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Product investigation of the gas phase ozonolysis of 1-penten-3-ol, *cis*-2-penten-1-ol and *trans*-3-hexen-1-ol

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Abstract

It is well known that the ozonolysis of organic compounds leads to the formation of oxygenated products, which can increase the oxidizing ability of the atmosphere. In this work, the products of the gas phase reactions of ozone with three unsaturated alcohols: 1-penten-3-ol (1P3OL), *cis*-2-penten-1-ol (c-2P1OL) and *trans*-3-hexen-1-ol (t-3H1OL) were investigated. The products formation yields were determined at 298 K and 760 Torr, in dry condition, in a 63 L pyrex reactor. The analysis of the products was performed in situ using Fourrier transform infrared (FTIR) spectroscopy (ie technique) and solid phase microextraction sampling in conjunction with gas chromatography coupled to mass spectrometry (SPME/GC-MS) (ie technique). The average yields of primary products were (in %): formaldehyde (62±12) and 2-hydroxybutanal (46±10) for the reaction of O_3 with 1-penten-3-ol; glycolaldehyde (56±14) and propanal (40±10) for the reaction of O_3 with *cis*-2-penten-1-ol; propanal (63±8) and 3-hydroxypropanal (43±10) for the reaction of O_3 with *trans*-3-hexen-1-ol. As for secondary products, their average yields were (in %): propanal (12±4) and acetaldehyde (10±4) for the ozonolysis of 1-penten-3-ol; acetaldehyde (13±5), 2-hydroxypropanal (10±2) and methylglyoxal (3±1) for the ozonolysis of *cis*-2-penten-1-ol, acetaldehyde (30±4), glycolaldehyde (16±4) and methylglyoxal (8±3) for the ozonolysis of *trans*-3-hexen-1-ol. The obtained yields were compared to the values available in literature. Based on the results obtained in this study, plausible reaction mechanisms of the ozonolysis of these unsaturated alcohols have been proposed.

Keywords: Biogenic volatile organic compounds (BVOC); Unsaturated alcohols; Ozonolysis; Products formation yields; Reaction mechanisms

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1. Introduction

To improve our knowledge on the atmospheric fate of organic compounds and their transformation to other secondary pollutants, more information on products formation and reaction mechanisms are needed. Biogenic volatile organic compounds (BVOCs) emitted by vegetation are the main source of VOC emissions in the troposphere (Guenther et al., 1995; Kesselmeier and Staudt, 1999; Williams et al., 2013). Other sources, such as the oceans, are considered to be minor sources (Broadgate et al., 1997; Ciuraru et al., 2015; Yassaa et al., 2008). Biogenic sources contribute to more than 90% of global VOC emissions where 1150×10^{12} g of Carbon result from BVOC per year (Guenther et al., 1995). Such BVOCs mainly include isoprenoids or terpenoids $(C_5H_8)_n$ like monoterpenes (n = 2) responsible for plant odors and sesquiterpenes (n = 3). The latter is considered as major products of essential oils stored by plants. BVOCs also include species of other families like alkanes, alkenes, oxygenated volatile organic compounds (OVOC) such as carbonyls, alcohols, esters, ethers and acids. These compounds play a dominant role in the chemistry of the lower troposphere and the atmospheric boundary layer (Fuentes et al., 2000).

Additionally, certain OVOCs are released from damage occurring in the leaves (grazing, cutting, harvesting, freezing and drying). The main result is C5 and C6 unsaturated alcohols and aldehydes known as "green leaf volatiles" released by plants in response to injury (Davis and Burkholder, 2011; Hatanaka, 1993; Nakamura and Hatanaka, 2002). Their emission depends on temperature, intensity of solar radiation, humidity and other physical and meteorological parameters (Karl et al., 2001b). Among the most widely documented wound-induced emissions are a series of C5 and C6 compounds and their derivatives. These compounds are detected in the atmosphere, especially C6 compounds, with concentrations varying between 0.01 µg (C) / g of dry matter and 1.30 mg (C) / g of dry matter or 1.9 g (C) / m^2 (Davis et al., 2007; Davis and Burkholder, 2011; Fall, 1999; Fisher et al., 2003; Fuentes et al., 2000; Grosjean et al., 1993; Grosjean and Grosjean, 1995; Hatanaka, 1993; Heiden et al., 2003; Karl et al., 2001a, 2001b; Kirstine et al., 1998; Lin et al., 2016; Nakamura and Hatanaka, 2002; Orlando et al., 2001). Hexenols are mainly derived from linoleic and linolenic acids, wounding, drying and pathogen attack (Heiden et al., 2003; Pfrang et al., 2008). Meanwhile, pentenols like 1-penten-3-ol and 2-penten-1-ol can be emitted into the atmosphere from freeze-damaged leaves, with concentrations of the order of ppbv, resulting from the peroxidation of fatty acids or for microbiological protection purpose (Davis and Burkholder, 2011; Karl et al., 2001b; Orlando et al., 2001).

2

66   Their atmospheric lifetime is influenced by the presence of the C = C double bond which
67   facilitates their oxidation by the photo-oxidants (OH, NO_3 and O_3) (Davis and Burkholder,
68   2011). These processes can contribute to the formation of other oxygenated species like
69   carbonyl and carboxylic acids, tropospheric ozone and secondary organic aerosols (SOA)
70   (Coates and Butler, 2015; Jenkin and Hayman, 1999) which would affect the tropospheric
71   composition as well as the climate. It is therefore important not only to study their reactivity
72   toward these oxidants but also to determine the type and the products yields of the formed
73   compounds.

74   The oxidation reactions of C5 and C6 unsaturated alcohols with OH radicals has been
75   relatively well studied (Davis and Burkholder, 2011; Gibilisco et al., 2013; Le Calvé et al.,
76   2000; Mellouki et al., 2003; Orlando et al., 2001; Papagni et al., 2009). However, studies of
77   the atmospheric degradation of these compounds (alcohols > C4) by ozone are still limited to
78   few studies. The rate coefficients of the ozonolysis of the compounds considered during the
79   present investigation have been determined at room temperature and as a function of
80   temperature in previous studies (Kalalian et al., 2020). The atmospheric lifetime of C5-C6
81   unsaturated alcohols were calculated and found to vary from few minutes to few days,
82   indicating that their lifetimes were affected by the local chemical composition and the
83   location of their emission sources (Grosjean and Grosjean, 1994; Kalalian et al., 2020; Lin et
84   al., 2016; O'Dwyer et al., 2010). Moreover, other studies have focused their attention on the
85   determination of the products formed during the ozonolysis reactions of different unsaturated
86   alcohols like 3-buten-1-ol, 2-buten-1-ol, 3-buten-2-ol, 2-methyl-3-buten-2-ol, 2-buten-1,4-
87   diol, *cis*-2-penten-1-ol, 1-penten-3-ol, *cis*-3-hexen-1-ol, and have established reaction
88   mechanisms (Aschmann et al., 1997; Grosjean et al., 1993; Grosjean and Grosjean, 1995;
89   O'Dwyer et al., 2010). In the studies of Grosjean et al. (1993) and Grosjean and Grosjean,
90   (1995), carbonyl products were isolated as 2,4-dinitrophenyl hydrazones by sampling the
91   reaction mix through small C_{18} cartridges covered by 2,4-dinitrophenylhydrazine (DNPH) and
92   then analyzed by liquid chromatography. Experiments were performed at room temperature
93   and at atmospheric pressure and at 50% of relative humidity. In addition, O'Dwyer et al.
94   (2010) determined the primary products of the ozonolysis reaction of 1-penten-3-ol and *cis*-2-
95   penten-1-ol by FTIR and GC-MS at room temperature and atmospheric pressure and at a
96   relative humidity (RH) lower than 1%. To the extent of our knowledge, no mechanistic study
97   of the ozonolysis reaction of *trans*-3-hexen-1-ol exists in the literature.

98   Thus, in order to improve our understanding on the mechanisms occurring in these processes

99   and enrich the mechanistic databases, further experimental work on products investigation is

100   still required due to discrepancies in some of the experimental products formation yields.

101   Keeping in view the above facts, in this work, the products of the gas phase ozonolysis of

102   three unsaturated alcohols 1-penten-3-ol (C_5) (1P3OL), *cis*-2-penten-1-ol (C_5) (c-2P1OL) and

103   *trans*-3-hexen-1-ol (C_6) (t-3H1OL) were identified using state of the art analytical techniques

104   and their corresponding yields were determined at 298 K and 760 Torr. Attempts have been

105   made to provide plausible reaction mechanisms for the ozonolysis of the targeted alkenols as

106   well. This work will provide complementary information, in terms of products identification

107   and reaction pathways, to previous studies for C5 alcohols (Aschmann et al., 1997; Grosjean

108   et al., 1993; Grosjean and Grosjean, 1995; O'Dwyer et al., 2010) and a first reported

109   mechanistic study for *trans*-3-hexen-1-ol. This information is crucial for the development of

110   reliable atmospheric chemistry models in order to predict the formation of photo-oxidants

111   such as the formation of secondary organic aerosols.

