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1 **An experimental study of the gas-phase reaction between Cl atoms and**
2 ***trans*-2-pentenal: kinetics, products and SOA formation**

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22

23 **Abstract**

24 The gas-phase reaction of trans-2-pentenal (T2P) with Cl atoms was studied at atmospheric
25 pressure and room temperature. A rate coefficient of $(2.56 \pm 0.83) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was
26 obtained using the relative rate method and isoprene, cyclohexane and ethanol as reference
27 compounds. The kinetic study was carried out using a 300-L Teflon bag simulation chamber
28 (IMT Lille Douai-France) and a 16-L Pyrex cell (UCLM-Ciudad Real-Spain), both coupled to
29 the Fourier transform infrared (FTIR) technique. Gas-phase products and secondary organic
30 aerosol (SOA) formation were studied at UCLM using a 16-L Pyrex cell and a 264-L quartz
31 simulation chamber coupled to the FTIR and gas-chromatography-mass spectrometry (GC-
32 MS) techniques. HCl, CO, and propanal were identified as products formed from the studied
33 reaction and quantified by FTIR, being the molar yield of the latter $(5.2 \pm 0.2)\%$. Formic acid
34 was identified as a secondary product and was quantified by FTIR with a yield of $(6.2 \pm 0.4)\%$.
35 In addition, 2-chlorobutanal and 2-pentenoic acid were identified, but not quantified, by GC-
36 MS as products. The SOA formation was investigated using a fast mobility particle sizer
37 spectrometer. The observed SOA yields reached maximum values of around 7% at high
38 particle mass concentrations. This work provides the first study of the formation of gaseous
39 and particulate products for the reaction of Cl with T2P. A reaction mechanism is suggested
40 to explain the formation of the observed gaseous products. The results are discussed in terms
41 of the structure-reactivity relationship, and the atmospheric implications derived from this
42 study are commented as well.

43

44 **Keywords:** Unsaturated aldehyde, kinetics, mechanism, organic aerosols, atmospheric
45 lifetimes

46

47 1. Introduction

48 It is well known that non-methane biogenic volatile organic compounds (BVOCs) account for
49 approximately 90% of VOCs present in the atmosphere. BVOCs play an important role in the
50 chemistry of the troposphere since their oxidation provides major reaction pathways for the
51 formation of Secondary Organic Aerosols (SOAs) (Hoffmann et al., 1997, Griffin et al.,
52 1999). In addition, the reactivity of BVOCs has an impact on the HO_x (OH + HO₂), NO_x (NO
53 + NO₂) and the tropospheric ozone budgets. Therefore, it is important to understand the
54 oxidation of BVOCs in the atmosphere to assess their role in the troposphere's chemistry. This
55 is crucial for atmospheric models to predict the formation of atmospheric photo-oxidants,
56 SOA and the HO_x cycle (Kanakidou et al., 2005, Rudich et al., 2007).

57 Unsaturated aldehydes are BVOCs that may be emitted into the atmosphere from the
58 enzymatic oxidation of linolenic and linoleic acids present in vegetation in response to stress
59 (Winer et al. 1992, Hatanaka, 1993, Heiden et al., 2003, Seco et al., 2007).

60 They may also be formed in situ as a result of the oxidation of dienes in the atmosphere
61 (Orlando and Tyndall, 2002). Besides their emission from biogenic sources, unsaturated
62 aldehydes are also emitted into the atmosphere from anthropogenic sources such as the
63 combustion of wood, polymers, tobacco and gasoline (Magneron et al., 2002) and from
64 chemical industries (Graedel and Crutzen, 1986).

65 Atmospheric mixing ratios of unsaturated aldehydes are in the order of ppb. For instance, the
66 mixing ratio of acrolein, the smallest unsaturated aldehyde, in several cities was reported to be
67 up to 12 ppb (Seaman et al., 2006, Faroon et al., 2008). Larger unsaturated aldehydes, such as
68 trans-2-pentenal (T2P), have also been detected in the atmosphere with mixing ratios of a few
69 ppb in soybean seeds after anaerobic incubation (Gardner et al., 1996). T2P is also emitted by
70 vegetation such as orange (Moshonas et al., 1973), tomato (Tandon et al., 2000) and black tea
71 (Yamanishi et al., 1972). Besides, T2P is emitted directly from food products such as olive oil

72 (Angerosa et al., 2000, Masella et al., 2019), milk powder (Cheng et al., 2019), wine (Saison
73 et al., 2009, Martins et al., 2013), dry sausages, cheese and bread (Bianchi et al., 2007) or
74 during food preparation as clam frying (Cheng et al., 2019). T2P has also been detected in
75 human breath (Ruzsanyi et al., 2002) and cigarette smoke (Hatai et al., 2019). Further, this
76 species is used to protect crop plants from pests and weeds (Rodríguez-Kabana et al.,
77 2008).

78 Like other unsaturated aldehydes, once emitted into the atmosphere, T2P is expected to be
79 removed mainly by reaction with OH and NO₃ radicals and by photolysis during the daytime
80 (Houk, 1976, Calvert et al., 2011). However, reactions with chlorine (Cl) atoms may play an
81 important role in the removal of these species in the atmosphere and maybe competitive with
82 those due to the OH radicals. Heterogeneous ClNO₂ formation in polluted environments has
83 been shown as a major route for the production of reactive gas-phase chlorine due to
84 photolysis (Wang et al., 2019, Faxon et al., 2015). In coastal areas and in polluted northern
85 hemisphere areas, the concentration of Cl atoms reaches 1×10^5 atoms cm⁻³ (Pszenny et al.,
86 1993, Spicer et al., 1998, Ezell et al., 2002, Tackett et al., 2007) and 5×10^4 atoms cm⁻³
87 (Hossaini et al., 2016), respectively, making the reactions of Cl with VOCs a potentially
88 significant elimination route in the atmosphere for these species. Therefore, the study of these
89 processes is necessary to assess the fate of these species in the atmosphere and to better
90 evaluate the atmospheric implications of their oxidation processes.

91 To our knowledge, the rate coefficient for the T2P+Cl reaction, k_{T2P} , was measured by
92 Rodríguez et al., 2005 by a relative method at room temperature and an atmospheric pressure
93 of air and N₂ in a Teflon bag using the GC-FID (Flame ionization detector).

94 The value provided by Rodríguez et al., $(1.31 \pm 0.19) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, is the only
95 experimental data for k_{T2P} . However, an estimation of k_{T2P} , calculated using the Structure-

96 Activity Relationships (SARs) method, $3.47 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is not in agreement
97 with the experimental value (Teruel et al., 2009). This value is close to the gas kinetic limit
98 for such a bimolecular elementary reaction. To elucidate this discrepancy, the present paper
99 describes the determination of the rate coefficient k_{T2P} and aims at evaluating the impact of the
100 Cl + T2P reaction in the removal of T2P in the atmosphere. In addition to the kinetic
101 investigation, the identification and quantification of the gas-phase products and the SOA
102 formation induced by reaction R1 are provided for the first time in the present work.

103 2. Materials and methods

104 2.1. Kinetic study

105 The kinetic study was carried out at $296 \pm 2 \text{ K}$ and $730 \pm 20 \text{ Torr}$ of air by a relative method
106 using two set-ups described below.

107 2.1.1. D-ASC chamber (IMT Lille Douai, France)

108 A detailed presentation of this experimental set-up can be found elsewhere (Turpin et al.,
109 2006), and only a brief description is given here. The Douai Atmospheric Simulation
110 Chamber (hereafter D-ASC) is a 300-L Teflon bag enclosed inside a wooden box and
111 equipped with a 2-L multiple-reflection optical cell with 10 m of optical path coupled to an
112 FTIR spectrometer (Nicolet 550). The IR spectra of the gaseous samples (T2P and the
113 reference compound and/or reaction products) were recorded with a resolution of 0.5 cm^{-1} in
114 the spectral range $4000\text{-}650 \text{ cm}^{-1}$ by accumulating 32 interferograms. In our experiments, Cl
115 atoms were generated from the photolysis of molecular chlorine using 1 or 2 actinic lamps
116 (Philips TMX 200 LS, emitting in the range 300-460 nm, $\lambda_{\text{max}} = 365 \text{ nm}$), which were fixed
117 on the internal walls of the box. All reactions were studied in purified zero air (relative
118 humidity $< 2 \text{ ppm}$, CO and CO₂ $< 80 \text{ ppb}$). T2P and the reference compounds were injected

119 into the Teflon bag using syringes. The sampling was made automatically each 5 min for
 120 analysis by FTIR. At the end of each experiment, the Teflon bag and the optical cell were
 121 cleaned several times by filling with zero air followed by pumping.

122 **2.1.2. 16-L cell (University of Castilla La Mancha UCLM - Ciudad Real, Spain)**

123 This experimental set-up was described in detail elsewhere (Ballesteros et al., 2009, Sleiman
 124 et al., 2014), and only a brief outline is provided here. It consists of a 16-L Pyrex White-type
 125 cell that has 96 m of the optical path. The cell is equipped with a Nexus 870 Thermo Nicolet
 126 FTIR spectrometer. IR spectra were recorded with a resolution of 2 cm^{-1} in the IR spectral
 127 range of 4000 to 650 cm^{-1} . The cell is surrounded by 4 actinic lamps (Philips TL-K 40 W,
 128 $\lambda_{max} = 365\text{ nm}$). All experiments were carried out in synthetic air (purity 99.999%, Air
 129 Liquide). The introduction of reactants in the gas-phase was done by expansion from a glass
 130 manifold system. At the end of each experiment, the cell was cleaned by filling with air and
 131 pumping down to 10^{-2} mbar several times.

