than 20%.

459 It is also possible to compare the reactivity of 3H3M2B to that of other
 460 hydroxyketones for which the hydroxyl group is attached to the carbon atom located
 461 in the α position with respect to the carbonyl group, namely 1-hydroxy-2-butanone, 3-
 462 hydroxy-2-butanone and 4-hydroxy-3-hexanone. The kinetic rate constants of the
 463 gas-phase reaction of OH radicals with these compounds are ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):
 464 $(7.7 \pm 0.7) \times 10^{-12}$ (Aschmann et al., 2000), $(9.60 \pm 0.30) \times 10^{-12}$ (Messaadia et al.,
 465 2013) and $(15.1 \pm 3.1) \times 10^{-12}$ (Aschmann et al., 2000) for 1-hydroxy-2-butanone, 3-
 466 hydroxy-2-butanone and 4-hydroxy-3-hexanone, respectively. As expected, the
 467 reactivity of 3H3M2B towards OH radicals is lower than that of the other α -
 468 hydroxyketones by at least one order of magnitude. This lower reactivity can be
 469 attributed to the lack of secondary or tertiary H-atoms in the structure of the 3H3M2B
 470 molecule.

471

472 4. Atmospheric implications

473 The photolysis frequency of 3H3M2B determined in the present work is specific
 474 to the experimental setup used and cannot be directly applied for the estimation of
 475 the atmospheric lifetime. However, the 3H3M2B atmospheric photolysis frequency
 476 ($J_{3\text{H3M2B}}^{\text{atm}}$) can be estimated using the known photolysis frequencies of actinometers
 477 (acetone and acetaldehyde) in the troposphere ($J_{\text{actin}}^{\text{atm}}$) through the following equation:

$$478 \quad J_{3\text{H3M2B}}^{\text{atm}} = J_{3\text{H3M2B}} \times \frac{J_{\text{actin}}^{\text{atm}}}{J_{\text{actin}}} \quad (\text{VIII})$$

479 Taking into account the experimental photolysis rate constants of 3H3M2B
 480 $J_{3\text{H3M2B}}$ and actinometer J_{actin} measured in the reaction chamber allows to estimate
 481 an average photolysis frequency of 3H3M2B in the troposphere of
 482 $J_{3\text{H3M2B}}^{\text{atm}} = 0.0095 \text{ h}^{-1}$. A global uncertainty of about 70% is associated with $J_{3\text{H3M2B}}^{\text{atm}}$
 483 principally due to the uncertainties on J_{actin} of at least 50% (Calvert et al., 2011).
 484 Furthermore, using the absorption cross sections of 3H3M2B (Messaadia et al.,
 485 2012) and the actinic flux at 40°N, 1st July and 20° zenithal angle enables calculating
 486 an upper limit of the 3H3M2B photolysis frequency $J_{3\text{H3M2B},\text{max}}$ of 0.094 h^{-1} in the
 487 atmosphere (assuming a 3H3M2B quantum yield of 1 over the whole absorption
 488 range). Finally, comparing the estimated and maximum $J_{3\text{H3M2B}}$ values yields an
 489 effective quantum yield of $\Phi = J_{3\text{H3M2B}}^{\text{atm}} / J_{3\text{H3M2B},\text{max}} = 0.0095 / 0.094 \approx 0.10$ for 3H3M2B
 490 in the atmosphere with around 80% combined uncertainty.

491 Data on atmospheric photolysis frequencies of hydroxyketones are very
 492 scarce in the literature. The estimated photolysis frequency of 3H3M2B in the
 493 troposphere is roughly a factor two higher than the J value for hydroxyacetone (HA):
 494 $J_{\text{HA}}^{\text{atm}} \approx (0.0054 \pm 0.0018) \text{ h}^{-1}$ while a factor two lower than the higher limit determined
 495 for 4-hydroxy-4-methyl-2-pentanone (4H4M2P) $J_{\text{4H4M2P}}^{\text{atm}} \leq 0.018 \text{ h}^{-1}$ (Calvert et al.,
 496 2011). The atmospheric lifetime of 3H3M2B can then be calculated according to:

$$497 \quad \tau_{\text{3H3M2B}}^{\text{atm}} = \frac{1}{J_{\text{3H3M2B}}^{\text{atm}}} \quad (\text{IX})$$