112   **2. Experimental section**

113   In this work, an Atmospheric Simulation Chamber (ASC) was used. It consisted of a Pyrex

114   reactor (Volume = 63L) connected to a FTIR spectrometer and to a GC-MS. Experiments

115   were carried out at room temperature (T = 298 ± 2 K) and at a pressure of 760 torr in the

116   presence of an excess of cyclohexane used as scavenger of OH radicals. The experimental

117   setup consisted of a triple jacket pyrex reactor transparent to the photolytic light at

118   wavelength greater than 290 nm. This reactor is composed of a multiple reflections cell

119   (length: 200 cm; diameter: 20 cm) with a water flow between the two jackets of the reactor

120   allowing it to maintain the temperature at 298±2 K. The pressure inside the reactor could vary

121   from few mTorr to 1000 Torr. However, in our experimental conditions, the pressure was

122   around 760 Torr. The chamber was equipped with golden mirrors which permitted to vary the

123   optical path, which was set at 56 m in this work and connected to a FTIR spectrometer

124   (Bruker Equinox 55) operating in the range 4000 - 400 cm^{-1} with a resolution of 2 cm^{-1}.

125   During an experiment, 40 to 60 IR spectra were collected. Spectra were recorded every 3

126   minutes and each spectrum constitutes an average of 100 scans to improve the signal to noise

127   ratio. A GC-MS (Thermo Fisher, column: Agilent DB-5MS, 30 m x 0.25 mm x 0.25 μm,

128   carrier gas: Helium) was also used and it consisted of off-line measurements with the use of

129   SPME fibers for the sampling. The different parameters used in GC-MS are summarized in

130 **SM-1 supporting materials** and further details of the experimental methodology are given in
131 previous publications (Al Rashidi et al., 2014; Kalalian et al., 2020, 2017; Laversin et al.,
132 2016).

133 Both FTIR and SPME/GC-MS techniques were used to monitor the reagents and products
134 concentrations during experiments. The integrated IR bands for the studied compounds were:
135 930 -950 cm^{-1} for 1P3OL; 920-960 cm^{-1} for c-2P1OL and 939-987 cm^{-1} for t-3H1OL. These
136 bands correspond to the =C-H deformation and were used to monitor the concentration of the
137 corresponding alcohols. However, analysis in GC-MS were performed using the Total Ion
138 Current (TIC) mode in order to identify all the compounds formed during the ozonolysis
139 reaction.

140 One should note that the ozonolysis of unsaturated alcohols generates carbonyl, bi-carbonyl
141 and hydroxy-carbonyl compounds. Among these compounds, propanal, glycolaldehyde,
142 acetaldehyde were commercially available, while other compounds such as glyoxal,
143 methylglyoxal and 2-hydroxybutanal were synthesized following the methods given by
144 Horowitz et al. (2001) and Lockhart et al. (2013), Staffelbach et al. (1995) and Fessner et al.
145 (2000), respectively. The purity of the synthesized compounds was checked by GC and FTIR
146 and were further purified by repeated freeze-pump-thaw cycles before use. As for
147 formaldehyde, this compound was prepared by heating paraformaldehyde around 120 °C. A
148 slow flow of nitrogen gas was used to drive the formed formaldehyde into the cell through a
149 cooling trap in order to eliminate water and polymerized products. Formaldehyde
150 concentration was then controlled by UV spectroscopy. The same procedure was also
151 followed for glycolaldehyde dimer to generate gas phase glycoladehyde as a reference
152 standard.

153 Calibration curves for all the above-mentioned species were made by both FTIR and
154 SPME/GC-MS. Thus, the products of the ozonolysis reactions of targeted alkenols were
155 identified and quantified by comparison with previously established standard spectra in IR
156 and GC-MS.

157 Prior to any experiment a background check was performed to avoid any carry over from a
158 previous experiment. During each experiment, a concentration of (3-4) × 10^{14} molecules cm^{-3}
159 of alcohols and (9-20) × 10^{15} molecules cm^{-3} of cyclohexane used as OH scavenger, were
160 introduced into the simulation chamber by an air flow after the vaporization of their
161 corresponding liquid standards. Ozone was generated by an ozonizer. The ozone generator

162 used is composed of a double walled pyrex cylinder placed between two copper electrodes
163 and connected to a high frequency generator KIKUSUI-PCCR 500LE, having a single-phase
164 output with a nominal capacity of 500 VA. Ozone is produced by dissociation of the oxygen
165 flowing between the two electrodes. The ozone-oxygen mixture is diluted with dry air at the
166 outlet of the ozonizer and directed to a 12 cm long cylindrical pyrex cell, designed to carry
167 out UV measurements and thus control the quantity of ozone introduced into the simulation
168 chamber. The ozone concentration was monitored at 270 nm at the output of the cell by a
169 CCD camera (Avantes). Ozone was then introduced into the reactor with a continuous flow of
170 1 mL/min (corresponding to a concentration of the order of 2 x 10^{12} molecules cm $^{-3}$).

171   At the same time, solid phase microextraction (SPME) fibers specifically
172 polydimethylsiloxane / divinylbenzene (PDMS / DVB) were used for sampling. These fibers
173 were previously doped with o- (2, 3, 4, 5, 6 - pentafluorobenzyl) hydroxylamine (PFBHA)
174 (Bourdin and Desauziers, 2014; Reisen et al., 2003). The derivatization conditions were taken
175 from Reisen et al. (2003). This implies an exposure of the PDMS/DVB fiber for one hour in
176 the head space of a vial containing 4 mL of the aqueous solution of PFBHA (0.4g/L) and
177 agitated with a magnetic stirrer. These conditions ensure a maximum coating of the fiber by
178 the PFBHA and a sufficient quantity of oxime for the detection. The formed carbonyls in the
179 simulation chamber adsorb on the PFBHA-doped fiber and form the corresponding oxime.
180 Samples were taken approximately every 15 minutes by exposing the doped PDMS/DVB
181 fiber into the simulation chamber for 5 minutes. The fibers were then taken from the chamber
182 and were thermally desorbed at 220° C in the GC-MS injector.

183 The ozonolysis of the targeted unsaturated alcohols were performed in 3 to 6 replicas. The
184 values of the obtained yields correspond to the average of the determinations made by FTIR
185 and SPME/GC-MS. The uncertainty on the obtained yields corresponds to twice the standard
186 deviation (2σ) and that on the total yield was determined using the error propagation. The
187 carbon balances were also calculated for each time interval of the experiment (every 15
188 minutes).

189 The purities of the used chemicals were as follows: 1-penten-3-ol (>98%), *cis*-2-penten-1-ol
190 (≥96%), *trans*-3-hexen-1-ol (97%), cyclohexane (≥99%), propanal (≥97%), acetaldehyde
191 (≥99.5%), glycolaldehyde dimer (≥95%), methylglyoxal (40% in H_2O), paraformaldehyde (>
192 95%), formic acid (≥95%), propanoic acid (≥99.5%), glyoxal trimer dihydrate (≥95%) and
193 PFBHA (≥98%). All these chemicals were provided by Sigma Aldrich and Santa Cruz and

194 were used without further purification. The gases were supplied by Air Liquide: Air
195 (>99.9999%), O_2 (>99.999%), He (>99.999%).

3. Results and discussion

3.1. Products formation yields

198 IR spectra at three different reaction times of the reaction of ozone with 1P3OL, c-2P1OL
199 and t-3H1OL are shown in **SM-2 in the supporting materials**. The approach used to quantify
200 the observed products with the FTIR spectroscopy is based on spectrum subtractions. **SM-3**
201 **and SM-4** in the supporting materials show the different steps involved in spectra
202 subtractions for 1P3OL and c-2P1OL to determine the concentrations and the formation
203 yields of the observed products. Subtraction of a spectra recorded at time, t of the reaction
204 time from the initial spectrum leads to a spectrum (R), which contains only the corresponding
205 peaks for reaction products. Their formation was confirmed by SPME/GC-MS following the
206 formation of their corresponding oxime. However, for t-3H1OL, the identification of the
207 products was only made by GC-MS due to the lack of a reference for the 3-hydroxypropanal.
208 Examples of chromatograms for the ozonolysis of 1P3OL, c-2P1OL and t-3H1OL are given
209 **in SM-5 in the supporting materials.**

210 Moreover, the molar fractions of the reagents and the identified products were calculated
211 according to:

$$Molar\ fraction = \frac{C \times T \times R}{N_A \times P}$$

212 where, C is the concentration of the reagents or the products (molecules cm^{-3}), T is the
213 temperature (K), R is the gas constant (R = 8.314 J mol^{-1}K^{-1}), N_A is the Avogadro number (N$_A$
214 = 6.022 x 10^{23} mol^{-1}) and P is the pressure (Pascal).