132 **2.1.3. Rate coefficient determination**

133 The relative rate coefficient of the gas-phase reaction of T2P with Cl was measured in the
 134 presence of a reference compound (isoprene, cyclohexane or ethanol) using either the D-ASC
 135 chamber or the 16-L cell. The experimental conditions used in this study are summarized in
 136 Table 1. The reactions of interest are the simultaneous reactions of T2P and the reference
 137 compound with chlorine atoms, with rate coefficients as k_{T2P} and k_{Ref} , respectively:



138

139 Before starting the kinetic study, tests were carried out to check the stability of T2P and the
 140 reference compounds by quantifying dark reactions (loss onto the walls and potential reaction
 141 with Cl₂) and photolysis processes. The loss rate coefficients due to dark reactions and to
 142 photolysis are defined as $k_{WL,X}$ and $k_{PL,X}$, where X compound could be either T2P or reference
 143 compound. The values are summarized in Table 1. The rate coefficients, k_L , accounting for all
 144 these secondary loss processes are included in Eq. 1. They typically represent from 6 to 15%
 145 of the logarithm components according to the reference compound employed in the
 146 experiments. The time evolution of the concentration of T2P and the reference compound is,
 147 then, described by the following expression:

$$\ln\left(\frac{[T2P]_0}{[T2P]_t}\right) - k_{L,T2P}t = \frac{k_{T2P}}{k_{Ref}} \left[\ln\left(\frac{[Ref]_0}{[Ref]_t}\right) - k_{L,Ref}t \right] \quad (Eq. 1)$$

148 where $[T2P]_0$, $[Ref]_0$ and $[T2P]_t$, $[Ref]_t$ are the concentrations of T2P and the reference
 149 compound at times $t=0$ and t , respectively, and $k_{L,T2P}$ and $k_{L,Ref}$ are the loss rate coefficients
 150 due to secondary processes for T2P and the reference compound, respectively. The linear
 151 least-square analysis at zero intercept of the $\ln([T2P]_0/[T2P]_t) - k_{L,T2P}t$ against
 152 $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}t$ plot yields k_{T2P}/k_{Ref} . The rate coefficient of T2P toward chlorine
 153 atoms k_{T2P} was then calculated using the known rate coefficient k_{Ref} .

154 During the experiments performed in the D-ASC chamber, isoprene was used as the reference
 155 compound considering a Cl-rate coefficient $k_{Isoprene}$ of $(4.80 \pm 1.25) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 156 This value is the average of those provided by (Ragains and Finlayson-Pitts, 1997, Fantechi et
 157 al., 1998 and Orlando et al., 2003). In the 16-L cell, two reference compounds were
 158 employed: ethanol ($k_{Ethanol} = (1.0 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2006) and
 159 cyclohexane ($k_{Cyclohexane} = (2.90 \pm 1.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This latter rate coefficient is
 160 the average of six values given by (Atkinson and Aschmann, 1985, Wallington et al., 1988,
 161 Rowley et al., 1992, Aschmann and Atkinson, 1995, Li and Pirasteh, 2006, Anderson et al.,

162 2007). The error in k_{Ref} represents twice the standard deviation calculated from the averages
 163 of individual k_{Ref} .

164 The reagents (T2P and the reference compound) consumption in the D-ASC chamber was
 165 monitored as a function of time, using the following IR spectral features: 1175-1115 cm^{-1} and
 166 942-855 cm^{-1} for T2P and isoprene, respectively. In the 16-L cell, the IR spectral features
 167 used were as follows: 1750-1700 cm^{-1} for T2P, 2890-2830 cm^{-1} for cyclohexane and 930-840
 168 cm^{-1} for ethanol. Once in the reactor, the gas mixture was allowed to stabilize for 40 min in
 169 the D-ASC chamber and 10 min in the 16-L cell. Indeed, the stabilization time of reagents is
 170 dependent on the volume of the reactor. The initial concentrations of T2P, reference
 171 compounds and Cl_2 were obtained based on the injected amounts (D-ASC) or the pressure
 172 measurements (16-L cell) and are summarized in Table 1.

173 The overall error Δk_{T2P} in the individual rate coefficient comes from statistical errors Δk_{T2P}
 174 (*stat*) and systematic errors Δk_{T2P} (*syst*) as follows:

$$\Delta k_{T2P} = \sqrt{\Delta k_{T2P} (stat)^2 + \Delta k_{T2P} (syst)^2} \quad (Eq. 2)$$

175 Statistical errors $\Delta k_{T2P} (stat)$ are calculated according to the following equation:

$$\frac{\Delta k_{T2P} (stat)}{k_{T2P}} = \frac{\Delta(Slope)}{Slope} + \frac{\Delta k_{Ref}}{k_{Ref}} \quad (Eq. 3)$$

176 $\Delta(Slope)$ comes from the determination of the slope in Eq. 1 and results from the least-squares
 177 analysis of Figure 1. Δk_{Ref} is the uncertainty on the rate coefficient of the used reference
 178 compounds. In this work, this value represents two standard deviations obtained from the
 179 averaging of several values of k_{Ref} found in the literature, as explained above. Systematic
 180 errors $\Delta k_{T2P} (syst)$ are estimated to 10%. They come mainly from the uncertainty in measuring
 181 the concentrations of the reagents (measurements of the areas of the spectroscopic peaks,

182 possible interference, and temperature instability). To minimize this error, 32 IR spectra were
183 recorded for each experiment.

184 **2.2. Mechanistic study**

185 In independent experiments without adding a reference compound, the products formed
186 during the gas-phase reaction of T2P with chlorine atoms were identified and quantified using
187 two different detection methods: FTIR spectroscopy, coupled to the 16-L cell described
188 above, and GC-MS technique, coupled to the 264-L Pyrex chamber (Ciudad Real-
189 Atmospheric Simulation Chamber, CR-ASC), described below.

190 In the 16-L Pyrex cell, the concentrations of T2P and the formed products were followed in
191 situ by monitoring the evolution of their IR absorption bands. The IR spectral features used
192 for this analysis were as follows: 1180-1120 cm^{-1} for T2P, 875-817 cm^{-1} for propanal, 1840-
193 1780 cm^{-1} for formic acid, 2230-2060 cm^{-1} for CO and 3100-2600 cm^{-1} for HCl. Examples of
194 measured spectra are shown in Figure S1. The identification of the products was done using
195 standard reference libraries of IR spectra.

196 The CR-ASC set-up was presented in detail elsewhere (Ballesteros et al., 2009), and only a
197 brief description is provided here. It consists of a 264-L Pyrex cylindrical reactor with four
198 quartz windows on the sides. The chamber is surrounded by a set of 8 actinic lamps (Philips
199 BL TL 40W/10 1SL/25, emitting in the range 340-400 nm, $\lambda_{\text{max}} = 365$ nm) used to generate
200 Cl atoms from the photolysis of Cl_2 . A GC-MS apparatus (Thermo Electron, Trace GC Ultra
201 and DSQ II) was employed to analyze the gas mixture from the chamber. The Solid-Phase
202 Micro-Extraction (SPME) technique was used for sampling the mixture using a 50/30 μm
203 divinylbenzene/carboxen/polydimethylsiloxane fiber as an absorber. The coated fiber was
204 exposed to the gas mixture during an optimized time of 15 min. The fiber samples were then

205 thermally desorbed in the heated (at 523 K) GC injection port, and the products were analyzed
206 by GC-MS by using temperature ramps that ranged between 313 and 573 K. The
207 identification of the reaction products was carried out by using the electronic impact
208 ionization mass spectrum of each retention time. The consumption of T2P and the formation
209 of the products were examined by monitoring the areas of corresponding chromatographic
210 peaks observed at a certain retention time. The initial concentration of T2P and Cl₂ used for
211 the mechanistic study are summarized in Table 2. Examples of a chromatogram and obtained
212 mass spectra of the detected products are shown in Figure S2.

213 **2.3. Secondary Organic Aerosol (SOA) study**

214 **2.3.1. Experimental apparatus**

215 The set-up used has already been presented elsewhere (Antiñolo et al., 2019). Hence, only a
216 brief description will be given here with a special emphasis on the specificities of the present
217 work. The study of the SOA formation in reaction R1 was carried out at 296±2 K and 730±20
218 Torr of synthetic air using both the CR-ASC and the 16-L cell-described above. Ranges of
219 initial concentrations of T2P and Cl₂ were (1.56-9.23)×10¹⁴ molecule cm⁻³ and (1.55-
220 15.8)×10¹⁴ molecule cm⁻³, respectively. The loss of T2P, necessary to quantify the SOA yield,
221 was measured using the FTIR spectrometer described in section 2.1.2. Cl atoms were
222 generated in the CR-ASC as described in section 2.2.

223 A Fast Mobility Particle Sizer (FMPS) spectrometer (TSI 3091) was used to measure the
224 number of particles formed with diameters ranging between 5.6 and 560 nm. Although it
225 allows a time resolution of 1 s, averaged values for 1 min were considered in the present
226 investigation. Mass concentrations were determined using an SOA density of 1.4 g.cm⁻³,
227 which corresponds to the recommended value of Hallquist et al., 2009.

