



**HAL**  
open science

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

Asma Grira, M. Antiñolo, André Canosa, Alexandre Tomas, E. Jiménez,  
Gisèle El Dib

### ► To cite this version:

Asma Grira, M. Antiñolo, André Canosa, Alexandre Tomas, E. Jiménez, et al.. An experimental study of the gas-phase reaction between Cl atoms and trans-2-pentenal: Kinetics, products and SOA formation. *Chemosphere*, 2021, 276, pp.130193. 10.1016/j.chemosphere.2021.130193 . hal-03195966

**HAL Id: hal-03195966**

**<https://hal.science/hal-03195966>**

Submitted on 21 Apr 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

3           Asma Grira<sup>1,2</sup>, María Antiñolo<sup>3,4,\* #</sup>, André Canosa<sup>1</sup>, Alexandre Tomas<sup>2</sup>, Elena Jiménez<sup>3,4</sup>,  
4           Gisèle El Dib<sup>1,\*</sup>

5  
6           <sup>1</sup>*CNRS, IPR (Institut de Physique de Rennes)-UMR 6251. Université de Rennes, F-35000 Rennes, France*

7           <sup>2</sup>*IMT Lille Douai, Institut Mines-Télécom, Univ. Lille, Center for Energy and Environment, F-59000 Lille,*  
8           *France*

9           <sup>3</sup>*Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-*  
10           *La Mancha, Avda. Camilo José Cela 1B, E-13071, Ciudad Real, Spain*

11           <sup>4</sup>*Instituto de Investigación en Combustión y Contaminación Atmosférica (ICCA), Universidad de Castilla-*  
12           *La Mancha, Camino de Moledores s/n, E-13071, Ciudad Real, Spain*

13  
14  
15           <sup>#</sup>Currently at: Escuela de Ingeniería Industrial y Aeroespacial, Universidad de Castilla-La  
16           Mancha, Avenida Carlos III s/n. Real Fábrica de Armas. E-45071, Toledo, Spain.

17  
18           \*Corresponding authors:

19           Gisèle El Dib Phone: +33 2 23 23 56 80; email: gisele.eldib@univ-rennes1.fr

20           Maria Antinolo Phone: +34 9 26 29 53 00; Ext. 3446; email: Maria.Antinolo@uclm.es

21

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<sub>x</sub> (OH + HO<sub>2</sub>), NO<sub>x</sub> (NO  
53 + NO<sub>2</sub>) 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<sub>x</sub> 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 NO<sub>3</sub> 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 ClNO<sub>2</sub> 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  $1 \times 10^5$  atoms cm<sup>-3</sup> (Pszenny et al.,  
86 1993, Spicer et al., 1998, Ezell et al., 2002, Tackett et al., 2007) and  $5 \times 10^4$  atoms cm<sup>-3</sup>  
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 N<sub>2</sub> in a Teflon bag using the GC-FID (Flame ionization detector).

94 The value provided by Rodríguez et al.,  $(1.31 \pm 0.19) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 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  $k_{\text{T2P}}$  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  $0.5 \text{ cm}^{-1}$  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 CO<sub>2</sub>  $< 80 \text{ ppb}$ ). 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  $2\text{ cm}^{-1}$  in the IR spectral  
 127 range of 4000 to  $650\text{ cm}^{-1}$ . 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 Cl<sub>2</sub>) 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  $\Delta k_{T2P}$  in the individual rate coefficient comes from statistical errors  $\Delta k_{T2P}$   
 174 (*stat*) and systematic errors  $\Delta k_{T2P}$  (*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.  $\Delta k_{Ref}$  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  $\text{cm}^{-1}$  for T2P, 875-817  $\text{cm}^{-1}$  for propanal, 1840-  
193 1780  $\text{cm}^{-1}$  for formic acid, 2230-2060  $\text{cm}^{-1}$  for CO and 3100-2600  $\text{cm}^{-1}$  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  $\text{Cl}_2$ . 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  $\mu\text{m}$   
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 Cl<sub>2</sub> 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 Cl<sub>2</sub> were (1.56-9.23)×10<sup>14</sup> molecule cm<sup>-3</sup> and (1.55-  
220 15.8)×10<sup>14</sup> molecule cm<sup>-3</sup>, 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<sup>-3</sup>,  
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  $\mu\text{m}$  cut cyclone  
229 at a 10 L  $\text{min}^{-1}$  flow rate, and a 10 L  $\text{min}^{-1}$  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  $\text{Cl}_2$  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  $\alpha$  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  $\Delta k_{T2P}$  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  $(2.56\pm 0.83)\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> 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 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) 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 ( $5.9\times 10^{-11}$  and  $2.70\times 10^{-10}$   
282 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively), gives  $k_{T2P} = 1.39 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 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 C<sub>3</sub>-C<sub>7</sub> 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 NO<sub>3</sub> 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  $\sigma_{\text{sys}}$  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  $\text{cm}^{-1}$  region, according to Wallington et al. (1996), and 2-chlorobutanal considering the  
349 peak typical for a carbonyl group ( $1750 \text{ cm}^{-1}$ ), 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-C<sub>2</sub>H<sub>4</sub>  
356 for the two Cl isotopes), 77 (M-C(O)H), and 41 (C<sub>3</sub>H<sub>5</sub>), 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-H<sub>2</sub>O) 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 ( $\alpha$ ) or on the double-bonded carbon furthest from  
377 the aldehydic group ( $\beta$ ). As seen in Scheme 1, the  $\alpha$ -addition forms the  
378  $\text{CH}_3\text{CH}_2\text{CHClC(O)H}$  radical, which will react with  $\text{O}_2$  followed by a reaction with  $\text{RO}_2$  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 ( $\text{ClC(O)C(O)H}$ ), formyl  
382 chloride  $\text{HC(O)Cl}$  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 ( $\text{C(O)HCHClC(O)H}$ ) 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  $\beta$ -addition mechanism proceeds through the  $\text{CH}_3\text{CH}_2\text{CHClCHC(O)H}$  radical, which will  
387 react with  $\text{O}_2$  followed by a reaction with  $\text{RO}_2$  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 ( $\text{C(O)HC(O)H}$ )  
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  $\text{RO}_2$ . Glyoxal ( $\text{C(O)HC(O)H}$ ) 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  $\text{O}_2$  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  $\text{HCl}$ . In the presence of  $\text{O}_2$ , 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  $\text{HO}_2$ . 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  $\text{RO}_2$  and generates  
404 the  $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}$  radical. This radical can decompose to carbon dioxide ( $\text{CO}_2$ ) 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  $\text{O}_2$ . The reaction of this later with  $\text{RO}_2$  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  $\text{RO}_2$  may also lead to propanal and  $\text{CO}$  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  $\beta$ -addition channel and observed in this work (2-chlorobutanal) could not be  
412 quantified. Among the products expected to occur from the  $\alpha$ -addition channel, only propanal  
413 and  $\text{CO}$  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 Cl<sub>2</sub> with  
417  $M_{SOA,max}$ . A clear dependency of  $M_{SOA,max}$  on the amount of Cl<sub>2</sub> 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 Cl<sub>2</sub> 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 ( $2\sigma$ ).