498 The calculated lifetime of 3H3M2B with respect to photolysis is about 4 - 5
 499 days. An atmospheric lifetime of 15 days due to reaction with OH[•] radicals is
 500 estimated according to the equation $\tau = 1/k_{\text{3H3M2B}} \times [\text{OH}^{\bullet}]$ by using a 24 h daytime
 501 average global tropospheric OH[•] concentration of $1 \times 10^6 \text{ molecule cm}^{-3}$ (Atkinson et
 502 al., 1997). Thus, it is clear that photolysis is the major oxidation pathway for 3H3M2B
 503 in the gas-phase. It should be noted that other heterogeneous loss processes for
 504 3H3M2B including physical processes (dry deposition) and uptake by clouds followed
 505 by wet deposition may be important. Regional impacts should thus be expected for
 506 3H3M2B: photolysis of 3H3M2B represents a source of acetone and formaldehyde,
 507 affecting the atmospheric oxidative capacity and the tropospheric ozone budget.

508 The data obtained in this work suggest that the reactivity of hydroxycarbonyls
 509 may be very sensitive to their chemical structures. While the OH[•] reaction is
 510 generally the major tropospheric loss process for hydroxycarbonyls, the absence of
 511 H-atom in the β position to the carbonyl group of 3H3M2B strongly depletes its
 512 reactivity towards OH[•] radicals and consequently enhances the importance of the
 513 photolysis channel in the atmosphere.
 514

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 525

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Tables and Figures

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Table 1: Experimental conditions used for the reaction of 3H3M2B with OH radicals in the Pyrex simulation chamber coupled to a FTIR spectrometer.

	3H3M2B + OH → products
Temperature (K)	298-356
Pressure (Torr)	500-600
Reference compound	Tert-butyl alcohol
Optical path (m)	24-56
[3H3M2B] ₀ (ppm)	10-50
[Reference] ₀ (ppm)	10-50
Spectral range (cm ⁻¹): 3H3M2B	990-950 and 3530-3480
Spectral range (cm ⁻¹): reference	1060-1000 and 3665-3620

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Table 2: Photolysis frequencies, global quantum yields and product yields (corrected for wall loss and photolysis) of the photolysis of 3H3M2B in the absence and presence of OH-scavenger. Errors represent the global uncertainty (2 σ).

Experiments		
	Without OH-scavenger	With OH-scavenger
[3M3H2B] ₀ (ppm)	18 - 60	9 - 52
J _{3H3M2B} (h ⁻¹)	0.33 ± 0.02	0.24 ± 0.02
Φ _{3H3M2B} (270-390 nm)	-	0.79 ± 0.30
Molar yields of primary products (%)		
Acetone	86 ± 13	98 ± 14
Formaldehyde	16 ± 4	23 ± 4
Methanol	6 ± 1	11 ± 3 ^a 6 ± 1 ^b
2,3-butanedione	1.7 ± 0.5	0.4 ± 0.14
Methylglyoxal ^c	0.11 ± 0.05	0
Hydroxyacetone	NQ ^d	NQ ^d

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- ^a: OH-scavenger: m-xylene
^b: OH-scavenger: carbon monoxide
^c: yield without photolysis correction
^d: NQ: not quantified