228 The gas mixture from the CR-ASC chamber entered in the FMPS through a 1 μm cut cyclone
229 at a 10 L min^{-1} flow rate, and a 10 L min^{-1} filtered exhaust flow rate from the FMPS was then
230 directed to the 16-L cell for FTIR measurements and then again to the CR-ASC, closing the
231 circuit and allowing mixing of the gases in the system. Data were recorded with both FTIR
232 and FMPS typically during 80 min as follows: 10 min before starting the reaction (dark
233 measurements), 50 min under irradiation, followed by 20 min in dark conditions.

234 2.3.2. Determination of the SOA production

235 The SOA yield Y_{SOA} is defined by the following equation:

$$Y_{SOA} = \frac{M_{SOA}}{\Delta[T2P]} \quad (\text{Eq. 4})$$

236 From the time evolutions of the SOA mass production M_{SOA} and the reactant consumption
237 $\Delta[T2P]$, it is possible to plot M_{SOA} as a function of $\Delta[T2P]$ and determine Y_{SOA} from the slope.
238 Both M_{SOA} and $\Delta[T2P]$ were corrected to account for their loss in the dark when no Cl
239 reaction is taking place, as explained in a previous study (Antiñolo et al. 2019). The loss of
240 M_{SOA} was characterized during the last 20 min of each experiment under the dark conditions
241 from the FMPS measurements, and its rate coefficient was in the $(5.22\text{--}6.97)\times 10^{-4} \text{ s}^{-1}$ range.
242 $\Delta[T2P]$ was corrected considering the FTIR measurements of T2P in the first 10 min of the
243 experiment under dark conditions from which it was possible to detect a loss rate coefficient
244 within the $(1.16\text{--}20.8)\times 10^{-4} \text{ s}^{-1}$ range. Tests were also done to confirm that no SOA was
245 formed during the Cl_2 dark reaction or exposure of T2P under the light.

246 In each experiment, M_{SOA} reaches a maximum value $M_{SOA,max}$ which is directly correlated to
247 the SOA yield Y_{SOA} . Indeed, SOA formation can be described by the one-product model
248 proposed by (Pankow, 1994) for which the following equation was recommended by (Odum
249 et al., 1996):

$$Y_{SOA} = M_{SOA,max} \left(\frac{\alpha K_p}{1 + M_{SOA,max} K_p} \right) \quad (Eq. 5)$$

250 where α is the mass-based gas-phase stoichiometric coefficient of a model product, and K_p
 251 represents its gas-particle partitioning equilibrium constant. The present study allows us to
 252 obtain these coefficients as explained in the discussion section 3.3.

253 2.4. Chemicals

254 The reagents employed were obtained from the following sources: T2P ($\geq 95\%$, Sigma-
 255 Aldrich), isoprene (99%, Sigma-Aldrich), cyclohexane (99.9%, Sigma-Aldrich), ethanol
 256 ($\geq 99.5\%$, Sigma-Aldrich), Cl_2 (10% in N_2 , Air Products) at IMT Lille Douai and Cl_2 (99.8%,
 257 Sigma-Aldrich) at UCLM.

258 3. Results and discussion

259 3.1. Kinetic study

260 The plots of $\ln([T2P]_0/[T2P]_t) - k_{L,T2P}t$ vs. $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}t$ are presented in Figure 1.
 261 Relative rate coefficients were obtained for each reference compound. Individual and average
 262 k_{2TP} are summarized in Table 3. The good linearity with a correlation coefficient greater than
 263 98% and an intercept close to zero for all the reference compounds indicates that no other
 264 secondary reactions occur. The error reported on the average rate coefficient shown in Table 3
 265 is two standard deviations. The overall error Δk_{T2P} in the individual rate coefficient values
 266 ranges from 24 to 42%.

267 Two determinations for the rate coefficient of the studied reaction exist in the literature: an
 268 experimental value, $(1.31 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Rodríguez et al., 2005), and a rate
 269 coefficient estimated using the SAR method, $3.47 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Teruel et al.,

270 2009). The present value of $(2.56\pm 0.83)\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ lays between these two
271 values.

272 k_{T2P} obtained in the present work is found to be higher than that provided by Rodríguez et al.,
273 also obtained using a relative method, by about a factor of 2. In Rodríguez et al.'s work, the
274 losses of T2P and the reference compounds (ethane, propene and 1-butene) were monitored
275 by GC-FID detection. The source of discrepancy with Rodríguez et al.'s work is not clear.
276 First, the Cl-rate coefficients for the reference compounds used by Rodríguez et al. cannot be
277 the reason for this discrepancy. These rate coefficients (in cm³ molecule⁻¹ s⁻¹) were
278 $(5.85\pm 0.55)\times 10^{-11}$ (Hitsuda et al., 2001), $(2.31\pm 0.29)\times 10^{-10}$ (Stutz et al., 1998) and
279 $(3.00\pm 0.40)\times 10^{-10}$ (Orlando et al., 2003) for ethane, propene and 1-butene, respectively.
280 Indeed, a re-evaluation of the value obtained by Rodríguez et al., for k_{T2P} using the rate
281 coefficients recommended by IUPAC, 2006 for ethane and propene (5.9×10^{-11} and 2.70×10^{-10}
282 cm³ molecule⁻¹ s⁻¹, respectively), gives $k_{T2P} = 1.39 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, which remains
283 within the error bars given by these authors. The only difference that we can find between the
284 two works, apart of the used technique, is that in Rodríguez et al.'s work the losses were not
285 corrected although that wouldn't explain the discrepancy. It is important to note that in the
286 present work, the rate coefficient of the reaction of T2P with Cl was measured in two
287 different set-ups under different conditions. Very close rate coefficients values were obtained
288 making our reported value reliable. The rate coefficient of the reaction of T2P with Cl atoms
289 estimated by Teruel et al., 2009 using the SAR method is 25% higher than that determined in
290 the present work. The source of this discrepancy is probably the uncertainties of the SAR
291 method that aims to estimate rate coefficients based on the reactivity of other compounds
292 considering only their structure.

293 As generally observed for VOCs, Cl atoms are more reactive than OH radicals toward these
294 species because they are stronger electrophiles than OH radicals. As expected, then, the rate
295 coefficient for reaction R1 is almost 1 order of magnitude greater than the rate coefficient for
296 the OH + T2P reaction, $3.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average from (Davis et al., 2007) and
297 (Albaladejo et al., 2002)).

298 In Table 4, the rate coefficients of the reactions of a series of C₃-C₇ unsaturated aldehydes
299 with Cl atoms are displayed. Our result confirms that the structure of unsaturated aldehydes
300 has a very small impact on their reactivity towards Cl atoms, as was previously observed
301 (Ullerstam et al., 2001, Colmenar et al., 2015)) opposite to their reactivity towards OH and
302 NO₃ radicals (Tables S1 and S2). The reactivity towards Cl seems to be fairly independent of
303 the substitution on the olefinic carbons for unsaturated aldehydes, as stated by Blanco et al.,
304 2010.

305 To evaluate the effect of the -CHO group on the reactivity, a comparison between the
306 reactions of Cl with a series of unsaturated aldehydes to those with the corresponding alkenes
307 would be useful. Unfortunately, no data are available in the literature for the reaction of Cl
308 with *trans*-2-pentene, the corresponding alkene of T2P. However, data for other unsaturated
309 aldehydes and their corresponding alkenes are available. The rate coefficients of the reactions
310 of Cl with crotonaldehyde and 3-methyl-2-butenal (see Table 4) are 34% and 36% lower than
311 those with *trans*-2-butene ($3.58 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ provided by Kaiser et al., 2007) and
312 2-methyl-propene ($3.38 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ provided by Blanco et al., 2010),
313 respectively. This may be due to the negative inductive effect of the carbonyl-containing
314 group, which may deactivate the double bond toward the Cl atom addition. However, this
315 decrease in reactivity due to the electron-withdrawing effect may be compensated by the fact
316 that the -CHO group is a reactive site. This was discussed in the study carried out by

317 (Thévenet et al., 2000), where the rate coefficient of the reaction of Cl with acrolein
318 ($2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was compared to that for propene ($2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
319 and was shown to be slightly higher within uncertainties showing that the $-\text{CHO}$ group is a
320 reactive site, although H abstraction from the $-\text{CHO}$ group remains a minor channel
321 compared to the Cl-addition to the double bond, which is likely to be the major one as stated
322 by these authors.

323 **3.2. Mechanistic study**

324 **3.2.1. Molar yields of reaction products**

325 This work represents the first mechanistic study on the T2P+Cl reaction. It has been carried
326 out at $296 \pm 2 \text{ K}$ and $730 \pm 20 \text{ Torr}$ of total pressure. By FTIR, HCl, CO, propanal and formic
327 acid were identified and quantified as products formed from the studied reaction (Figure S1).
328 Figure 2 shows a typical concentration vs. time profile for the consumption of T2P and the
329 formation of products. The plots of the $[Product]_t$ vs. $\Delta[T2P]$ for propanal and formic acid are
330 shown in Figure 3. $[Product]_t$ is the product concentration at a time t , $\Delta[T2P]$ is the consumed
331 concentration of T2P at a time t . For propanal, a correction of its concentration was done
332 according to the method described by Ceacero-Vega et al. (2012) and considering the IUPAC
333 recommendation for the rate coefficient of the Cl-reaction of propanal: $1.3 \times 10^{-10} \text{ cm}^3$
334 $\text{molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al. 2006).