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  $\tau_{Cl}$  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  $1 \times 10^3$  atoms  $\text{cm}^{-3}$  averaged over 24 hours  
441 (Wingenter et al., 1999). With this value, a  $\tau_{Cl}$  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  $1 \times 10^5$  molecule  $\text{cm}^{-3}$  (Singh et al., 1996) and  
444  $5 \times 10^4$  atoms  $\text{cm}^{-3}$  (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  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  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) ( $3.33 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ ). A short lifetime (5 hours) of T2P is calculated for  
450 its reaction with  $\text{NO}_3$  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 =  $26^\circ$ ). 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- $\text{NO}_x$  conditions), the formation of CO  
469 may contribute to photochemical pollution via its OH-reaction, which produces  $\text{CO}_2$  and H  
470 atoms that quickly combine with  $\text{O}_2$  to form  $\text{HO}_2$  radicals regenerating OH and producing  $\text{O}_3$   
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  $\text{NO}_x$ -free conditions will evolve by including  $\text{RO}_2 +$   
474  $\text{NO}$  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  $Y_{\text{SOA}}$  with the maximum SOA mass is well-described by a  
480 one-product absorptive model that yielded the Odum's parameters  $\alpha$  and  $K_p$ , the latter being  
481 two orders of magnitude lower than the one reported for  $\alpha$ -pinene,  $\beta$ -pinene and d-limonene  
482 (Cai and Griffin, 2006). Even though the uncertainties in  $Y_{\text{SOA}}$  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  $\beta$ -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.

#### 494 **Acknowledgement**

495 The authors are grateful to the INSU-LEFE French program, the IEA program funded by  
496 CNRS France and the Brittany Council. IMT Lille Douai acknowledges funding by the  
497 French ANR agency under contract No. ANR-11-LabX-0005-01 CaPPA (Chemical and  
498 Physical Properties of the Atmosphere), the Région Hauts-de-France, the Ministère de  
499 l'Enseignement Supérieur et de la Recherche (CPER Climibio), and the European Fund for  
500 Regional Economic Development. This research was also funded by the Consejería de  
501 Educación, Cultura y Deportes de la Junta de Comunidades de Castilla-La Mancha through  
502 the project SBPLY/19/180501/000052 and the University of Castilla-La Mancha (UCLM)  
503 through the project 2019-GRIN-27175 (*Ayudas para la financiación de actividades de*  
504 *investigación dirigidas a grupos*). M. Antiñolo acknowledges UCLM *Plan Propio de*  
505 *Investigación* for funding her research contract.