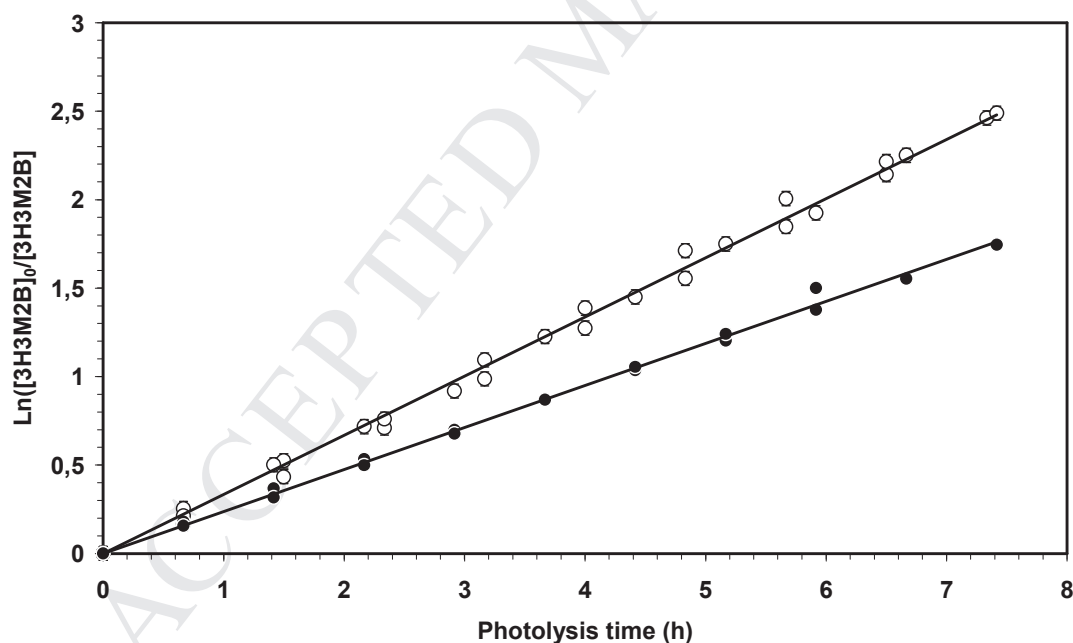
668 **Table 3: Average rate constants for the reactions of 3H3M2B with OH**
 669

Temperature (K)	k_{3H3M2B}/k_{ref}	$k_{3H3M2B} (/ 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
298	0.67 ± 0.01	7.3 ± 1.0
298	0.69 ± 0.01	7.4 ± 1.0
298	0.75 ± 0.02	8.1 ± 1.0
		$7.6 \pm 0.5^*$
314	0.81 ± 0.01	9.2 ± 2.0
315	0.78 ± 0.01	8.9 ± 2.0
		$9.0 \pm 0.3^*$
334	0.81 ± 0.01	9.6 ± 1.5
334	0.75 ± 0.02	8.9 ± 1.5
335	0.76 ± 0.02	9.0 ± 1.5
		$9.2 \pm 0.4^*$
353	0.97 ± 0.01	12.0 ± 2.0
356	0.73 ± 0.02	9.2 ± 2.0
		$10.6 \pm 2.0^*$

* uncertainties correspond to the standard deviation of the rate constant

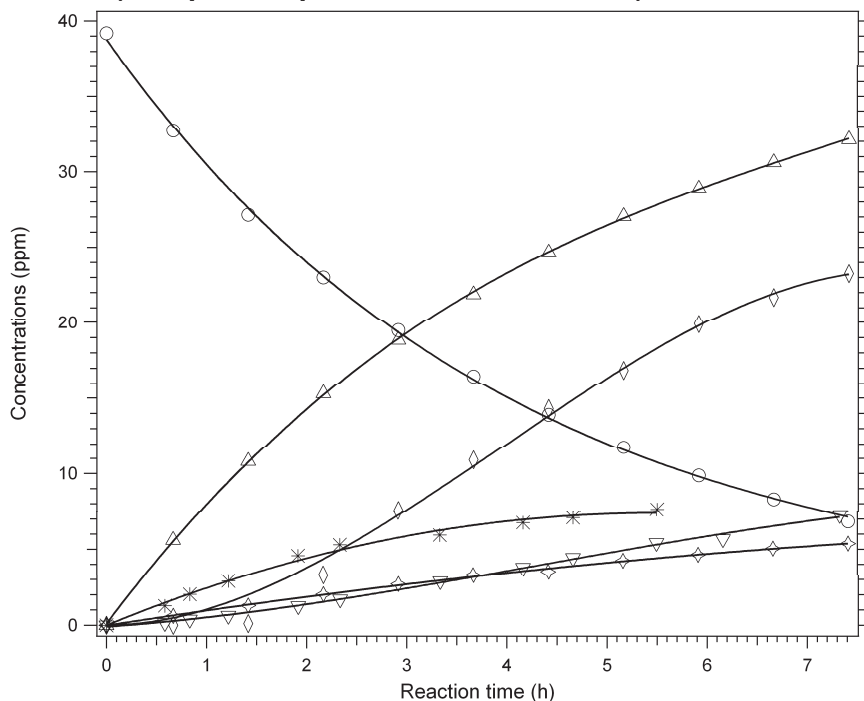
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Figure 1: Kinetic plots of 3H3M2B photolysis. Empty symbols are for experiments without OH-scavenger (3 experiments), while full symbols are for experiments with excess m-xylene as OH-scavenger (2 experiments).