215 The temporal evolution profiles of the species involved in the reaction processes are presented
216 in **Figure 1.** All identified products belong to the family of aldehydes and hydroxyaldehydes.
217 **Figure 1** shows that the concentrations of the identified products are almost stable after 70
218 minutes of reaction time. Beyond this time, a slight consumption is observed for hydroxy-
219 carbonyls and bi-carbonyls; however, a slight increase is observed for glycolaldehyde and
220 propanal for the reaction of c-2P1OL. These variations remain included in the molar fraction
221 uncertainty interval.

222 The carbon balance was also determined for each time interval of the experiment according
223 to:

$$\text{Carbon balance} = \frac{\sum(\text{molar fraction of species at time } t \ \times \ \text{species carbon atom number})}{\text{molar fraction of reagents at time } t_0 \ \times \ \text{reagent carbon atom number}} \times 100$$

224 Results plotted in **Figure 1** show that a carbon deficit was observed when the rate of
225 consumption of the starting reagent exceeded 30%. At the end of the reaction the carbon
226 deficit can reach up to 50% for 1P3OL, 65% for c-2P1OL and 60% for t-3H1OL. This is due
227 to the possible formation of additional products in the reactor that could not be detected or
228 identified by the used analytical techniques on account of the limitation associated to the
229 derivatization agent, lack in reference standards and the detection limit of the instruments.
230 The incomplete carbon balance might also result from an interaction between the gas and the
231 aerosol phase. In fact, in the study of O'Dwyer et al. (2010), the formation of secondary
232 organic aerosol (SOA) for the ozonolysis of unsaturated alcohols (1-penten-3-ol and *cis*-2-
233 penten-1ol) was observed with yields ranging from $0.13 - 0.17$. However, we do not have the
234 means to do these SOA measurements in our laboratory.

235 The formation yields of primary (2-hydroxybutanal and formaldehyde for 1P3OL,
236 glycolaldehyde and propanal for c-2P1OL, 3-hydroxypropanal and propanal for t-3H1OL)
237 and secondary products (propanal and acetaldehyde for 1P3OL, acetaldehyde, 2-
238 hydroxypropanal, and methylglyoxal for c-2P1OL, and glycolaldehyde, methylglyoxal and
239 acetaldehyde for t-3H1OL) for the reaction of O_3 with 1P3OL, c-2P1OL and t-3H1OL were
240 determined by plotting their concentration as a function of that of the alcohol for increasing
241 times by FTIR and SPME/GC-MS **(Figures 2-4).** The formation yields correspond to the
242 slopes of the plotted curves. The average yields obtained by both techniques are summarized
243 in **Table 1.** The formation yields of primary carbonyl exceed 100% (108 ± 16 for 1-penten-3-ol
244 and 106 ± 13 for *trans*-3-hexen-1-ol respectively), as the formed primary carbonyls can also be
245 produced via the reactions of Criegee intermediates.

246 Uncertainty on the average yields are twice the standard deviation. This uncertainty originated
247 mainly from systematic errors due to the used analytical techniques to monitor and quantify
248 the identified compounds. For FTIR analysis, uncertainty on yield is mainly due to errors
249 related to spectra subtraction as well as the area integration of spectroscopic peaks
250 corresponding to both the reagent and the identified products. To reduce this error, more than
251 40 IR spectra were collected during an experiment and each spectrum constituted an average
252 of 100 scans. For GC/MS analysis, errors are related to chromatographic peak's integration

253   and standard calibration curves. To minimize this error, preliminary tests were performed to

254   optimise SPME-GC/MS method. In addition, experiments were performed in 3-6 replicas.

255   The yields obtained by both techniques are in good agreement with a difference that do not

256   exceed 20-25%. However, the obtained results by FTIR have higher uncertainties related

257   mainly to peak substractions, which are systematic errors that cannot be avoided. As

258   expected, large error (more than 30%) is mainly observed for species with low concentrations.

259   These yields were compared to previous literature studies for 1P3OL and c-2P1OL (Grosjean

260   and Grosjean, 1995; O'Dwyer et al., 2010). As for the ozonolysis of t-3H1OL, to the best of

261   our knowledge, no study exists in the literature. The different experimental conditions of this

262   current study and those of the literature are listed **in SM-6 in the supporting materials.**

263   The major products identified during the ozonolysis of 1-penten-3-ol were formaldehyde (62

264   ± 12)% and 2-hydroxybutanal (46 ± 10)% **(Table 1).** For 2-hydroxybutanal yields, a 35%

265   discrepancy is observed when compared with the values obtained by Grosjean and Grosjean,

266   (1995), whereas it agrees well with the values reported by O'Dwyer et al. (2010). As for

267   formaldehyde yields, 45% and 21% discrepencies are observed with the yields determined by

268   Grosjean and Grosjean, (1995) and O'Dwyer et al. (2010), respectively. Our results are in

269   good agreement with those of O'Dwyer et al. (2010) who conducted their study at the same

270   relative humidity (RH<1%) as was kept in the present study. The substantial discrepancy with

271   the results of Grosjean and Grosjean, (1995) might be linked to the different relative humidity

272   conditions used. Minor products such as propanal and acetaldehyde have been identified and

273   quantified with yields of (12 ± 4)% and (10 ± 4)% respectively. Acetaldehyde was not

274   quantified by Grosjean and Grosjean, (1995) and O'Dwyer et al. (2010). Formic acid was

275   observed but not quantified by O'Dwyer et al. (2010). However, it was not detected in this

276   study.

277   As for the ozonolysis of *cis*-2-penten-1-ol, the major products identified and quantified were

278   glycolaldehyde (56 ± 14)% and propanal (40 ± 10)% as listed in **Table 1.** For glycolaldehyde

279   yields, 5% and 23% discrepancies are obtained with the values obtained by Grosjean and

280   Grosjean, (1995) and O'Dwyer et al. (2010), respectively. As for propanal yields, 28% and

281   3% discrepancies are observed with the values of Grosjean and Grosjean, (1995) and

282   O'Dwyer et al. (2010) respectively. The experimental data obtained for the main products

283   (propanal and glycolaldehyde) are in good agreement with those determined by Grosjean and

284   Grosjean, (1995) and O'Dwyer et al. (2010) with an average difference of 17% and 13%, in

285 their respective yields. Other compounds such as 2-hydroxypropanal, methylglyoxal and
286 acetaldehyde have also been observed with the percentage yields of (10 ± 2)%, (3±1)% and
287 (13 ± 5)%, respectively. Traces of formaldehyde were also detected but could not be
288 quantified. In their study of ozonolysis of c-2P1OL, O'Dwyer et al. (2010) have only
289 identified acetaldehyde, whereas Grosjean and Grosjean, (1995) identified and quantified
290 acetaldehyde, methylglyoxal and formaldehyde. It should be noted that Grosjean and
291 Grosjean, (1995) assumed that glycolaldehyde, hydroxycarbonyls (2-hydroxypropanal and 2-
292 hydroxybutanal) reacted with the acidic DNPH to form the DNPH derivatives of the
293 corresponding di-carbonyls, namely glyoxal, methylglyoxal and 2-oxobutanal. Thus, the 2-
294 hydroxypropanal was measured as methylglyoxal-DNPH using the available reference
295 standard.

296 It should be noted that, relative humidity may affect the products yields during the ozonolysis
297 of unsaturated compounds. In fact several studies, concerning the ozonolysis of alkenes, have
298 shown that the slightly different amounts of water vapour present in the chambers could affect
299 the reaction pathways of the Criegee intermediates and thus alter product distributions and the
300 generation of OH radicals (Hasson et al., 2001 ; O'Dwyer et al., 2010 ; Wegener et al., 2007).
301 Indeed, the humidity can accelerate the formation of organic hydroperoxides via the
302 hydroperoxide channels. Thus, more experiments for the ozonolysis of other unsaturated
303 compounds, under different relative humidities are still needed.

304

305 **3.2. Hydroxyl group effect on primary carbonyl formation yields**
306 To better understand the effect of a hydroxyl substituent on primary carbonyl formation
307 yields, the formation yields of the products resulting from the ozonolysis of 1P3OL, c-2P1OL
308 and t-3H1OLwere compared to those of their homologous alkenes **(Table 2).** 1P3OL, c-
309 2P1OL and t-3H1OL were compared to 1-pentene, *cis*-2-pentene and *trans*-3-hexene,
310 respectively. These alkenes have the same geometric configuration and the same position of
311 the double bond as that present in the targeted alcohols. The ozonolysis of 1-pentene was
312 performed by Atkinson et al. (1995) in a 7900 L Teflon chamber at 296 ± 2 K and 740 Torr
313 total pressure of purified air at ~5% relative humidity and in the presence of OH scavenger
314 (cyclohexane or n-octane) using FTIR spectroscopy and GC-FID. The ozonolysis of *cis*-2
315 pentene and *trans*-3-hexene were carried out by Grosjean et al. (1996) and Grosjean and
316 Grosjean, (1997) in a 3.7-3.9 m^3 Teflon film chambers covered with black plastic. The
317 experiments were performed in the presence of cyclohexane as OH scavenger, at T=286-

318   296K, at atmospheric pressure and at a relative humidity of 55 ± 10% using C18 cartridges

319   coated with 2,4-dinitrophenylhydrazine (DNPH) analyzed by liquid chromatography.