506

507 **References**

- 508 Albaladejo, J., Ballesteros, B., Jiménez, E., Martín, P. and Martínez, E., 2002. A PLP-LIF  
509 kinetic study of the atmospheric reactivity of a series of C4–C7 saturated and  
510 unsaturated aliphatic aldehydes with OH. *Atmospheric Environment*, 36(20), pp.3231-  
511 3239.
- 512 Anderson, R.S., Huang, L., Iannone, R. and Rudolph, J., 2007. Measurements of the <sup>12</sup>C/<sup>13</sup>C  
513 kinetic isotope effects in the gas-phase reactions of light alkanes with chlorine  
514 atoms. *The Journal of Physical Chemistry A*, 111(3), pp.495-504.
- 515 Angerosa, F., Mostallino, R., Basti, C. and Vito, R., 2000. Virgin olive oil odour notes: their  
516 relationships with volatile compounds from the lipoxygenase pathway and secoiridoid  
517 compounds. *Food Chemistry*, 68(3), pp.283-287.
- 518 Antiñolo, M., Asensio, M., Albaladejo, J. and Jiménez, E., 2020. Gas-Phase Reaction of  
519 trans-2-Methyl-2-butenal with Cl: Kinetics, Gaseous Products, and SOA  
520 Formation. *Atmosphere*, 11(7), p.715.
- 521 Antiñolo, M., del Olmo, R., Bravo, I., Albaladejo, J. and Jiménez, E., 2019. Tropospheric fate  
522 of allyl cyanide (CH<sub>2</sub>CHCH<sub>2</sub>CN): Kinetics, reaction products and secondary organic  
523 aerosol formation. *Atmospheric Environment*, 219, p.117041.
- 524 Aschmann, S.M. and Atkinson, R., 1995. Rate constants for the gas-phase reactions of  
525 alkanes with Cl atoms at 296±2 K. *International Journal of Chemical Kinetics*, 27(6),  
526 pp.613-622.
- 527 Atkinson, R. and Aschmann, S.M., 1985. Kinetics of the gas phase reaction of Cl atoms with  
528 a series of organics at 296±2 K and atmospheric pressure. *International journal of  
529 chemical kinetics*, 17(1), pp.33-41.
- 530 Atkinson, R., Baulch, D.L., Cox, R.A., Hampson Jr, R.F., Kerr, J.A., Rossi, M.J. and Troe, J.,  
531 1997. Evaluated kinetic, photochemical and heterogeneous data for atmospheric  
532 chemistry: Supplement V. IUPAC Subcommittee on Gas Kinetic Data Evaluation for  
533 Atmospheric Chemistry. *Journal of Physical and Chemical Reference Data*, 26(3),  
534 pp.521-1011.
- 535 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., ... &  
536 Subcommittee, I. U. P. A. C. (2006). Evaluated kinetic and photochemical data for  
537 atmospheric chemistry: Volume II—gas phase reactions of organic  
538 species. *Atmospheric chemistry and physics*, 6(11), 3625-4055.
- 539 Ballesteros, B., Ceacero-Vega, A.A., Garzon, A., Jimenez, E. and Albaladejo, J., 2009.  
540 Kinetics and mechanism of the tropospheric reaction of tetrahydropyran with Cl  
541 atoms. *Journal of Photochemistry and Photobiology A: Chemistry*, 208(2-3), pp.186-  
542 194.
- 543 Bianchi, F., Careri, M., Mangia, A. and Musci, M., 2007. Retention indices in the analysis of  
544 food aroma volatile compounds in temperature-programmed gas chromatography:  
545 Database creation and evaluation of precision and robustness. *Journal of separation  
546 science*, 30(4), pp.563-572.
- 547 Blanco, M.B., Barnes, I. and Teruel, M.A., 2010. FTIR gas-phase kinetic study of the  
548 reactions of Cl atoms with (CH<sub>3</sub>)<sub>2</sub>C=CHC(O)H and CH<sub>3</sub>CH=CHC(O)OCH<sub>3</sub>. *Chemical  
549 Physics Letters*, 488(4-6), pp.135-139.



- 550 Cai, X. and Griffin, R.J., 2006. Secondary aerosol formation from the oxidation of biogenic  
551 hydrocarbons by chlorine atoms. *Journal of Geophysical Research:*  
552 *Atmospheres*, 111(D14).
- 553 Cai, X., Ziemba, L.D. and Griffin, R.J., 2008. Secondary aerosol formation from the oxidation  
554 of toluene by chlorine atoms. *Atmospheric Environment*, 42(32), pp.7348-7359.
- 555 Calvert, J., Mellouki, A., & Orlando, J. (2011). Mechanisms of atmospheric oxidation of the  
556 oxygenates.
- 557 Canosa-Mas, C.E., Cotter, E.S., Duffy, J., Thompson, K.C. and Wayne, R.P., 2001. The  
558 reactions of atomic chlorine with acrolein, methacrolein and methyl vinyl  
559 ketone. *Physical Chemistry Chemical Physics*, 3(15), pp.3075-3084.
- 560 Ceacero-Vega, A. A., Ballesteros, B., Bejan, I., Barnes, I., Jiménez, E., & Albaladejo, J.  
561 (2012). Kinetics and mechanisms of the tropospheric reactions of menthol, borneol,  
562 fenchol, camphor, and fenchone with hydroxyl radicals (OH) and chlorine atoms  
563 (Cl). *The Journal of Physical Chemistry A*, 116(16), 4097-4107.
- 564 Cheng, H., Erichsen, H., Soerensen, J., Petersen, M.A. and Skibsted, L.H., 2019. Optimising  
565 water activity for storage of high lipid and high protein infant formula milk powder  
566 using multivariate analysis. *International Dairy Journal*, 93, pp.92-98.
- 567 Colmenar, I., Martín, P., Cabañas, B., Salgado, S., Tapia, A. and Martínez, E., 2015. Reaction  
568 products and mechanisms for the reaction of n-butyl vinyl ether with the oxidants OH  
569 and Cl: Atmospheric implications. *Atmospheric Environment*, 122, pp.282-290.
- 570 Davis, M.E., Gilles, M.K., Ravishankara, A.R. and Burkholder, J.B., 2007. Rate coefficients  
571 for the reaction of OH with (E)-2-pentenal, (E)-2-hexenal, and (E)-2-  
572 heptenal. *Physical Chemistry Chemical Physics*, 9(18), pp.2240-2248.
- 573 Ezell, M.J., Wang, W., Ezell, A.A., Soskin, G. and Finlayson-Pitts, B.J., 2002. Kinetics of  
574 reactions of chlorine atoms with a series of alkenes at 1 atm and 298 K: structure and  
575 reactivity. *Physical Chemistry Chemical Physics*, 4(23), pp.5813-5820.
- 576 Fantechi, G., Jensen, N.R., Saastad, O., Hjorth, J. and Peeters, J., 1998. Reactions of Cl atoms  
577 with selected VOCs: Kinetics, products and mechanisms. *Journal of atmospheric  
578 chemistry*, 31(3), pp.247-267.
- 579 Faxon, C. B., Bean, J. K., & Ruiz, L. H. (2015). Inland concentrations of Cl<sub>2</sub> and ClNO<sub>2</sub> in  
580 Southeast Texas suggest chlorine chemistry significantly contributes to atmospheric  
581 reactivity. *Atmosphere*, 6(10), 1487-1506.
- 582 Gardner, H.W., Grove, M.J. and Salch, Y.P., 1996. Enzymic pathway to ethyl vinyl ketone  
583 and 2-pentenal in soybean preparations. *Journal of Agricultural and Food  
584 Chemistry*, 44(3), pp.882-886.
- 585 Graedel, T.E. and Crutzen, P.J., 1986. The role of atmospheric chemistry in environment-  
586 development•• Interactions. *Sustainable Development of the Biosphere*. Clark, WC  
587 and Munn, RE (eds.). Cambridge University Press, Cambridge, pp.213-251.
- 588 Griffin, R.J., Cocker III, D.R., Flagan, R.C. and Seinfeld, J.H., 1999. Organic aerosol  
589 formation from the oxidation of biogenic hydrocarbons. *Journal of Geophysical  
590 Research: Atmospheres*, 104(D3), pp.3555-3567.
- 591 Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M.,  
592 Dommen, J., Donahue, N.M., George, C., Goldstein, A.H. and Hamilton, J.F., 2009.