335 The molar yields obtained from the slopes of the plot depicted in Figure 3 are: $(5.2 \pm 0.2)\%$ and
336 $(6.2 \pm 0.4)\%$, for propanal and formic acid, respectively. The overall errors in the formation
337 yields are due to systematic errors σ_{sys} mentioned above and statistical errors resulting from a
338 least-squares analysis of the $[Product]_t$ vs. $\Delta[T2P]$ plots. CO is expected to be formed as a
339 primary product and also as a final product from the studied reaction and may be generated in
340 the oxidation of other species in the mechanism. For that reason, a molar yield for this

341 compound is not reported in this work. HCl yield is not reported either because it may be a
342 primary product, or it can be generated in the H-abstraction of other reaction products.
343 Propanal is expected to be formed as a primary product from the reaction of T2P with Cl.
344 Formic acid may be produced through the very rapid oxidation of other species generated in
345 the oxidation of T2P or as a consequence of heterogeneous reactions on the chamber walls
346 though no evidence of this phenomenon was observed in our experiments. The residual IR
347 spectrum presented in Figure S1 shows peaks that could correspond to ketene in the 2200-
348 2100 cm^{-1} region, according to Wallington et al. (1996), and 2-chlorobutanal considering the
349 peak typical for a carbonyl group (1750 cm^{-1}), the bands due to C-H bending and stretching
350 ($1500\text{-}1000 \text{ cm}^{-1}$ and $3000\text{-}2800 \text{ cm}^{-1}$, respectively) and the band that can correspond to the
351 C-Cl stretching ($1000\text{-}650 \text{ cm}^{-1}$). However, none of these two compounds could be confirmed
352 by FTIR or quantified given the lack of standards of these products.

353 Three of the peaks observed in the chromatogram obtained by GC-MS could be assigned to
354 reaction products (Figure S2). The peak detected at 4.03 min, for which the mass spectrum
355 (MS) shows peaks at $m/z = 106$ (molecular ion, M), 78 and 80 (fragment M-CO or M-C₂H₄
356 for the two Cl isotopes), 77 (M-C(O)H), and 41 (C₃H₅), could be assigned to 2-chlorobutanal,
357 and that would confirm the observations made by FTIR. A chlorinated product that could not
358 be identified was observed at 5.09 min retention time: its MS shows the isotopic pattern for Cl
359 in the 77 and 105 peaks, although it was not possible to clearly identify the molecular ion.
360 The last peak in the chromatogram, at 5.82 min, was attributed to 2-pentenoic acid, given that
361 in the MS there are peaks at $m/z = 100$ (M), 82 (M-H₂O) and 55 (M-C(O)OH). This
362 identification was confirmed by comparing the reference MS library installed in the CG-MS
363 software used in this study. The quantification of these products was not possible due to the
364 lack of standards. However, based on the area of the observed peaks in the chromatogram and
365 assuming the same response for all of them, it seems that the yield of 2-chlorobutanal and the

366 unidentified chlorinated product is higher than that for 2-pentenoic acid (Figure S2). The
367 carbon balance was calculated considering only propanal and CO. The obtained value was
368 shown to not exceed 15% at the end of the reaction showing that additional formed oxidation
369 products could not be detected or quantified.

370 3.2.2. Proposed reaction mechanism

371 As other unsaturated aldehydes (Canosa-Mas et al., 2001, Orlando and Tyndall, 2002,
372 Magneron et al., 2002), the degradation of T2P initiated by Cl atoms is expected to proceed
373 via two basic mechanisms: abstraction of the hydrogen atom from the -CHO group and/or
374 addition to the C=C double bond. In Scheme 1, the reaction pathways that may justify the
375 observed products are shown. The addition of a Cl atom may occur on two sites of the C=C
376 double bond: adjacent to the -C(O)H group (α) or on the double-bonded carbon furthest from
377 the aldehydic group (β). As seen in Scheme 1, the α -addition forms the
378 $\text{CH}_3\text{CH}_2\text{CHClC(O)H}$ radical, which will react with O_2 followed by a reaction with RO_2 to
379 lead to the corresponding chloroalkoxy radical $\text{CH}_3\text{CH}_2\text{C(O)HCHClC(O)H}$. The
380 decomposition of this chloroalkoxy radical may proceed via two channels. The first one leads
381 to the formation of propanal ($\text{CH}_3\text{CH}_2\text{C(O)H}$), 2-oxoacetylchloride (ClC(O)C(O)H), formyl
382 chloride HC(O)Cl and CO. Propanal may further react with Cl atoms to form HCl and
383 $\text{CH}_3\text{CH}_2\text{C(O)}$ radicals (Le Crâne et al., 2004). The second channel leads to the formation of
384 chloromalonaldehyde (C(O)HCHClC(O)H) and acetaldehyde $\text{CH}_3\text{C(O)H}$. Among these
385 products, only propanal and CO were observed and quantified in this work.

386 The β -addition mechanism proceeds through the $\text{CH}_3\text{CH}_2\text{CHClCHC(O)H}$ radical, which will
387 react with O_2 followed by a reaction with RO_2 to lead to the $\text{CH}_3\text{CH}_2\text{CHClC(O)HC(O)H}$
388 radical. This radical may decompose to lead to the formation of 2-chlorobutanal
389 ($\text{CH}_3\text{CH}_2\text{CHClC(O)H}$) identified by GC-MS, but not quantified and further to the formation
390 of CO identified and quantified by FTIR. The decomposition of the

391 $\text{CH}_3\text{CH}_2\text{CHClCOHC(O)H}$ radical may also lead to the formation of glyoxal (C(O)HC(O)H)
392 and 1-chloropropanal ($\text{CH}_3\text{CH}_2\text{C(O)Cl}$) after the conversion of the reaction of the
393 chloroperoxy radical $\text{CH}_3\text{CH}_2\text{C(O}_2\text{)HCl}$ with RO_2 . Glyoxal (C(O)HC(O)H) and 1-
394 chloropropanal were not observed in this work, suggesting that this channel either does not
395 occur in the timescale of the experiments or is a minor route in the mechanism. Note also that
396 glyoxal may be readily photolyzed under UV irradiation. The $\text{CH}_3\text{CH}_2\text{CHClC(O)HC(O)H}$
397 radical may react with O_2 to form chloropropylglyoxal ($\text{CH}_3\text{CH}_2\text{CHClC(O)C(O)H}$). This
398 product may be the unidentified one observed by GC-MS but could not be confirmed.

399 The H-abstraction from the $-\text{C(O)H}$ group may form the $\text{CH}_3\text{CH}_2\text{CHCHC(O)}$ radical and
400 HCl . In the presence of O_2 , the $\text{CH}_3\text{CH}_2\text{CHCHC(O)}$ radical may be converted to the peroxy
401 radical $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}_2$, which generates 2-pentenoic acid ($\text{CH}_3\text{CH}_2\text{CHCHC(O)OH}$)
402 and ozone in the presence of HO_2 . 2-pentenoic acid was detected in SPMS/GC-MS analysis.

403 On the other hand, the $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}_2$ radical may also react with RO_2 and generates
404 the $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}$ radical. This radical can decompose to carbon dioxide (CO_2) and
405 ethylvinyl radical ($\text{CH}_3\text{CH}_2\text{CHCH}$), which is converted to the $\text{CH}_3\text{CH}_2\text{CHCH(O}_2\text{)}$ radical in
406 the presence of O_2 . The reaction of this later with RO_2 may lead to the formation of butanal
407 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)H}$) not observed in this work. The reaction of $\text{CH}_3\text{CH}_2\text{CHCH(O}_2\text{)}$ with
408 RO_2 may also lead to propanal and CO formation, both quantified by FTIR in this work.

409 In the light of the discussion above, the relative contribution of addition and abstraction
410 channels in the suggested mechanism could not be determined. In fact, the product formed
411 only through the β -addition channel and observed in this work (2-chlorobutanal) could not be
412 quantified. Among the products expected to occur from the α -addition channel, only propanal
413 and CO were detected in this work. These products may also be formed through the other
414 channels, as mentioned before.

415 3.3. SOA study

416 Figure S3 shows the relationship between the initial concentration of T2P and Cl₂ with
417 $M_{SOA,max}$. A clear dependency of $M_{SOA,max}$ on the amount of Cl₂ introduced in the system was
418 observed, whereas no obvious correlation can be identified with the initial concentration of
419 T2P.

420 Typical aerosol size distributions at several reaction times for given initial concentrations of
421 T2P and Cl₂ are presented in Figure S4. In Figure 4, the SOA mass concentration M_{SOA} is
422 plotted as a function of the consumed T2P. The SOA yield Y_{SOA} is obtained from linear least-
423 squares analysis. The values of Y_{SOA} are summarized together with the experimental
424 conditions in Table 5. Despite the data scattering (Figure 5), the calculated Y_{SOA} fits
425 reasonably well to a one-product model (Odum et al., 1996), given by Equation 5. A least-
426 square regression on the data gives the following parameters: $\alpha = (9.95 \pm 2.52)\%$ and $K_p =$
427 $(6.00 \pm 2.68) \times 10^{-4} \text{ m}^3 \mu\text{g}^{-1}$. Uncertainties are statistics and represent two standard deviations
428 (2σ).

429 Many products result from the oxidation of a VOC, so this fitting allows for easy comparison
430 of yield curves, but, as reported by Cai and Griffin, 2006, the fitted parameters provide no
431 specific information about the real oxidation products and ascribing meaning to them should
432 be avoided.

433 The SOA formation yields for the reaction of other unsaturated compounds with Cl have been
434 previously determined. For *trans*-2-methyl-2-butenal, Y_{SOA} were recently determined to be
435 between 0.26 and 1.65% (Antiñolo et al., 2020). These SOA yields are a little lower than the
436 values determined in the present work for the reaction of Cl with T2P.