320   The branching ratio between the two potential routes for the ozonide to decompose seems

321   to be similar between the alcohols and their respective alkenes. This behavior has been also

322   observed for other mono- and di-substituted unsaturated alcohols, carbonyl compounds, ethers

323   and esters (Grosjean, 1996): no influence of the presence of oxygenated groups on the

324   branching ratios was observed. This similarity between alkenes and oxygenated compounds

325   such as alcohol, ether, carbonyl and ester show that the ozone addition to the C=C double

326   bond forms an ozonide and its decomposition follow the same route irrespective of the

327   structure of the compound. However, concerning the reactivity, the presence of functional

328   groups influences the kinetics of the ozonolysis in the gas phase where alkenes, unsaturated

329   ethers and unsaturated alcohols react more rapidly with ozone than aldehydes, ketones and

330   unsaturated esters (Grosjean, 1996).

331

332   **3.3. Mechanistic schemes**

333   As with olefinic compounds, the reaction between unsaturated alcohols and ozone starts by an

334   electrophilic addition of ozone to the C=C double bond to form a primary ozonide. The latter

335   is not stable and cleaves simultaneously to give two primary carbonyl compounds and two

336   intermediates called the "Criegee" intermediate (Atkinson and Arey, 2003). Based on the

337   identified products in IR and GC-MS analysis, and the available literature for other

338   unsaturated compounds (Atkinson, 1998; Finlayson-Pitts and Pitts, 2000; Johnson and

339   Marston, 2008; O'Dwyer et al., 2010), detailed mechanisms of the ozonolysis of 1P3OL, c-

340   2P1OL and t-3H1OL are established **(Figure 5 (a-c)).**

341   The total yields of the primary products of the O_3-reaction with 1-penten-3-ol, *cis*-2-penten-1-

342   ol and *trans*-3-hexen-1-ol are (108±16) %, (96±17) %, and (106±13) %, respectively.

343   The products formation yields summarized in **Table 1** show that there is no remarkable

344   preference between the evolution pathways of the Criegee bi-radical. In addition, the total

345   yields of the primary products exceed 100%. These results indicate that the observed yields

346   include the formation of these products by both primary (ozonide reactions) and secondary

347   reactions (CI reactions). Therefore, it is not easy to extract the preferential reaction pathway

348   that should be followed by both ozonide and Criegee intermediates.

349   The Criegee, $H_2C°OO°$ is produced during the ozonolysis of 1P3OL. Its decomposition leads

350   to the formation of other stable species such as HCHO, CO_2, CO, H_2O, H_2, OH and

351   HC(O)OH (Johnson and Marston, 2008). Determination of H_2O and CO_2 yields was not

352   attempted due to the interference of the background levels of these compounds in the reaction

353   chamber because part of the beam was exposed to air within the compartment. The stabilized

354   Criegee intermediate, CH_2OO can also undergo various reactions, including:

(i) Reaction with water to produce hydroxymethyl hydroperoxide $HOCH_2OOH$. The

356   latter can decompose in two ways to generate: (I) formic acid (HC(O)OH) and H_2O,

357   (II) formaldehyde (HCHO) and H_2O_2:

$$CH_2OO + H_2O \rightarrow HOCH_2OOH.; \qquad\qquad \rightarrow HC(O)OH + H_2O \qquad\qquad (I)$$
$$\rightarrow HCHO + H_2O_2 \qquad\qquad (II)$$

358   (ii) Reaction with HCOOH to form hydroperoxymethyl formate, $HC(O)OCH_2OOH$.

359   (iii) Reaction with HCHO to form formic acid HCOOH

360   However, no trace of formic acid was observed in FTIR or GC-MS. This might be linked

361   either to the very low concentration of formed formic acid (under the detection limit of the

362   instrument mainly FTIR) and to the fact that the experiments were conducted at a relative

363   humidity < 1%. Moreover, we assumed that the detected formaldehyde could not result from

364   the cited reactions as the study was conducted under dry condition (RH< 1%).

365   The Criegee, $CH_3CH_2CHOHC°HOO°$ formed during the ozonolysis of 1P3OL can evolve

366   mainly to form 2-hydroxybutanal (46±10)%, formaldehyde (62±12)%), propanal (12±4)%

367   and acetaldehyde (10±4)% (**Figure 5a)** (Grosjean and Grosjean, 1995; O'Dwyer et al., 2010)**.**

368   The pathway (c') corresponding to the formation of 2-hydroxybutanal and an oxygen atom O

369   (^{3}P) is considered as a minor pathway according to Finlayson-Pitts and Pitts, (2000). Propanal

370   has also been identified by O'Dwyer et al. (2010) and Grosjean and Grosjean, (1995) who

371   proposed that propanal could be produced from the unimolecular decomposition of excited

372   Criegee, as shown in **Figure 5a**. In addition, no chromatographic peak or band corresponding

373   to propanoic acid and 2-oxobutanal (lack of references) has been identified.

374   The Criegee, $CH_3CH_2CH°OO°$ formed during the reaction of O_3 with c-2P1OL and t-3H1OL

375   (Aschmann et al., 1997; Grosjean et al., 1993; Grosjean and Grosjean, 1995; O'Dwyer et al.,

376   2010) can evolve in five different pathways **(Figures 5b and 5c)**:

377	(i)	Production of an oxygen atom O (^{3}P) and propanal. This route is minor according
378		to Finlayson-Pitts and Pitts, (2000).
379	(ii)	Formation of OH radical and $CH_3CH_2C°O$. The latter can react with O_2 to give a
380		peroxypropenyl, which decomposes to form CO_2 and $CH_3CH_2°$. With an excess of
381		O_2, the ethyl radical leads to the formation of acetaldehyde quantified by
382		SPME/GC-MS with a yield of (13 ± 5)% for c-2P1OL and (30 ± 4)% for t-3-H1OL.
383	(iii)	Formation of ethane and CO_2. It was not possible to detect ethane by the used
384		analytical techniques.
385	(iv)	Formation of the hydroperoxyde $CH_3CH=CHOOH$ that can decompose in four
386		different pathways as shown in **Figures 5 (b-c).** 2-Hydroxypropanal has been
387		identified by FTIR in the case of c-2P1OL with a yield of (10 ± 2) %. Acetaldehyde
388		can also result from this way where it was quantified with a yield of (13 ± 5) % for
389		c-2P1OL and (30 ± 4) % for t-3H1OL. In addition to the above-mentioned
390		compound, methylglyoxal was identified with a yield of (8 ± 3) % for t-3H1OL and
391		(3 ± 1) % for c-2P1OL. This is in accord with the results obtained by Grosjean and
392		Grosjean, (1995) in the study of the ozonolysis of c-2P1OL, where acetaldehyde
393		and methylglyoxal were observed.
394	(v)	Formation of propanoic acid. This was observed neither in FTIR nor in
395		SPME/GC- MS.

396   The bi-radical $HOCH_2CH°OO°$, formed during the ozonolysis of c-2P1OL, can evolve into

397   three different pathways **(Figure 5b).** However, apart from glycolaldehyde, traces of

398   formaldehyde were observed but not quantified in GC-MS.

399   The bi-radical $OHCH_3CH_2C°HOO°$, formed during the ozonolysis of t-3H1OL (Aschmann et

400   al., 1997; Grosjean et al., 1993) evolves in five different routes **(Figure 5c):**

401	(i)	Formation of 3-hydroxypropanal and atomic oxygen. This is a minor pathway
402		according to Finlayson-Pitts and Pitts, (2000).
403	(ii)	Formation of hydroperoxide $OHCH_2CH = CHOOH$. The decomposition of this
404		hydroperoxide may follow 5 different routes as shown in **Figure 5c**. However,
405		only glycolaldehyde is observed and quantified in GC-MS with a yield of (16 ± 4)
406		%.

407   (iii)   Formation of OH radicals and $OHCH_2CH_2CO°$. In the presence of oxygen, the
408   latter, induce the formation of glycolaldehyde quantified in GC-MS with a yield of
409   (16 ± 4) %.
410   (iv)   Formation of CO_2, HO_2 and glycolaldehyde. Glycolaldehyde was identified and
411   quantified in GC / MS with a yield of (16 ± 4) %.
412   (v)   Formation of $OHCH_2CH_2C(O)OH$. This compound was not observed with the
413   existing analytical techniques used during the present investigation due to lack of
414   references.