- 593 The formation, properties and impact of secondary organic aerosol: current and  
594 emerging issues. *Atmospheric chemistry and physics*, 9(14), pp.5155-5236.
- 595 Hatai, M., Horiyama, S., Yoshikawa, N., Kinoshita, E., Kagota, S., Shinozuka, K. and  
596 Nakamura, K., 2019. trans-2-Pentenal, an Active Compound in Cigarette Smoke,  
597 Identified via Its Ability to Form Adducts with Glutathione. *Chemical and*  
598 *Pharmaceutical Bulletin*, 67(9), pp.1000-1005.
- 599 Hatanaka, A., 1993. The biogenesis of green odour by green  
600 leaves. *Phytochemistry*, 34(5), pp.1201-1218.
- 601 Heiden, A.C., Kobel, K., Langebartels, C., Schuh-Thomas, G. and Wildt, J., 2003. Emissions  
602 of oxygenated volatile organic compounds from plants Part I: Emissions from  
603 lipoxygenase activity. *Journal of atmospheric chemistry*, 45(2), pp.143-172.
- 604 Hitsuda, K., Takahashi, K., Matsumi, Y. and Wallington, T.J., 2001. Kinetics of the reactions  
605 of  $\text{Cl}^*(^2\text{P}_{1/2})$  and  $\text{Cl}^*(^2\text{P}_{3/2})$  atoms with  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{D}_8$ , n- $\text{C}_4\text{H}_{10}$ , and i- $\text{C}_4\text{H}_{10}$  at 298  
606 K. *Chemical physics letters*, 346(1-2), pp.16-22.
- 607 Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D., Flagan, R.C. and Seinfeld,  
608 J.H., 1997. Formation of organic aerosols from the oxidation of biogenic  
609 hydrocarbons. *Journal of Atmospheric Chemistry*, 26(2), pp.189-222.
- 610 Houk, K. N. (1976). The photochemistry and spectroscopy of  $\beta$ ,  $\gamma$ -unsaturated carbonyl  
611 compounds. *Chemical Reviews*, 76(1), 1-74.
- 612 Hossaini, R., Chipperfield, M.P., Saiz-Lopez, A., Fernandez, R., Monks, S., Feng, W.,  
613 Brauer, P. and Von Glasow, R., 2016. A global model of tropospheric chlorine  
614 chemistry: Organic versus inorganic sources and impact on methane  
615 oxidation. *Journal of Geophysical Research: Atmospheres*, 121(23), pp.14-271.
- 616 IUPAC 2006. URL: <http://publications.iupac.org/pac/reports/year/2006/index.html>.
- 617 Kaiser, E.W., Donahue, C.J., Pala, I.R., Wallington, T.J. and Hurley, M.D., 2007. Kinetics,  
618 Products, and Stereochemistry of the Reaction of Chlorine Atoms with cis- and trans-  
619 2-Butene in 10– 700 Torr of  $\text{N}_2$  or  $\text{N}_2/\text{O}_2$  Diluent at 297 K. *The Journal of Physical*  
620 *Chemistry A*, 111(7), pp.1286-1299.
- 621 Kalalian, C., Samir, B., Roth, E. and Chakir, A., 2019. UV absorption spectra of trans-2-  
622 pentenal, trans-2-hexenal and 2-methyl-2-pentenal. *Chemical Physics Letters*, 718,  
623 pp.22-26.
- 624 Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C.,  
625 Dingenen, R.V., Ervens, B., Nenes, A.N.C.J.S.E., Nielsen, C.J. and Swietlicki, E.,  
626 2005. Organic aerosol and global climate modelling: a review. *Atmospheric*  
627 *Chemistry and Physics*, 5(4), pp.1053-1123.
- 628 Le Crâne, J.P., Villenave, E., Hurley, M.D., Wallington, T.J., Nishida, S., Takahashi, K. and  
629 Matsumi, Y., 2004. Atmospheric chemistry of pivalaldehyde and isobutyraldehyde:  
630 Kinetics and mechanisms of reactions with Cl atoms, fate of  $(\text{CH}_3)_3\text{CC}(\text{O})$  and  
631  $(\text{CH}_3)_2\text{CHC}(\text{O})$  radicals, and self-reaction kinetics of  $(\text{CH}_3)_3\text{CC}(\text{O})\text{O}_2$  and  
632  $(\text{CH}_3)_2\text{CHC}(\text{O})\text{O}_2$  radicals. *The Journal of Physical Chemistry A*, 108(5), pp.795-805.
- 633 Li, Z. and Pirasteh, A., 2006. Kinetic study of the reactions of atomic chlorine with several  
634 volatile organic compounds at 240–340 K. *International journal of chemical*  
635 *kinetics*, 38(6), pp.386-398.