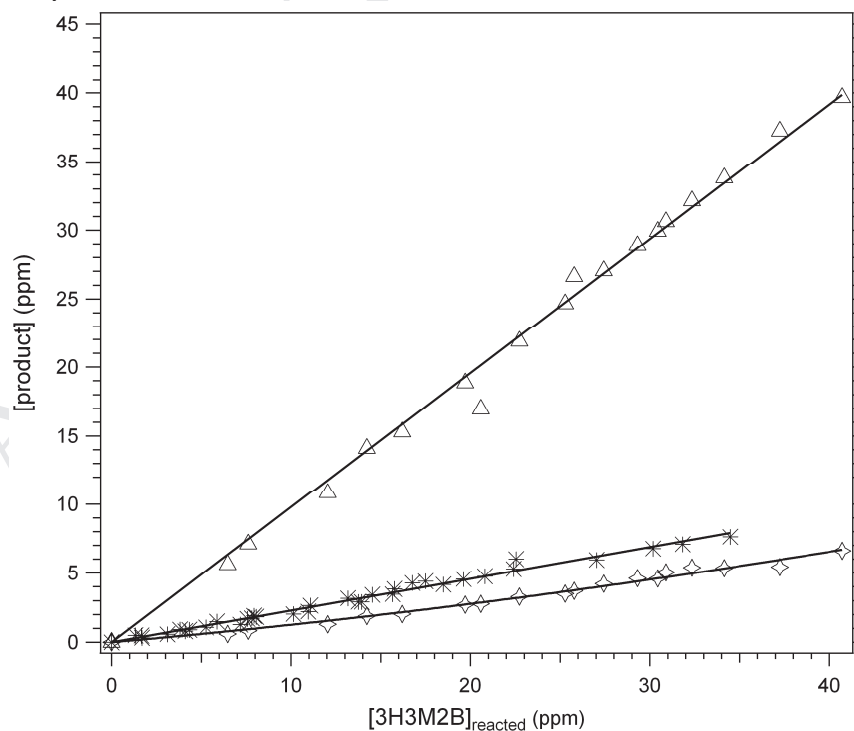


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678 **Figure 2: Time profiles of 3H3M2B and reaction products (experiment with m-**
 679 **xylene as OH-scavenger). Symbols: ○: 3H3M2B; △: Acetone; ◇: Acetic acid; *:**
 680 **Formaldehyde; ▽: Carbon monoxide; ◇: Methanol. Lines correspond to**
 681 **polynomial fits (except an exponential fit for 3H3M2B).**