415

4. Conclusion

Reaction products and mechanisms of the gas phase reaction of ozone with three unsaturated alcohols (1-penten-3-ol, *cis*-2-penten-1-ol and *trans*-3-hexen-1-ol) have been determined at room temperature and atmospheric pressure in an atmospheric simulation chamber. Both the FTIR and the GC-MS techniques were used to monitor the concentrations of the reagents and the formed products. This study shows that their ozonolysis leads to the formation of carbonyl and hydroxylcarbonyl products. These multifunctional species contribute to the increase of the oxidizing capacity of the atmosphere (HO_x formation, SOA).

Primary products of the ozonolysis of 1P3OL, c-2P1OL and t-3H1OL are found to be 2-hydroxybutanal and formaldehyde, glycolaldehyde and propanal and 3-hydroxypropanal and propanal, respectively. The total formation yields of these products are around 100%. Some secondary products have also been detected and quantified. The yields of primary and secondary products obtained in this work are close to those found in the literature. No preference between the primary ozonide decomposition pathways was found in the ozonolysis of the three unsaturated alcohols undertaken during the present study. Detailed mechanisms for the ozonolysis of the targeted compounds have been developed based on our observations and those available in the literature.

435

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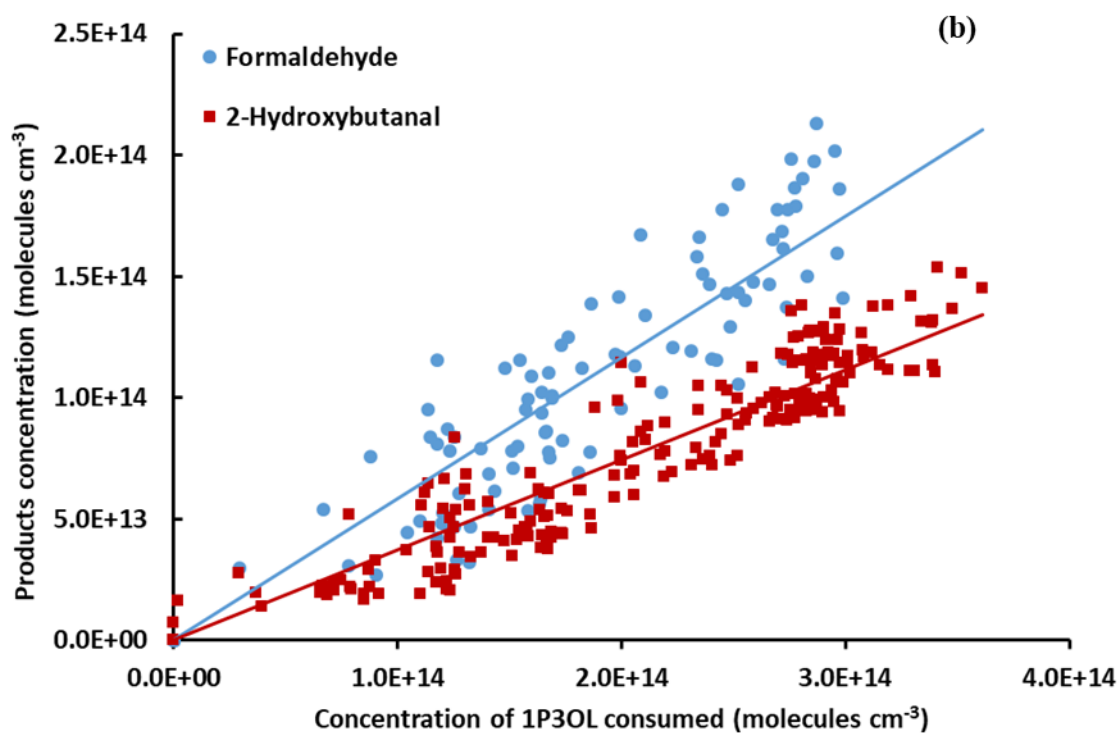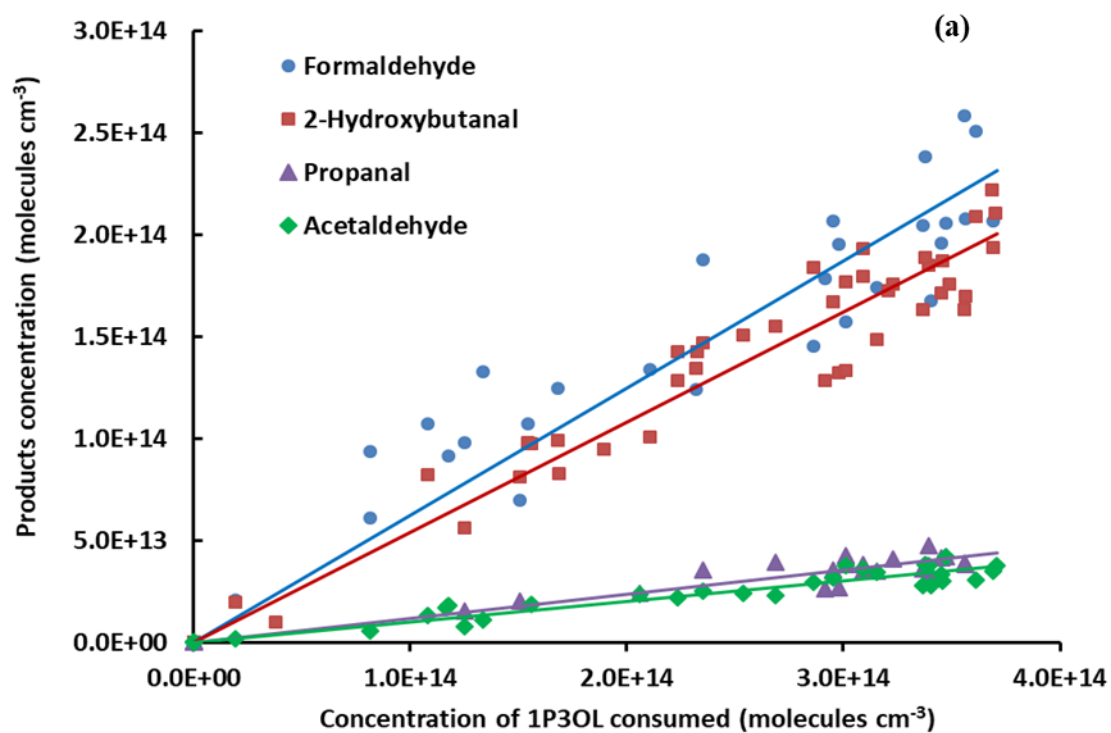597   https://doi.org/10.1071/EN08047