- 636 Magneron, I., Thevenet, R., Mellouki, A., Le Bras, G., Moortgat, G.K. and Wirtz, K., 2002. A  
637 study of the photolysis and OH-initiated oxidation of acrolein and trans-  
638 crotonaldehyde. *The Journal of Physical Chemistry A*, 106(11), pp.2526-2537.
- 639 Martins, R.C., Monforte, A.R. and Silva Ferreira, A., 2013. Port wine oxidation management:  
640 A multiparametric kinetic approach. *Journal of agricultural and food*  
641 *chemistry*, 61(22), pp.5371-5379.
- 642 Masella, P., Guerrini, L., Angeloni, G., Spadi, A., Baldi, F. and Parenti, A., 2019.  
643 Freezing/storing olives, consequences for extra virgin olive oil quality. *International*  
644 *Journal of Refrigeration*, 106, pp.24-32.
- 645 Moshonas, M.G., MG, M. and PE, S., 1973. Some newly found orange essence components  
646 including trans-2-pentenal. *Journal of Food Science*, 38, pp.360-361.
- 647 Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C. and Seinfeld, J.H., 1996.  
648 Gas/particle partitioning and secondary organic aerosol yields. *Environmental Science*  
649 *& Technology*, 30(8), pp.2580-2585.
- 650 Orlando, J.J. and Tyndall, G.S., 2002. Mechanisms for the reactions of OH with two  
651 unsaturated aldehydes: crotonaldehyde and acrolein. *The Journal of Physical*  
652 *Chemistry A*, 106(51), pp.12252-12259.
- 653 Orlando, J.J., Tyndall, G.S., Apel, E.C., Riemer, D.D. and Paulson, S.E., 2003. Rate  
654 coefficients and mechanisms of the reaction of Cl atoms with a series of unsaturated  
655 hydrocarbons under atmospheric conditions. *International Journal of Chemical*  
656 *Kinetics*, 35(8), pp.334-353.
- 657 Pankow, J.F., 1994. An absorption model of gas/particle partitioning of organic compounds in  
658 the atmosphere. *Atmospheric Environment*, 28(2), pp.185-188.
- 659 Pszenny, A.A.P., Keene, W.C., Jacob, D.J., Fan, S., Maben, J.R., Zetwo, M.P., Springer  
660 Young, M. and Galloway, J.N., 1993. Evidence of inorganic chlorine gases other than  
661 hydrogen chloride in marine surface air. *Geophysical Research Letters*, 20(8), pp.699-  
662 702.
- 663 Ragains, M.L. and Finlayson-Pitts, B.J., 1997. Kinetics and mechanism of the reaction of Cl  
664 atoms with 2-methyl-1, 3-butadiene (isoprene) at 298 K. *The Journal of Physical*  
665 *Chemistry A*, 101(8), pp.1509-1517.
- 666 Rodríguez, D., Rodríguez, A., Notario, A., Aranda, A., Diaz-de-Mera, Y. and Marínez, E.,  
667 2005. Kinetic study of the gas-phase reaction of atomic chlorine with a series of  
668 aldehydes.
- 669 Rodriguez-Kabana, R., Guertal, E.A., Walker, R.H. and Teem, D.H., Auburn University,  
670 2008. 2-Propenal and Related Enal Compounds for Controlling Plant Pests and Weeds  
671 in Soil. U.S. Patent Application 12/190,302.
- 672 Rowley, D.M., Lesclaux, R., Lightfoot, P.D., Noziere, B., Wallington, T.J. and Hurley, M.D.,  
673 1992. Kinetic and mechanistic studies of the reactions of cyclopentylperoxy and  
674 cyclohexylperoxy radicals with hydroperoxy radical. *The Journal of Physical*  
675 *Chemistry*, 96(12), pp.4889-4894.
- 676 Rudich, Y., Donahue, N.M. and Mentel, T.F., 2007. Aging of organic aerosol: Bridging the  
677 gap between laboratory and field studies. *Annu. Rev. Phys. Chem.*, 58, pp.321-352.
- 678 Ruzsanyi, V., Sielemann, S. and Baumbach, J.I., 2002. Determination of VOCs in human  
679 breath using IMS. *Int. J. Ion Mobility Spectrom*, 5, pp.45-48.