437 4. Atmospheric implications and conclusion

438 The atmospheric lifetime τ_{Cl} of T2P due to its reaction with Cl is estimated from k_{T2P} obtained
439 in this work according to the following equation: $\tau_{Cl} = 1/(k_{T2P} \times [Cl])$. $[Cl]$ represents the
440 global tropospheric concentration of Cl of 1×10^3 atoms cm^{-3} averaged over 24 hours
441 (Wingenter et al., 1999). With this value, a τ_{Cl} of 44 days is calculated. The reaction of T2P
442 with Cl may become significant in coastal areas and in polluted northern hemisphere areas
443 where the concentration of Cl atoms can reach 1×10^5 molecule cm^{-3} (Singh et al., 1996) and
444 5×10^4 atoms cm^{-3} (Hossaini et al., 2016), respectively, yielding to a lifetime shorter than 1
445 day which makes the reaction of T2P with Cl a potentially significant elimination route in the
446 atmosphere. The calculated lifetime of T2P due to its reaction with OH is 7 hours using a 24-h
447 average concentration of 1×10^6 molecules cm^{-3} for OH (Atkinson et al., 1997) and the average
448 of the rate coefficient values reported in the literature by (Davis et al., 2007) and (Albaladejo
449 et al., 2002) (3.33×10^{-11} cm^3 molecule $^{-1}$ s $^{-1}$). A short lifetime (5 hours) of T2P is calculated for
450 its reaction with NO_3 radicals showing that this process is an important removal pathway for
451 T2P during nighttime (Kalalian et al., 2019). These authors provided a lifetime of 9 days
452 towards reaction with ozone. The tropospheric lifetime considering the four chemical removal
453 pathways, is shorter than 3 hours. Further, the UV cross-sections of T2P have been recently
454 determined by Kalalian et al., 2019. A lower limit of 44 min was provided by these authors
455 for the T2P lifetime due to photolysis in the UV solar actinic region. This value was
456 calculated using a quantum yield of unity and a photolysis rate corresponding to June 30 at
457 midday for Paris (zenith angle = 26°). It should be noted however that the overall quantum
458 yield in the actinic region for T2P are not known and that for smaller unsaturated aldehydes
459 such as *trans*-crotonaldehyde it has been found to be quite small since Magneron et al., 2002
460 obtained an upper value of 0.03 for this species.

461 The degradation products (and molar yields) of T2P in the presence of air were HCl, CO, and
462 propanal ($5.2\pm 0.2\%$). Besides, chlorinated products, such as 2-chlorobutanal, were identified
463 as reaction products of the T2P + Cl reaction but could not be quantified. Highly oxidized
464 compounds, such as 2-pentenoic acid and formic acid ($6.2\pm 0.4\%$), were also detected in this
465 work. Formic acid can be produced as a consequence of heterogeneous reactions on the
466 chamber walls.

467 Given the formation of HCl, the T2P + Cl reaction may contribute to the acidity of marine
468 atmospheres. On the other hand, in polluted areas (high- NO_x conditions), the formation of CO
469 may contribute to photochemical pollution via its OH-reaction, which produces CO_2 and H
470 atoms that quickly combine with O_2 to form HO_2 radicals regenerating OH and producing O_3
471 in the troposphere. It is important to note that in polluted areas, the reaction of T2P with Cl
472 may be a source of other toxic molecules such as PAN type species. In addition, the chemical
473 mechanism displayed in Scheme 1 for NO_x -free conditions will evolve by including $\text{RO}_2 +$
474 NO and $\text{RO}_2 + \text{NO}_2$ reactions.

475 As observed in this work, the high particle mass concentration was due to the large amount of
476 T2P present in the system (22.5 ppm). In a real atmosphere, the mixing ratio of T2P is at ppb
477 levels. Considering the small SOA yield formed in the T2P + Cl reaction ($Y_{\text{SOA}} < 7\%$), it is
478 not expected that T2P could contribute to the formation of ultrafine particles in clean
479 atmospheres. The dependence of Y_{SOA} with the maximum SOA mass is well-described by a
480 one-product absorptive model that yielded the Odum's parameters α and K_p , the latter being
481 two orders of magnitude lower than the one reported for α -pinene, β -pinene and d-limonene
482 (Cai and Griffin, 2006). Even though the uncertainties in Y_{SOA} are high due to the lack of
483 knowledge in the SOA density, among other assumptions that were made, the determined

484 SOA yields are in the order of magnitude of those reported for the Cl + toluene reaction (Cai
485 et al., 2008) and other similar biogenic compounds as isoprene (Wang and Ruiz, 2017).

486 Additionally, insights in the reaction mechanism for the degradation of T2P initiated by Cl
487 atoms were reported here. From the obtained results, the first step of the reaction mechanism
488 seems to proceed mainly by H-abstraction of the aldehydic group and by β -addition of Cl
489 atoms to the double bond. The carbon balance calculated in this study did not exceed 15% at
490 the end of the reaction showing that additional oxidation products could not be detected or
491 quantified. Further studies, with complementary detection techniques, are clearly needed to
492 better understand the mechanism and accurately evaluate the carbon balance and the relative
493 contribution of addition and abstraction channels in this mechanism.

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Tables

Table 1. Experimental conditions used during our kinetic study.

Reactor	Lamps	Compound	Initial concentration ($\times 10^{13}$ molecule cm^{-3})	$k_{\text{WL},X} \pm \sigma_1^a$ ($\times 10^{-5}$ s^{-1})	$k_{\text{PL},X} \pm \sigma_2^a$ ($\times 10^{-5}$ s^{-1})
D-ASC	1-2	T2P	5.04 – 15.10	1.73 \pm 0.06 – 6.55 \pm 0.39	1.85 \pm 0.10 – 6.43 \pm 0.41
		Isoprene	5.90 – 14.80	0.50 \pm 0.12 – 2.42 \pm 0.07	0.54 \pm 0.16 – 2.68 \pm 0.12
		Cl ₂	25.00 – 37.26		
16-L cell	4	T2P	46.20 – 93.00	0.48 \pm 0.15 – 1.02 \pm 0.08	2.95 \pm 0.13 – 3.57 \pm 0.07
		Cyclohexane	57.60 – 66.00	0.11 \pm 0.09 – 1.07 \pm 0.21	
		Ethanol	74.40 – 110	1.72 \pm 0.07 – 2.08 \pm 0.40	
		Cl ₂	66.00 – 132		

^a: uncertainty is $\pm 1\sigma$.

Table 2. Experimental conditions used during the mechanistic study.

Reactor	Lamps	Compound	Initial concentration range ($\times 10^{14}$ molecule cm^{-3})
16-L cell (4 runs)	3	T2P	2.78-5.91
		Cl ₂	8.34-9.97
CR-ASC (2 runs)	8	T2P	9.05-9.64
		Cl ₂	8.34-8.76

Table 3. Rate coefficients for the reaction of T2P with Cl atoms at 296 ± 2 K and 730 ± 20 Torr.

Reactor	Reference compound	k_{T2P}/k_{Ref}	$k_{T2P} \pm \Delta k_{T2P}^a$ ($\times 10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹)
D-ASC	Isoprene (6 runs)	0.50 ± 0.04	2.40 ± 0.82
16-L Pyrex cell	Cyclohexane (2 runs)	0.79 ± 0.01	2.29 ± 0.92
	Ethanol (3 runs)	2.99 ± 0.08	2.99 ± 0.69
Average			2.56 ± 0.83^b

$k_{\text{Isoprene}} = (4.8 \pm 1.25) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (see section 2.1.3)

$k_{\text{Ethanol}} = (1.0 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (see section 2.1.3)

$k_{\text{Cyclohexane}} = (2.90 \pm 1.12) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (see section 2.1.3)

^a uncertainty calculated according to equations (4-5)

^b two standard deviations

Table 4. Summary of the rate coefficients for the reactions of a series of C₃-C₇ unsaturated aldehydes with Cl atoms.

Unsaturated aldehyde	k_{Cl} ($\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
Acrolein (CH ₂ =CH-CHO)	2.2 ± 0.3 2.2 ± 0.3 1.8 ± 0.3 2.5 ± 0.7	(Thévenet et al. 2000) (Canosa-Mas et al. 2001) (Ullerstam et al. 2001) (Wang et al. 2002)
Crotonaldehyde (CH ₃ -CH=CH-CHO)	2.6 ± 0.3 2.2 ± 0.4 3.2 ± 0.9	(Thévenet et al. 2000) (Ullerstam et al. 2001) (Wang et al. 2002)
3-methyl-2-butenal (CH ₃) ₂ C=CH-C(O)H	2.48 ± 0.71	(Blanco et al. 2010)
Trans-2-pentenal (CH ₃ -CH ₂ -CH=CH-CHO)	1.31 ± 0.19 3.47 2.53 ± 0.83	(Rodríguez et al. 2005) (Teruel et al. 2009) (SAR Estimation) This work
Trans-2-hexenal (CH ₃ -CH ₂ -CH ₂ -CH=CH-CHO)	1.92 ± 0.22	(Rodríguez et al. 2005)
Trans-2-heptenal (CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH=CH-CHO)	2.4 ± 0.29	(Rodríguez et al. 2005)

Table 5. Experimental conditions and results obtained for the SOA study.