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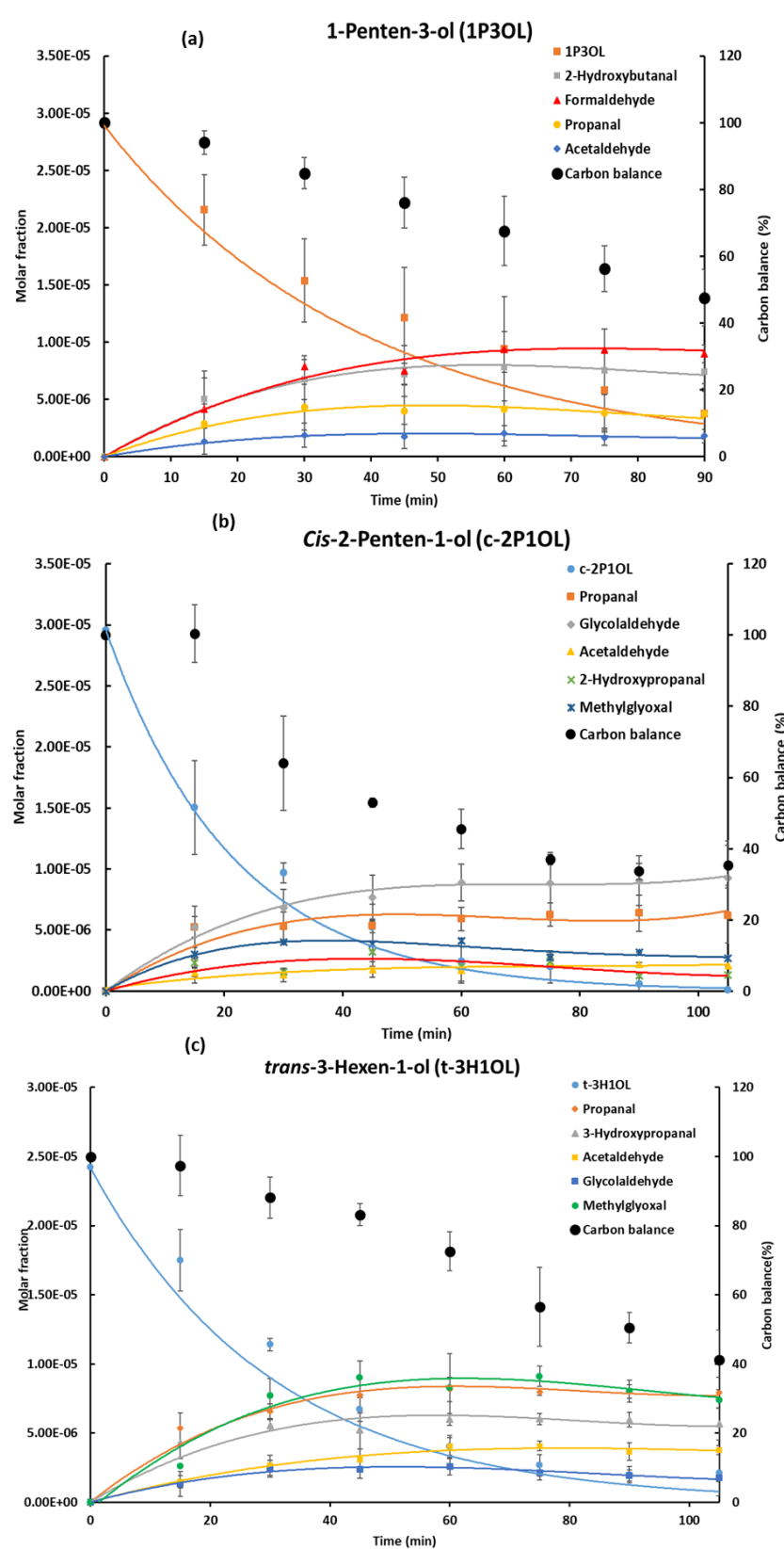
Figure 1: Carbon balance and temporal evolution of 1-penten-3-ol (a), *cis*-2-penten-1-ol (b) and *trans*-3-hexen-1-ol (c) and the formed products identified by SPME/GC-MS and by FTIR during their ozonolysis. Solid lines correspond to the points adjustments using a polynomial fit ($R^2 > 0.9$).
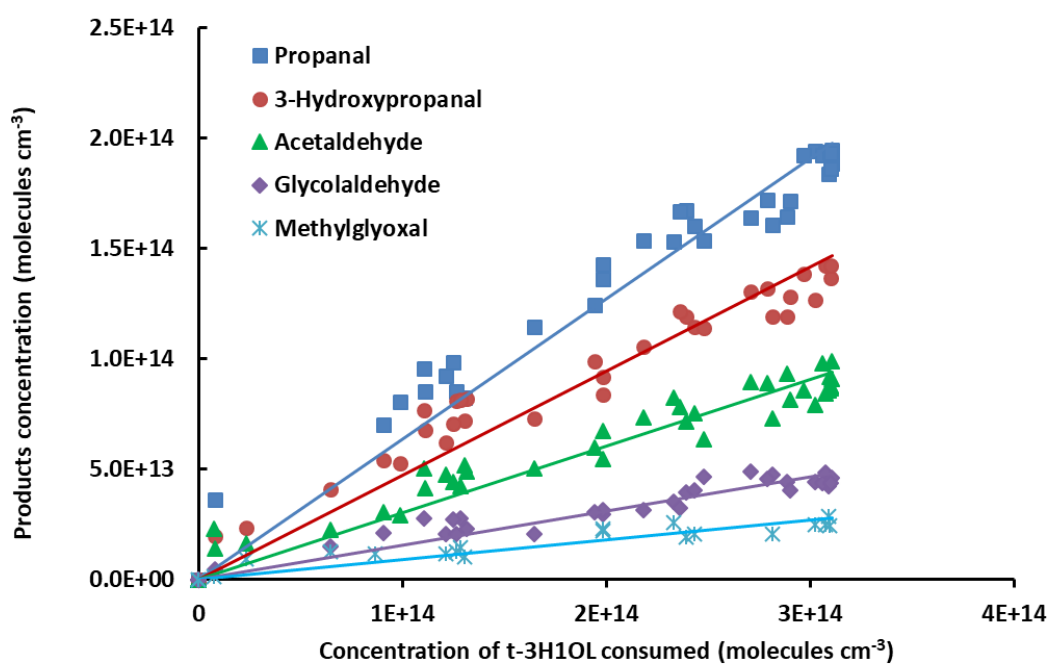
Figure 2: Formation yields for primary and secondary products observed during the ozonolysis of 1P3OL obtained by SPME/ GC- MS (a) and by FTIR (b).