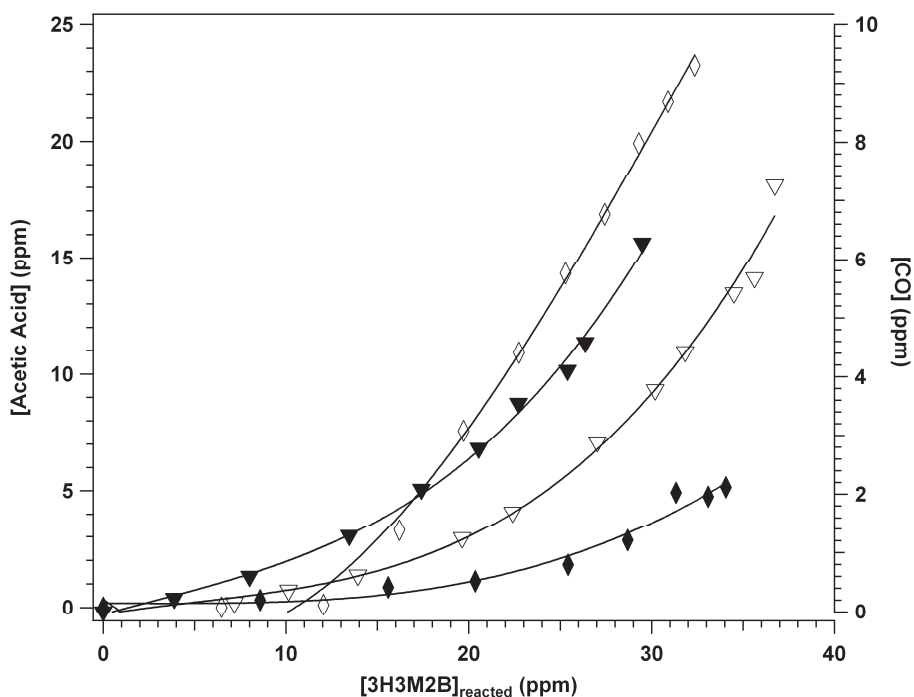


682 **Figure 3: △: Acetone, *: Formaldehyde and ◇: Methanol yield plots for**
 683 **experiments performed in the presence of m-xylene as OH-scavenger. Lines**
 684 **correspond to linear fits for acetone and formaldehyde and to a polynomial fit**
 685 **(second order) for methanol.**
 686



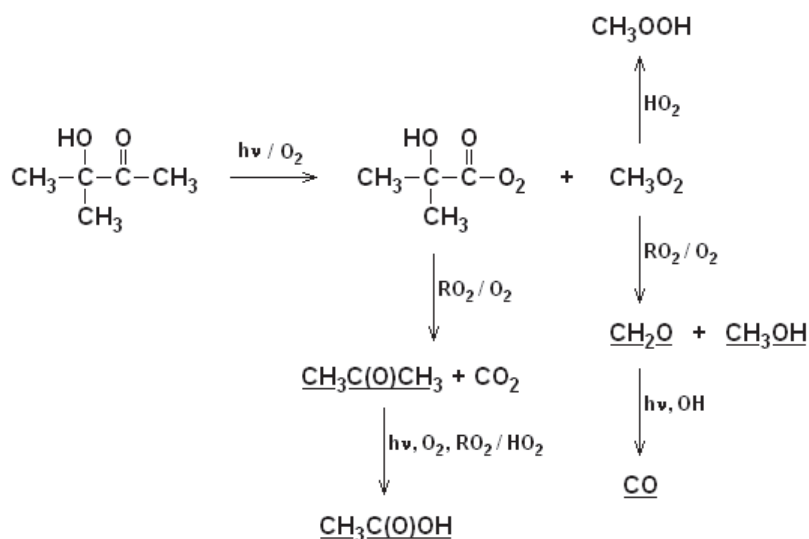
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688 Figure 4: Plots of acetic acid (diamonds - left scale) and carbon monoxide
 689 (triangles - right scale) formation against 3H3M2B reacted. Full symbols are for
 690 experiments without OH-scavenger, while empty symbols are for experiments
 691 with OH-scavenger. Full lines correspond to polynomial fits of the data to help
 692 visualizing the data points.
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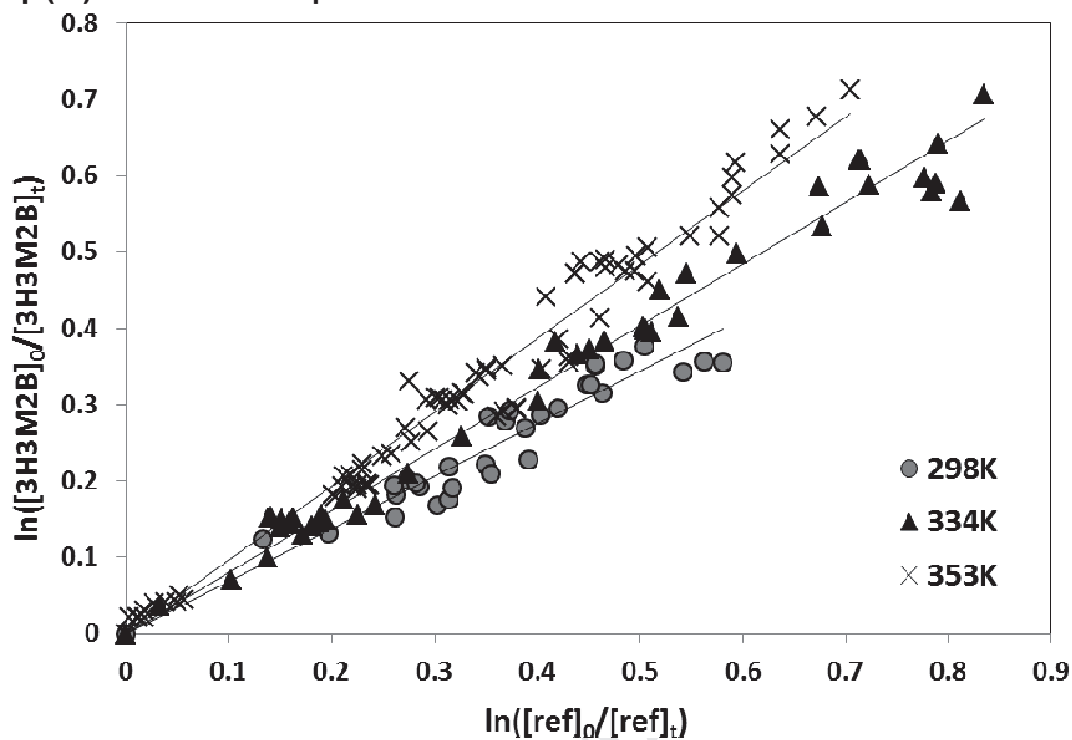
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Figure 5: Simplified reaction mechanism for the photolysis of 3H3M2B