$[T2P]_0$ ($\times 10^4 \mu\text{g m}^{-3}$)	$[Cl_2]_0$ ($\times 10^4 \mu\text{g m}^{-3}$)	$\Delta[T2P]$ ($\times 10^4 \mu\text{g m}^{-3}$)	$M_{SOA,max}$ ($\times 10^2 \mu\text{g m}^{-3}$)	Y_{SOA}^a (%)
8.03	1.86	1.80	1.20	0.82 ± 0.02
9.39	2.43	1.75	1.75	1.15 ± 0.02
13.14	4.28	3.08	3.42	1.34 ± 0.02
3.30	3.16	1.56	3.39	2.07 ± 0.09
12.62	8.45	4.75	9.11	2.15 ± 0.02
2.23	2.43	0.88	2.56	2.47 ± 0.08
5.75	8.07	3.36	8.18	2.59 ± 0.05
3.05	8.07	1.67	8.20	2.79 ± 0.08
2.99	8.33	1.62	9.72	3.79 ± 0.10
5.75	7.89	2.19	8.97	3.79 ± 0.10
9.32	13.74	2.79	13.48	4.26 ± 0.11
6.69	12.41	4.31	15.89	4.62 ± 0.27
2.23	7.00	1.35	9.88	4.77 ± 0.28
7.89	18.97	4.89	21.56	5.17 ± 0.39
6.59	16.10	4.43	16.62	5.24 ± 0.54
9.32	17.34	2.46	19.00	6.16 ± 0.10

^a Y_{SOA} is determined from the slope of $M_{SOA,max}$ vs. Y_{SOA} . Errors are 2σ .

Figure and Scheme Legends

Figure 1. Plot of $\ln([T2P]_0/[T2P]_t) - k_{L,T2Pt}$ vs. $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}t$ according to Eq. 1. Data obtained using the D-ASC (isoprene) and the 16L-cell (Cyclohexane and Ethanol).

Figure 2. Concentration-time profiles for T2P and the major products observed by FTIR using the 16-L cell.. Initial concentrations: 5.91×10^{14} molecule.cm⁻³ for T2P and 9.09×10^{14} molecule.cm⁻³ for Cl₂.

Figure 3. Product yields for HC(O)OH and propanal.

Figure 4. SOA mass concentration M_{SOA} produced from the T2P+Cl reaction as a function of the consumed T2P with an initial concentration of 4.03×10^{14} molecule.cm⁻³ for T2P and 6.72×10^{14} molecule.cm⁻³ for Cl₂. The SOA yield Y_{SOA} is obtained from a linear least-squares analysis.

Figure 5. Plot of SOA yield Y_{SOA} as a function of $M_{SOA,max}$ for the reaction between T2P and Cl.

Scheme 1. Proposed mechanism for the reaction of T2P with Cl atom: α -addition (a), β -addition (b) and H-abstraction (c).

Figures

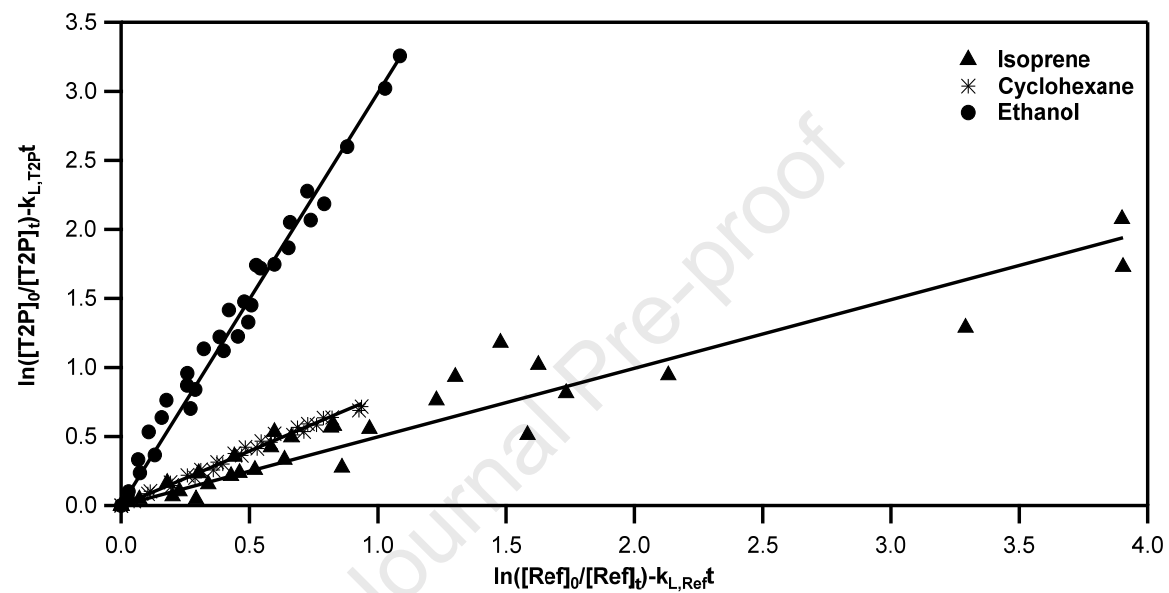


Figure 1. Plot of $\ln([T2P]_0/[T2P]_t) - k_{L,T2P}t$ vs. $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}t$ according to Eq. 1.

Data obtained using the D-ASC (isoprene) and the 16L-cell (Cyclohexane and Ethanol).

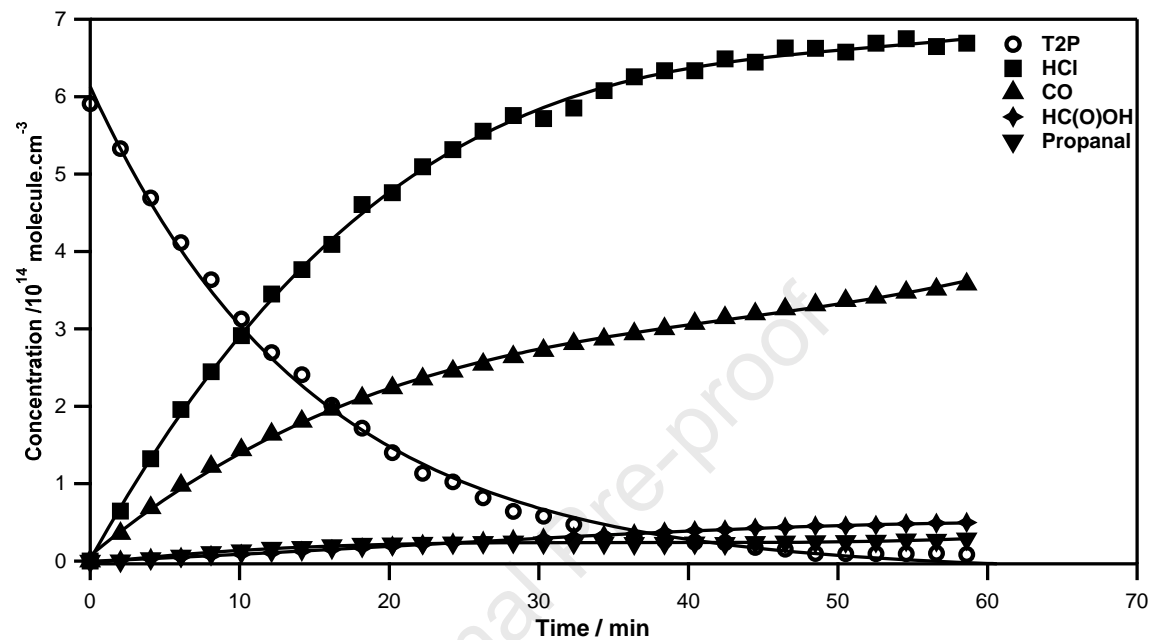


Figure 2. Concentration-time profiles for T2P and the major products observed by FTIR using the 16-L cell. Initial concentrations: 5.91×10^{14} molecule. cm^{-3} for T2P and 9.09×10^{14} molecule. cm^{-3} for Cl_2 .