- 680 Saison, D., De Schutter, D.P., Delvaux, F. and Delvaux, F.R., 2009. Determination of  
681 carbonyl compounds in beer by derivatisation and headspace solid-phase  
682 microextraction in combination with gas chromatography and mass  
683 spectrometry. *Journal of Chromatography A*, 1216(26), pp.5061-5068.
- 684 Seaman, V. Y., Charles, M. J., & Cahill, T. M. (2006). A sensitive method for the  
685 quantification of acrolein and other volatile carbonyls in ambient air. *Analytical*  
686 *chemistry*, 78(7), 2405-2412.
- 687 Seco, R., Penuelas, J., & Filella, I. (2007). Short-chain oxygenated VOCs: Emission and  
688 uptake by plants and atmospheric sources, sinks, and concentrations. *Atmospheric*  
689 *Environment*, 41(12), 2477-2499.
- 690 Singh, H.B., Thakur, A.N., Chen, Y.E. and Kanakidou, M., 1996. Tetrachloroethylene as an  
691 indicator of low Cl atom concentrations in the troposphere. *Geophysical Research*  
692 *Letters*, 23(12), pp.1529-1532.
- 693 Sleiman, C., El Dib, G., Ballesteros, B., Moreno, A., Albaladejo, J., Canosa, A. and Chakir,  
694 A., 2014. Kinetics and Mechanism of the Tropospheric Reaction of 3-Hydroxy-3-  
695 methyl-2-butanone with Cl Atoms. *The Journal of Physical Chemistry A*, 118(32),  
696 pp.6163-6170.
- 697 Spicer, C.W., Chapman, E.G., Finlayson-Pitts, B.J., Plastringe, R.A., Hubbe, J.M., Fast, J.D.  
698 and Berkowitz, C.M., 1998. Unexpectedly high concentrations of molecular chlorine  
699 in coastal air. *Nature*, 394(6691), pp.353-356.
- 700 Stutz, J., Ezell, M.J., Ezell, A.A. and Finlayson-Pitts, B.J., 1998. Rate constants and kinetic  
701 isotope effects in the reactions of atomic chlorine with n-butane and simple alkenes at  
702 room temperature. *The Journal of Physical Chemistry A*, 102(44), pp.8510-8519.
- 703 Tackett, P.J., Cavender, A.E., Keil, A.D., Shepson, P.B., Bottenheim, J.W., Morin, S., Deary,  
704 J., Steffen, A. and Doerge, C., 2007. A study of the vertical scale of halogen chemistry  
705 in the Arctic troposphere during Polar Sunrise at Barrow, Alaska. *Journal of*  
706 *Geophysical Research: Atmospheres*, 112(D7).
- 707 Tandon, K.S., Baldwin, E.A. and Shewfelt, R.L., 2000. Aroma perception of individual  
708 volatile compounds in fresh tomatoes (*Lycopersicon esculentum*, Mill.) as affected by  
709 the medium of evaluation. *Postharvest biology and technology*, 20(3), pp.261-268.
- 710 Teruel, M.A., Achad, M. and Blanco, M.B., 2009. Kinetic study of the reactions of Cl atoms  
711 with  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds at atmospheric pressure and structure  
712 activity relations (SARs). *Chemical Physics Letters*, 479(1-3), pp.25-29.
- 713 Thévenet, R., Mellouki, A. and Le Bras, G., 2000. Kinetics of OH and Cl reactions with a  
714 series of aldehydes. *International Journal of Chemical Kinetics*, 32(11), pp.676-685.
- 715 Turpin, E., Tomas, A., Fittschen, C., Devolder, P. and Galloo, J.C., 2006. Acetone- $h_6$  or- $d_6$  +  
716 OH reaction products: Evidence for heterogeneous formation of acetic acid in a  
717 simulation chamber. *Environmental science & technology*, 40(19), pp.5956-5961.
- 718 Ullerstam, M., Ljungström, E. and Langer, S., 2001. Reactions of acrolein, crotonaldehyde  
719 and pivalaldehyde with Cl atoms: structure–activity relationship and comparison with  
720 OH and NO<sub>3</sub> reactions. *Physical Chemistry Chemical Physics*, 3(6), pp.986-992.
- 721 Wallington, T.J., Skewes, L.M., Siegl, W.O., Wu, C.H. and Japar, S.M., 1988. Gas phase  
722 reaction of Cl atoms with a series of oxygenated organic species at 295  
723 K. *International journal of chemical kinetics*, 20(11), pp.867-875.

- 724 Wallington, T. J., Ball, J. C., Straccia, A. M., Hurley, M. D., Kaiser, E. W., Dill, M., ... &  
725 Bilde, M. (1996). Kinetics and mechanism of the reaction of Cl atoms with CH<sub>2</sub> CO  
726 (Ketene). *International journal of chemical kinetics*, 28(8), 627-635.
- 727 Wang, D.S. and Ruiz, L.H., 2017. Secondary organic aerosol from chlorine-initiated  
728 oxidation of isoprene. *Atmospheric Chemistry and Physics*, 17(22).
- 729 Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., ... & Liao, H.  
730 (2019). The role of chlorine in global tropospheric chemistry. *Atmospheric Chemistry  
731 and Physics*, 19(6), 3981-4003.
- 732 Winer, A. M., Arey, J., Atkinson, R., Aschmann, S. M., Long, W. D., Morrison, C. L., &  
733 Olszyk, D. M. (1992). Emission rates of organics from vegetation in California's  
734 Central Valley. *Atmospheric Environment. Part A. General Topics*, 26(14), 2647-  
735 2659.
- 736 Wingenter, O.W., Blake, D.R., Blake, N.J., Sive, B.C., Rowland, F.S., Atlas, E. and Flocke,  
737 F., 1999. Tropospheric hydroxyl and atomic chlorine concentrations, and mixing  
738 timescales determined from hydrocarbon and halocarbon measurements made over the  
739 Southern Ocean. *Journal of Geophysical Research: Atmospheres*, 104(D17),  
740 pp.21819-21828.
- 741 Yamanishi, T., Kita, Y., Watanabe, K. and Nakatani, Y., 1972. Constituents and composition  
742 of steam volatile aroma from Ceylon tea. *Agricultural and Biological  
743 Chemistry*, 36(7), pp.1153-1158.

## Tables

**Table 1.** Experimental conditions used during our kinetic study.

Reactor	Lamps	Compound	Initial concentration ( $\times 10^{13}$ molecule $\text{cm}^{-3}$ )	$k_{\text{WL},X} \pm \sigma_1^a$ ( $\times 10^{-5} \text{ s}^{-1}$ )	$k_{\text{PL},X} \pm \sigma_2^a$ ( $\times 10^{-5} \text{ s}^{-1}$ )
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 <sub>2</sub>	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 <sub>2</sub>	66.00 – 132		

<sup>a</sup>: uncertainty is  $\pm 1\sigma$ .