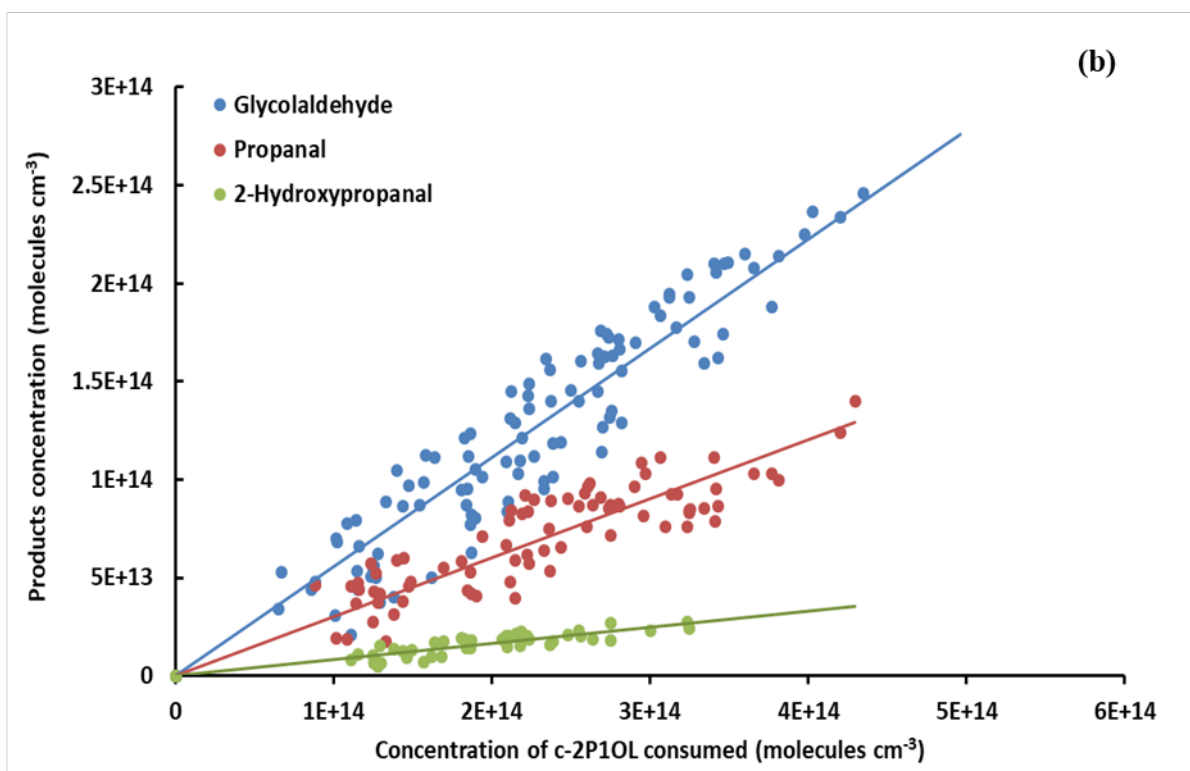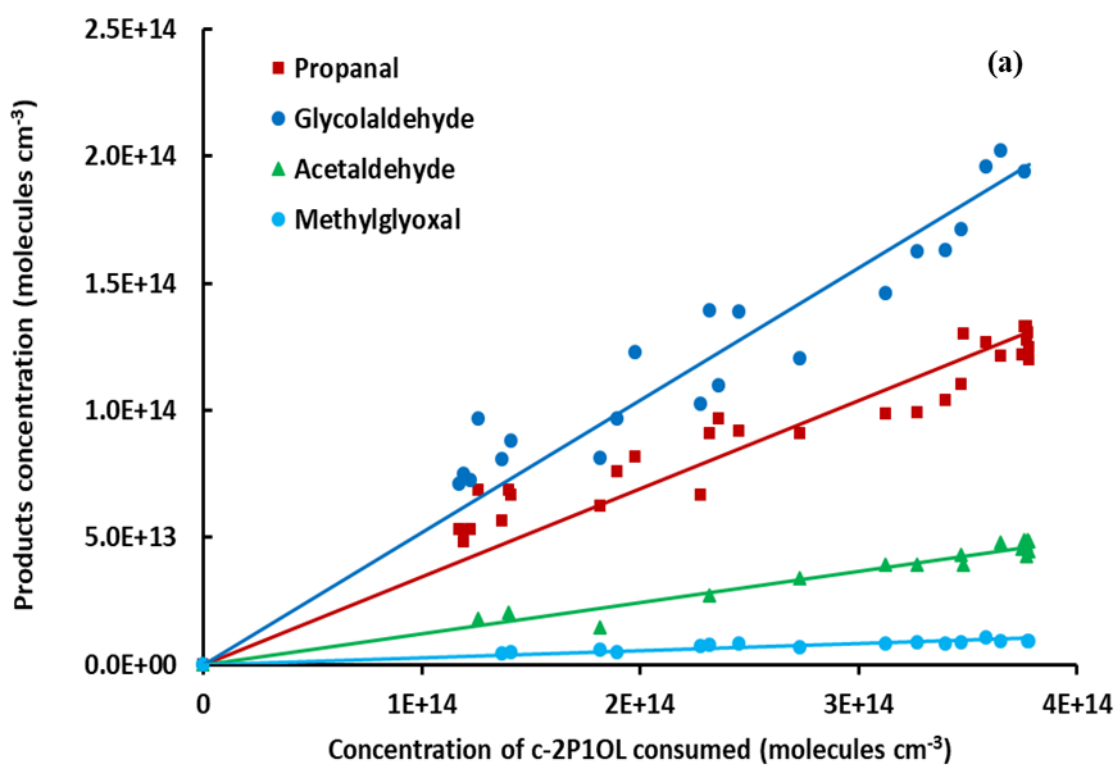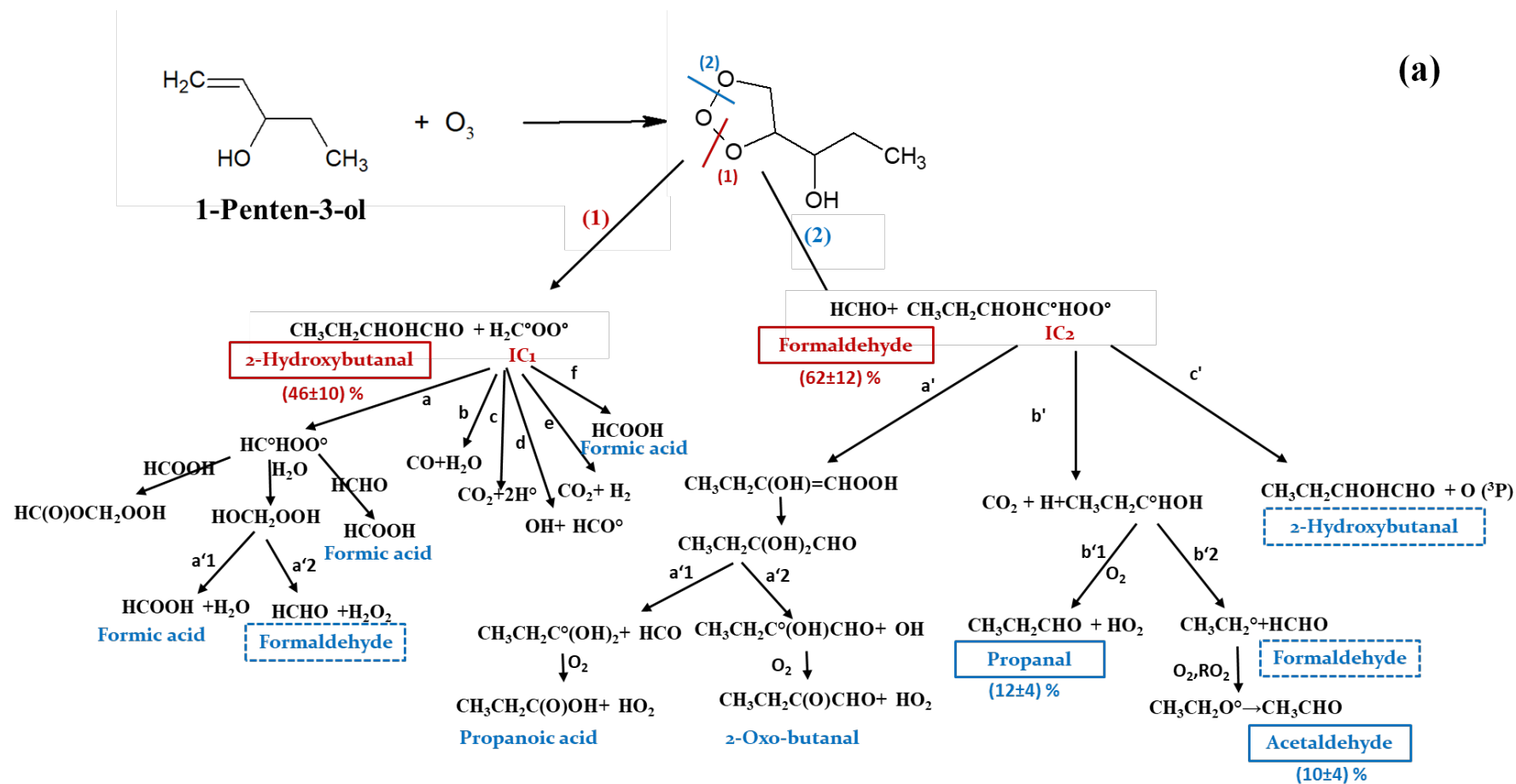
Figure 3: Formation yields for primary and secondary products observed during the ozonolysis of c-2P1OL obtained by SPME/GC - MS (a) and by FTIR (b).
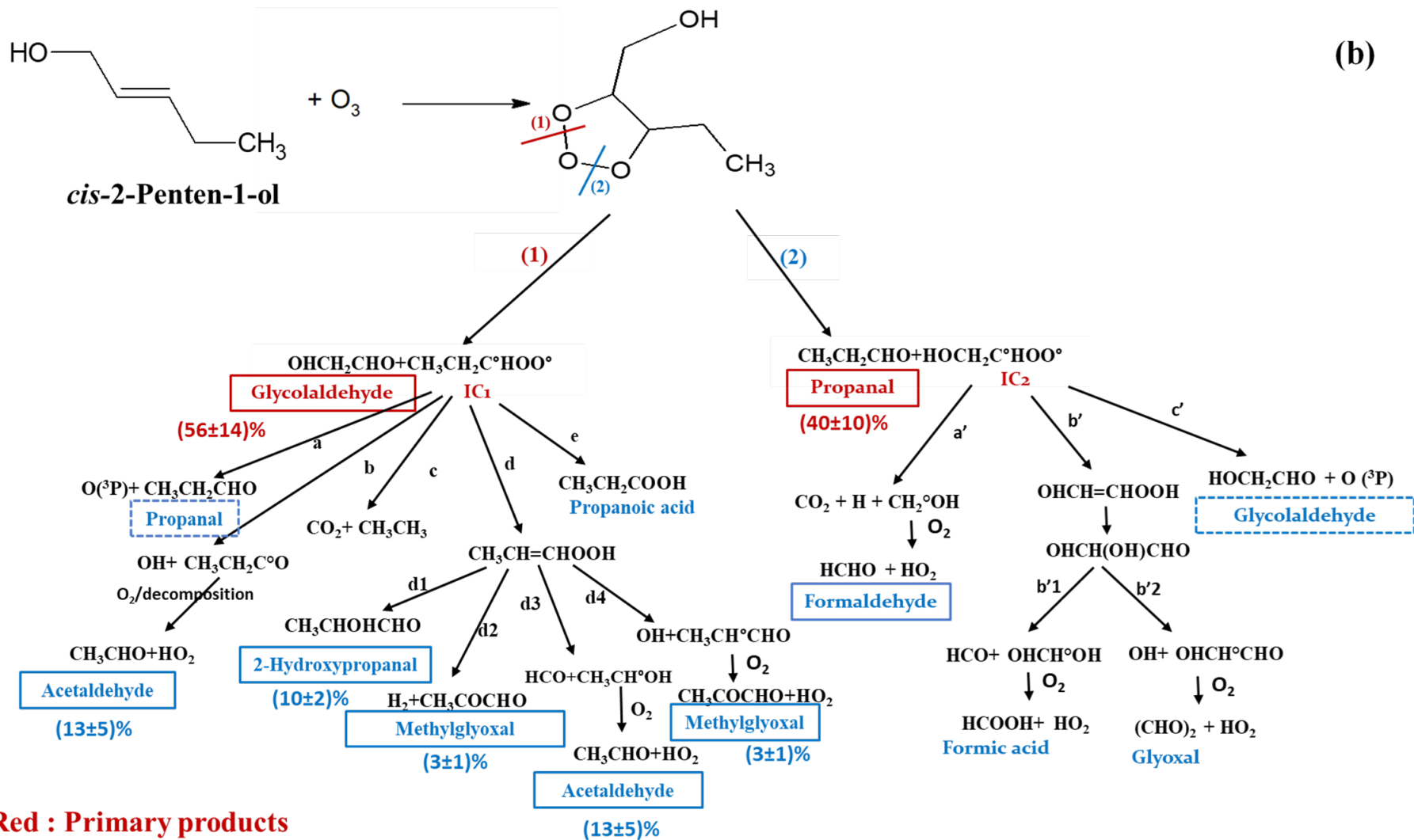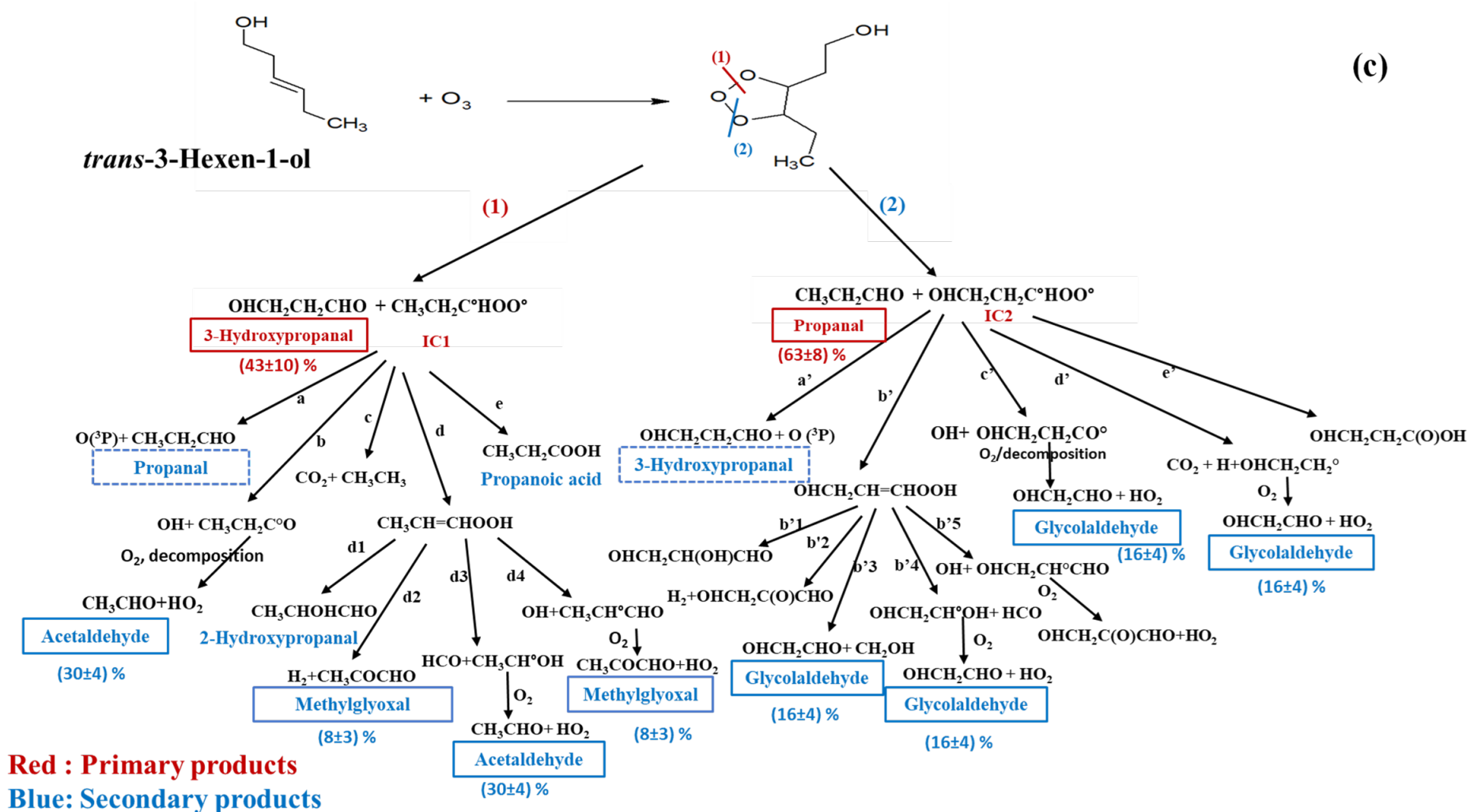
Figure 4: Formation yields for primary and secondary products observed during the ozonolysis of t-3H1OL obtained by SPME/GC - MS.