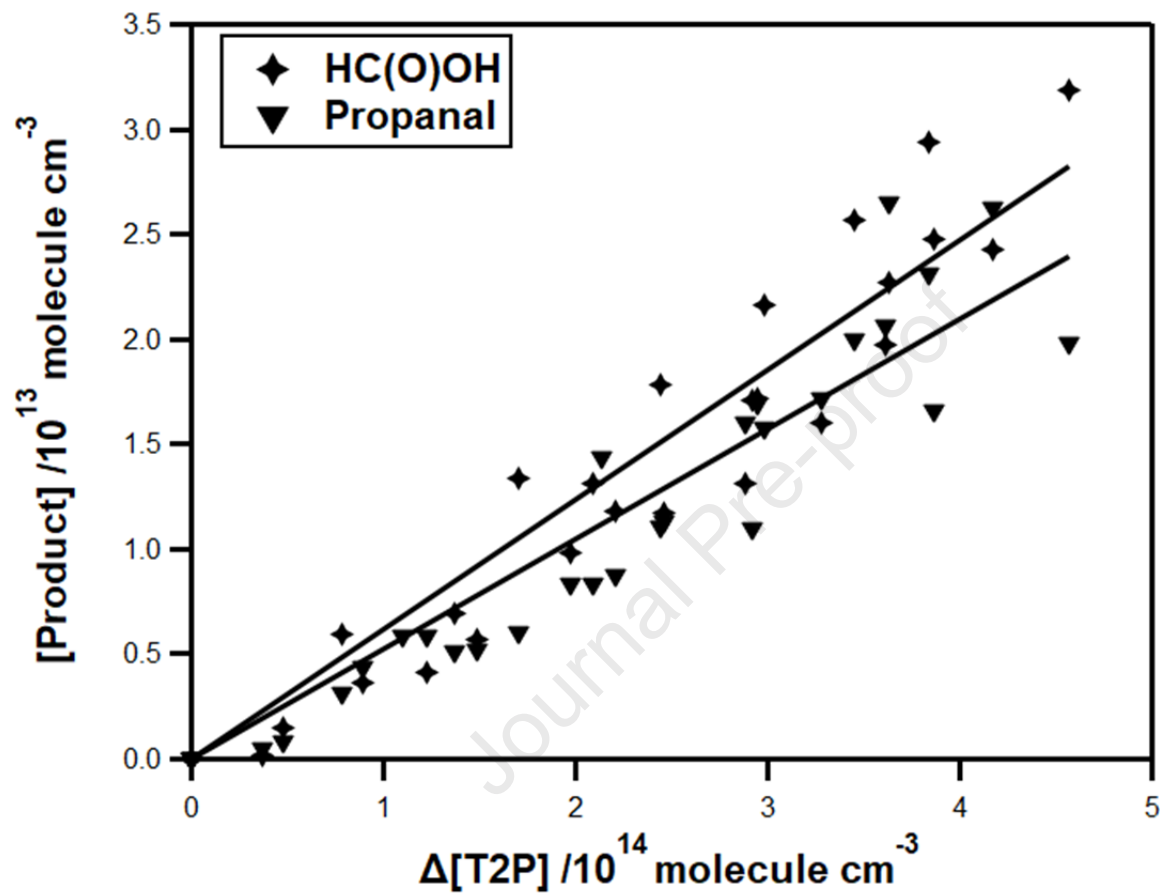


Figure 3. Product yields for HC(O)OH and propanal.

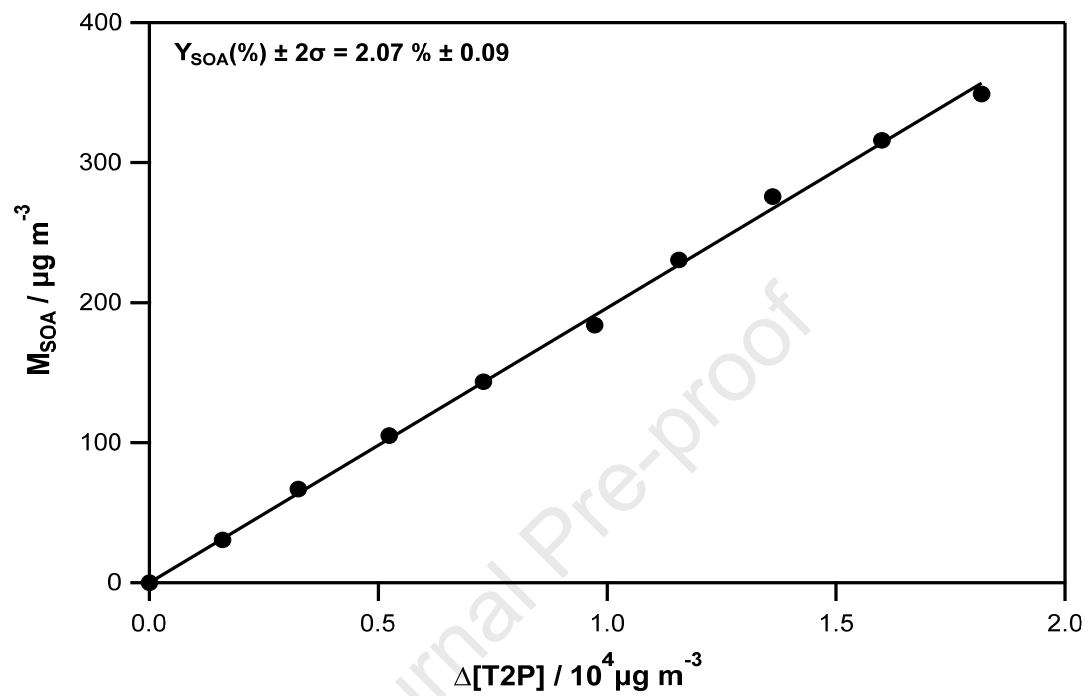


Figure 4. SOA mass concentration M_{SOA} produced from the T2P+Cl reaction as a function of the consumed T2P with an initial concentration of 4.03×10^{14} molecule. cm^{-3} for T2P and 6.72×10^{14} molecule. cm^{-3} for Cl_2 . The SOA yield Y_{SOA} is obtained from a linear least-squares analysis.