**Table 2.** Experimental conditions used during the mechanistic study.

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

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

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

$k_{\text{Isoprene}} = (4.8 \pm 1.25) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (see section 2.1.3)

$k_{\text{Ethanol}} = (1.0 \pm 0.2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (see section 2.1.3)

$k_{\text{Cyclohexane}} = (2.90 \pm 1.12) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (see section 2.1.3)

<sup>a</sup> uncertainty calculated according to equations (4-5)

<sup>b</sup> two standard deviations

**Table 4.** Summary of the rate coefficients for the reactions of a series of C<sub>3</sub>-C<sub>7</sub> unsaturated aldehydes with Cl atoms.

Unsaturated aldehyde	$k_{Cl}$ ( $\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
Acrolein (CH <sub>2</sub> =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 <sub>3</sub> -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 <sub>3</sub> ) <sub>2</sub> C=CH-C(O)H	2.48 ± 0.71	(Blanco et al. 2010)
Trans-2-pentenal (CH <sub>3</sub> -CH <sub>2</sub> -CH=CH-CHO)	1.31 ± 0.19 3.47 <b>2.53 ± 0.83</b>	(Rodríguez et al. 2005) (Teruel et al. 2009) (SAR Estimation) <b>This work</b>
Trans-2-hexenal (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH=CH-CHO)	1.92 ± 0.22	(Rodríguez et al. 2005)
Trans-2-heptenal (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -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	$0.82 \pm 0.02$
9.39	2.43	1.75	1.75	$1.15 \pm 0.02$
13.14	4.28	3.08	3.42	$1.34 \pm 0.02$
3.30	3.16	1.56	3.39	$2.07 \pm 0.09$
12.62	8.45	4.75	9.11	$2.15 \pm 0.02$
2.23	2.43	0.88	2.56	$2.47 \pm 0.08$
5.75	8.07	3.36	8.18	$2.59 \pm 0.05$
3.05	8.07	1.67	8.20	$2.79 \pm 0.08$
2.99	8.33	1.62	9.72	$3.79 \pm 0.10$
5.75	7.89	2.19	8.97	$3.79 \pm 0.10$
9.32	13.74	2.79	13.48	$4.26 \pm 0.11$
6.69	12.41	4.31	15.89	$4.62 \pm 0.27$
2.23	7.00	1.35	9.88	$4.77 \pm 0.28$
7.89	18.97	4.89	21.56	$5.17 \pm 0.39$
6.59	16.10	4.43	16.62	$5.24 \pm 0.54$
9.32	17.34	2.46	19.00	$6.16 \pm 0.10$

<sup>a</sup> $Y_{SOA}$  is determined from the slope of  $M_{SOA,max}$  vs.  $Y_{SOA}$ . Errors are  $2\sigma$ .

## 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:  $5.91 \times 10^{14}$  molecule.cm<sup>-3</sup> for T2P and  $9.09 \times 10^{14}$  molecule.cm<sup>-3</sup> for Cl<sub>2</sub>.

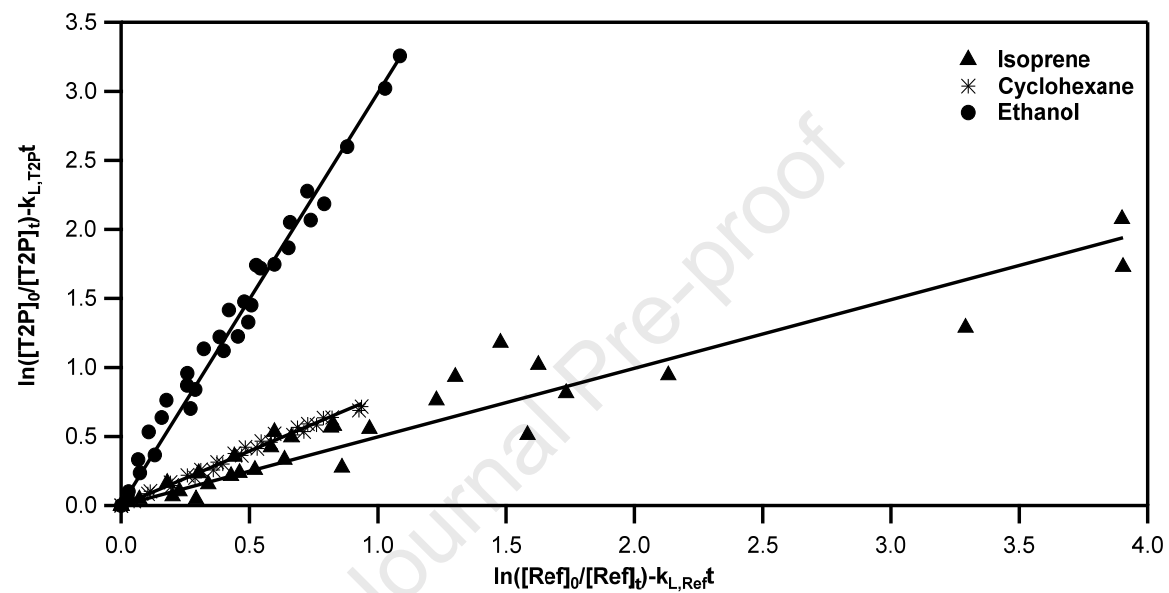
**Figure 3.** Product yields for HC(O)OH and propanal.

**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  $4.03 \times 10^{14}$  molecule.cm<sup>-3</sup> for T2P and  $6.72 \times 10^{14}$  molecule.cm<sup>-3</sup> for Cl<sub>2</sub>. 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.