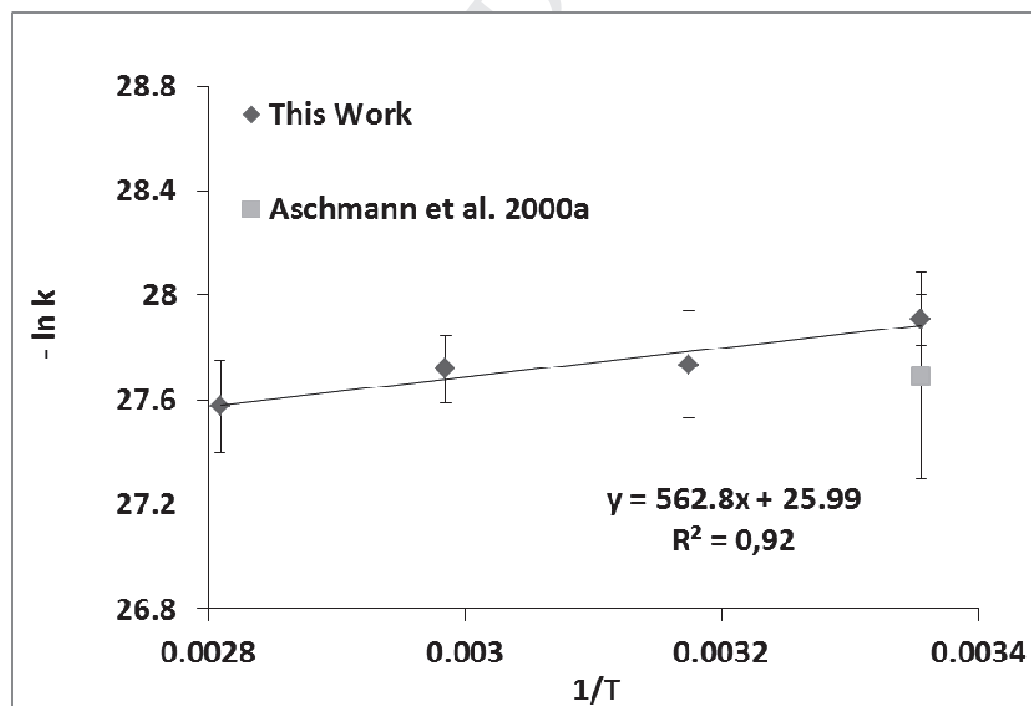
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700 Figure 6: Relative rate plots for the reaction of OH with 3H3M2B according to
 701 eq. (VI) at different temperatures



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Figure 7: Arrhenius plot for the OH + 3H3M2B reaction between 298 and 356 K



707

Reactivity of 3-hydroxy-3-methyl-2-butanone: Photolysis and OH reaction kinetics

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Highlights

- 3H3M2B photolysis is the major oxidation channel in the atmosphere
- Slight positive temperature dependence in the OH + 3H3M2B reaction kinetics
- Need for a better understanding of the atmospheric chemistry of oxygenated VOC