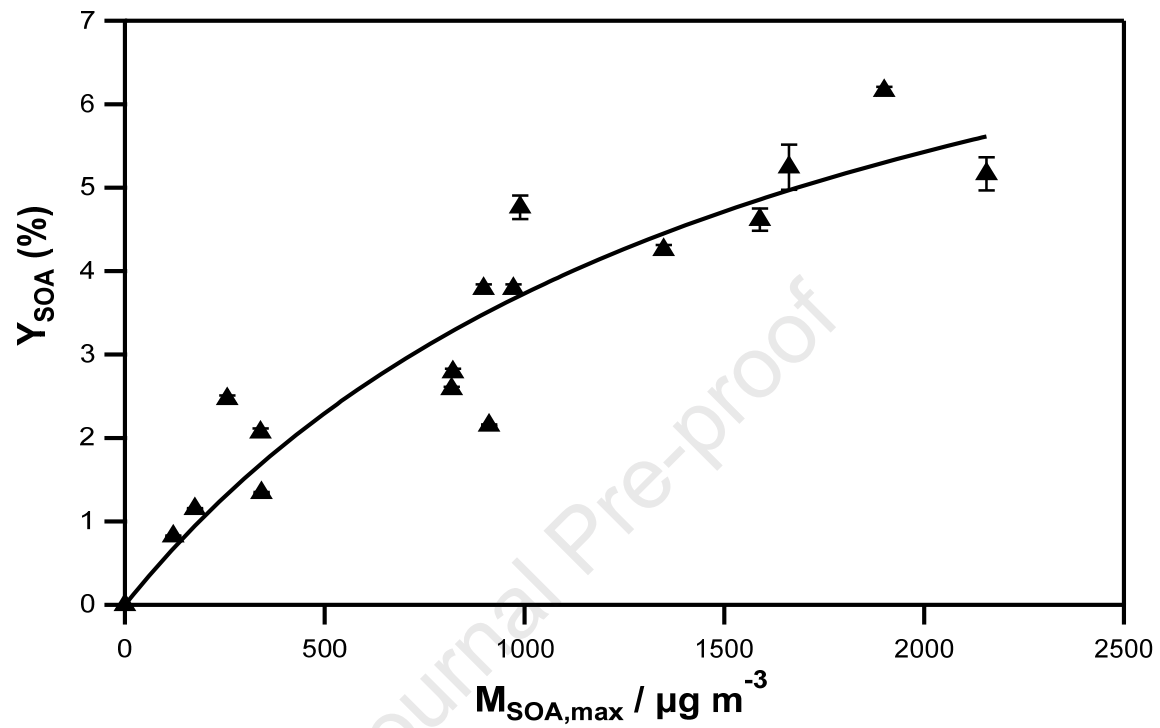
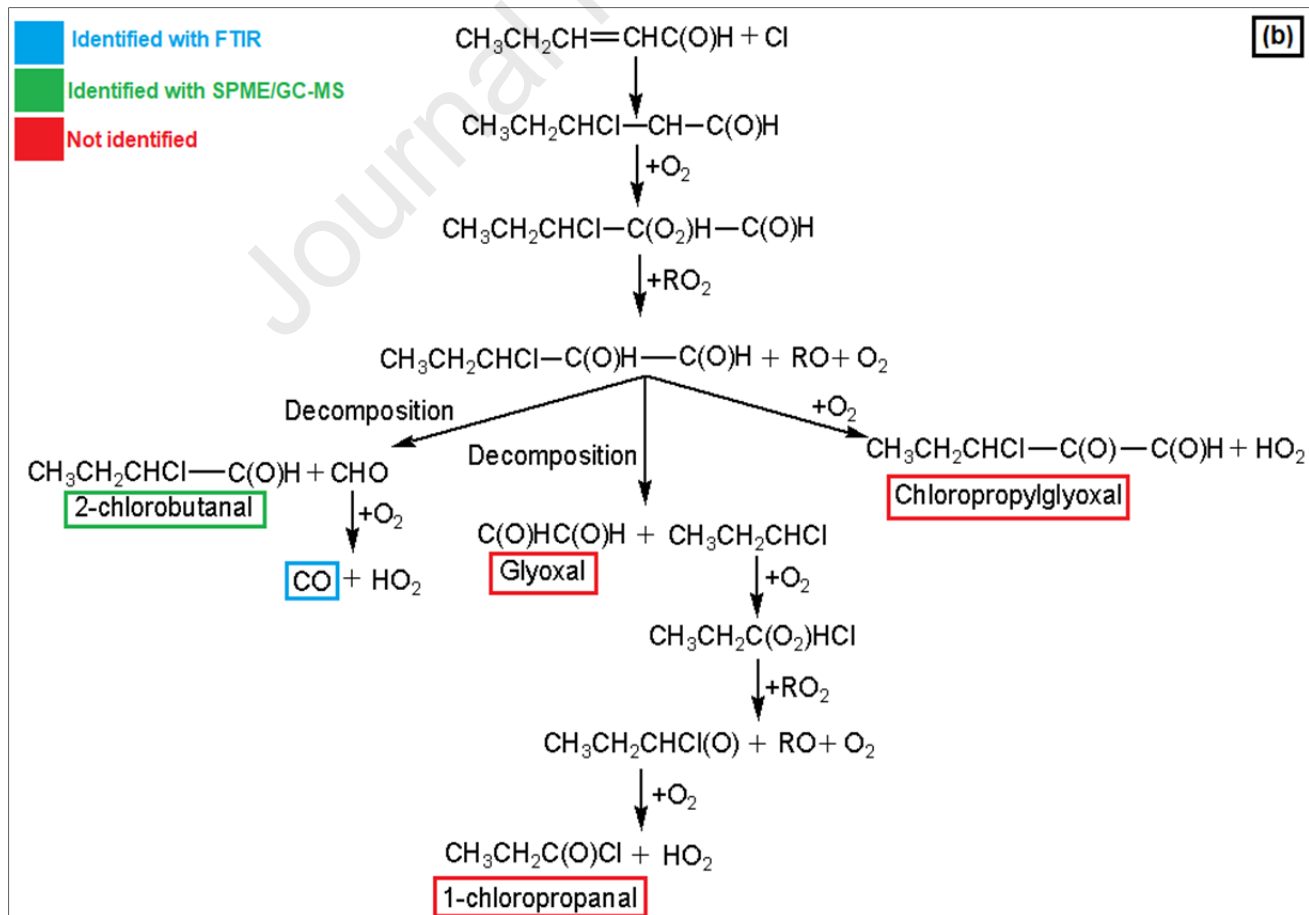
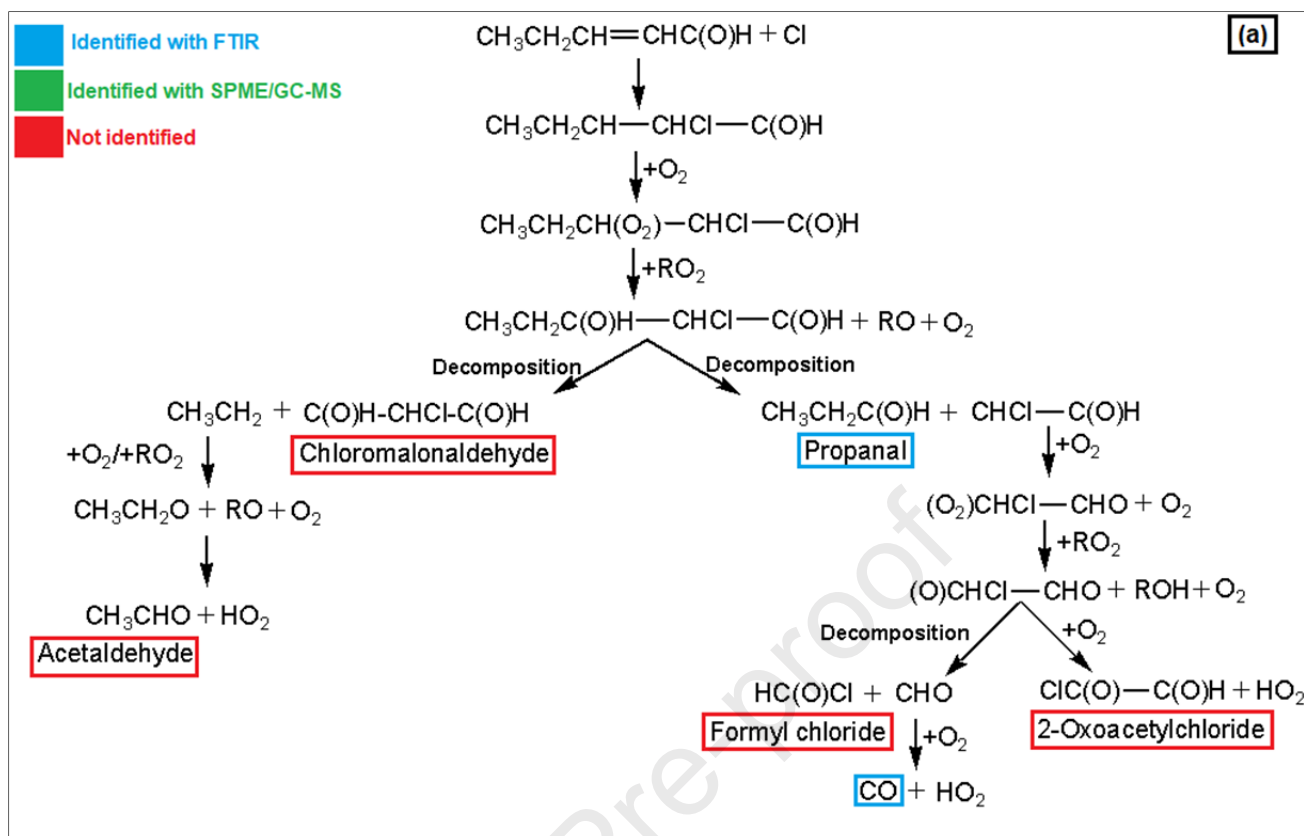
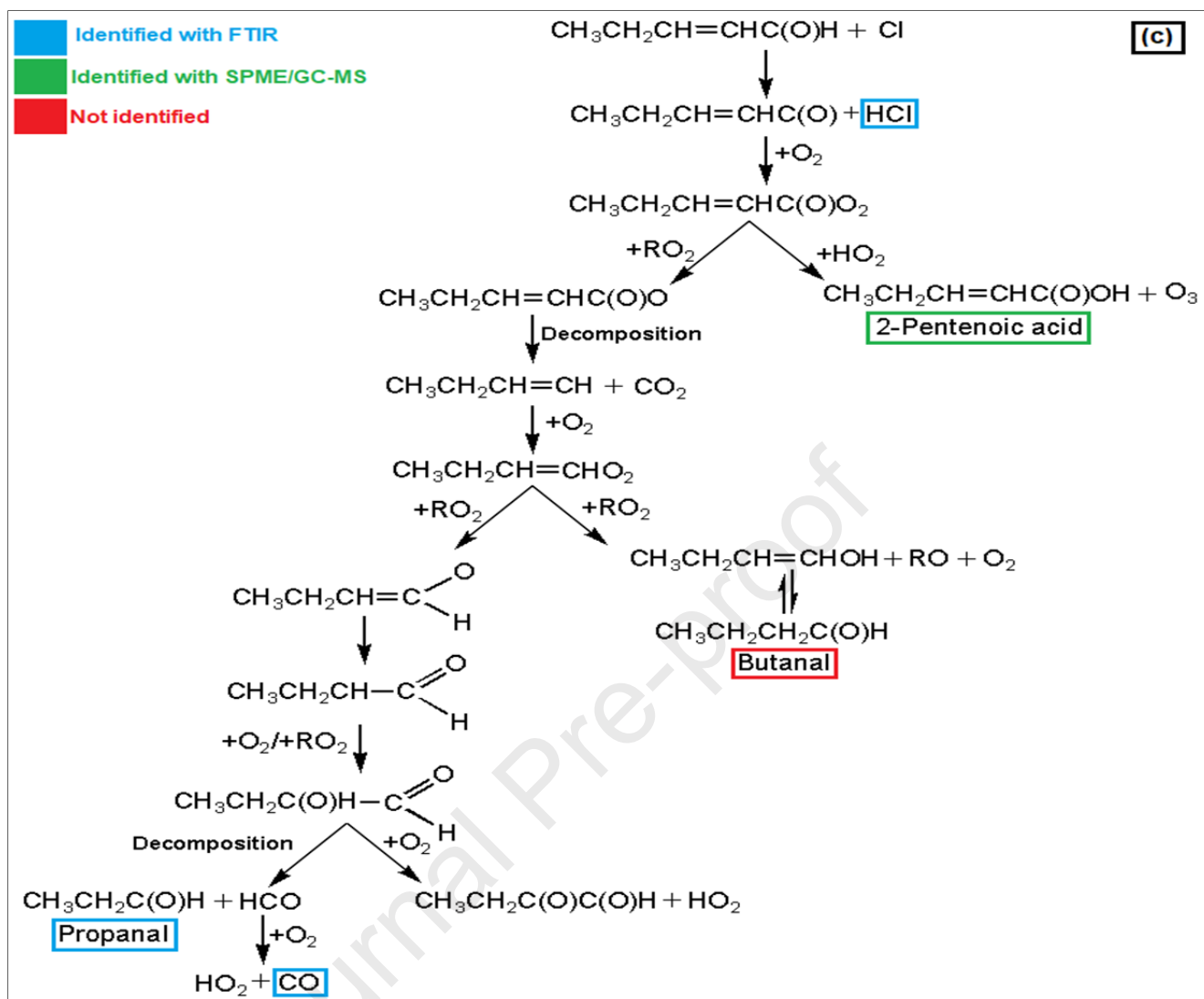


Figure 5. Plot of SOA yield Y_{SOA} as a function of $M_{SOA,max}$ for the reaction between T2P and Cl.





Scheme 1. Proposed mechanism for the reaction of T2P with Cl atom: α -addition (a), β -addition (b) and H-abstraction (c).

- A rate coefficient of $(2.56 \pm 0.83) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained for the reaction of T2P with Cl atoms under atmospheric conditions.
- This work is the first study of the gas-phase products and the SOA formation from the reaction of T2P with Cl.
- The T2P + Cl reaction may contribute to the acidity of marine atmospheres.
- The T2P + Cl reaction proceeds mainly by H-abstraction of the aldehydic group and by β -addition of Cl atoms to the double bond.
- Atmospheric lifetimes of T2P toward chemical removals are of few hours.

Journal Pre-proof

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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