(a)

Red : Primary products
Blue: Secondary products

(b)

HO — (structure) + O₃ → (cyclic ozonide structure with OH and CH₃)

cis-2-Penten-1-ol

(1) (red) / (2) (blue)

(1)

OHCH₂CHO+CH₃CH₂C°HOO°

Glycolaldehyde   IC₁

(56±14)%

a → O(³P)+ CH₃CH₂CHO
Propanal

OH+ CH₃CH₂C°O
O₂/decomposition

CH₃CHO+HO₂
Acetaldehyde
(13±5)%

b → CO₂+ CH₃CH₃

c → CH₃CH=CHOOH

d1 → CH₃CHOHCHO
2-Hydroxypropanal
(10±2)%

d2 → H₂+CH₃COCHO
Methylglyoxal
(3±1)%

d3 → HCO+CH₃CH°OH
↓ O₂
CH₃CHO+HO₂
Acetaldehyde
(13±5)%

d4 → OH+CH₃CH°CHO
↓ O₂
CH₃COCHO+HO₂
Methylglyoxal
(3±1)%

e → CH₃CH₂COOH
Propanoic acid

(2)

CH₃CH₂CHO+HOCH₂C°HOO°

Propanal   IC₂

(40±10)%

a' → CO₂ + H + CH₂°OH
↓ O₂
HCHO + HO₂
Formaldehyde

b' → OHCH=CHOOH
↓
OHCH(OH)CHO

b'1 → HCO+ OHCH°OH
↓ O₂
HCOOH+ HO₂
Formic acid

b'2 → OH+ OHCH°CHO
↓ O₂
(CHO)₂ + HO₂
Glyoxal

c' → HOCH₂CHO + O (³P)
Glycolaldehyde

Red : Primary products
Blue: Secondary products

Figure 5: Proposed reaction scheme for the gas phase ozonolysis of 1 penten-3-ol (a), *cis*-2-penten-1-ol (b) and *trans*-3-hexen-1-ol (c). The compounds framed with solid lines are detected in the present study whereas the one in the dotted frame corresponds to secondary pathways of the primary products.

Table 1: Comparison of the products identified and quantified during the ozonolysis of 1-penten-3-ol, *cis*-2-penten-1-ol and t*rans*-3-hexen-1-ol.

Unsaturated alcohol	Identified products	Average yields-this work (%)	Literature
1-Penten-3-ol	2-Hydroxybutanal [1,2]	46±10	30±5[a]
			46±3[b]
	Formaldehyde[1,2]	62±12	34±4[a]
			49±2[b]
	Propanal[2]	12±4	12±1[a]
			15±2[b]
	Acetaldehyde[2]	10±4	n.i.[a, b]
	Formic acid	-	n.i.[a]
			Identified but not quantified[b]
cis-2-Penten-1-ol	Glycolaldehyde[1,2]	56±14	53±4[a]
			43±4[b]
	Propanal[1,2]	40±10	51±2[a]
			39±3[b]
	Acetaldehyde[2]	13±5	8±1[a]
			Identified but not quantified[b]
	2-Hydroxypropanal[1]	10±2	n.i.[a, b]
	Formaldehyde[2]	Identified but not quantified	7±2[a]
			n.i.[b]
	Methylglyoxal	3±1-	4±1[a]
			n.i.[b]
trans-3-Hexen-1-ol	3-Hydroxypropanal[2]	43±10	
	Propanal[2]	63±8	
	Glycolaldehyde[2]	16±4	
	Acetaldehyde[2]	30±4	
	Methylglyoxal[2]	8±3	

a: Grosjean and Grosjean, (1995) ; b : O'Dwyer et al. (2010) ; [1]: detected in this work by FTIR; [2]: detected in this work by GC-MS, n.i..: not identified

Table 2: Comparison of the primary products formation yields (R) of unsaturated alcohols with their homologous alkenes.

Compounds	Primary products	R (%)	Homologous alkenes	Primary products	R (%)
1-Penten-3-ol	Formaldehyde	62±12	1-Pentene	Formaldehyde	60±6[a]
***cis*-2-Penten-1-ol**	Propanal	40±10	*cis*-2-Pentene	Propanal	51±3[b]
***trans*-3-Hexen-1-ol**	Propanal	63±8	*trans*-3-Hexene	Propanal	101±5[c]

a: Atkinson et al., (1995) ; b :Grosjean and Grosjean, (1997), c : Grosjean et al. (1996)

1-penten-3-ol

Cis-2-penten-1-ol

Trans-3-hexen-1-ol

+ O₃ →

(I)   (II)

Carbonyl 1   **IC 1**   **Carbonyl 2**   **IC 2**