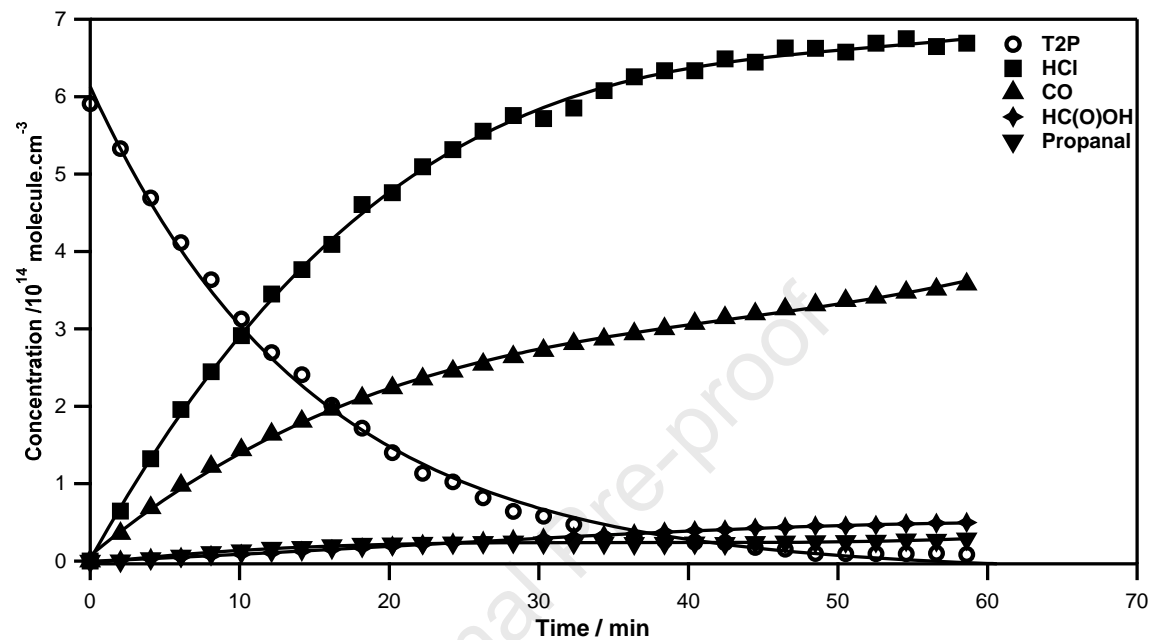
**Scheme 1.** Proposed mechanism for the reaction of T2P with Cl atom:  $\alpha$ -addition (a),  $\beta$ -addition (b) and H-abstraction (c).

## 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:  $5.91 \times 10^{14}$  molecule. $\text{cm}^{-3}$  for T2P and  $9.09 \times 10^{14}$  molecule. $\text{cm}^{-3}$  for  $\text{Cl}_2$ .

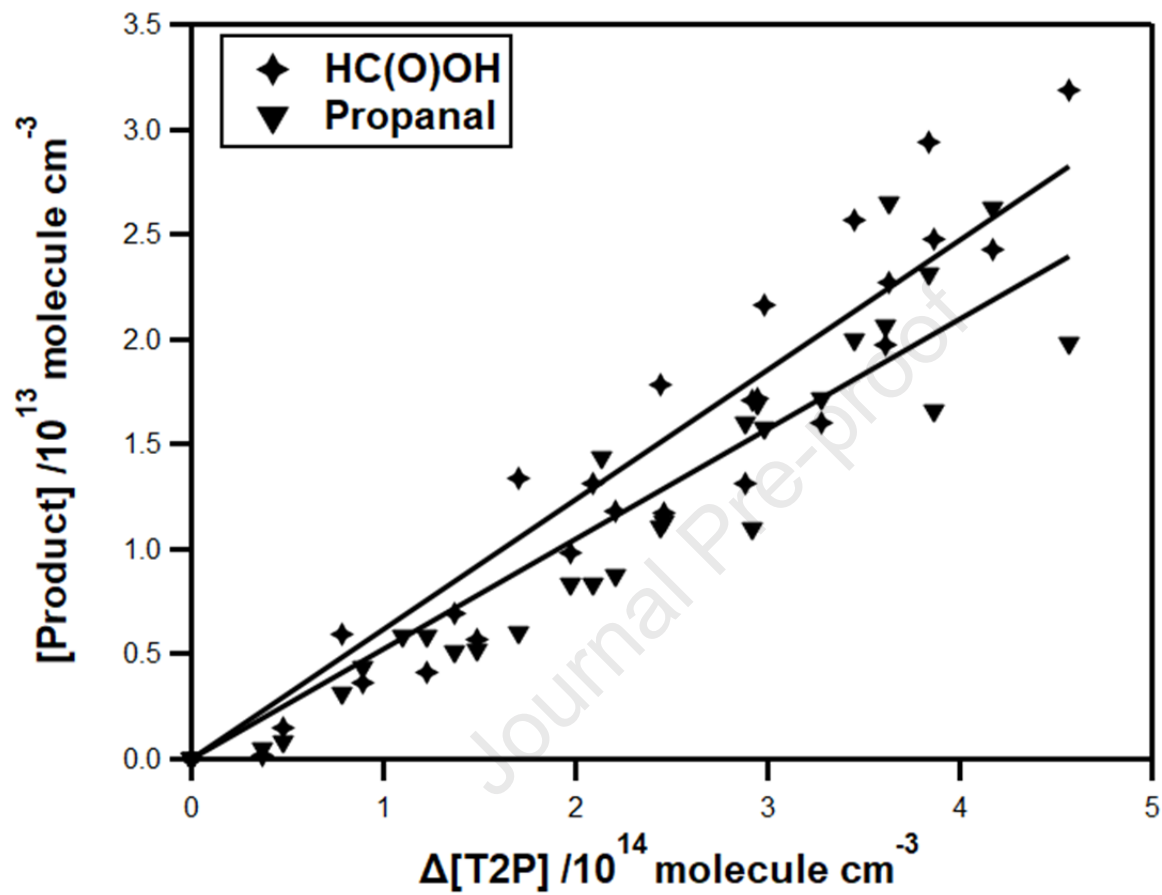
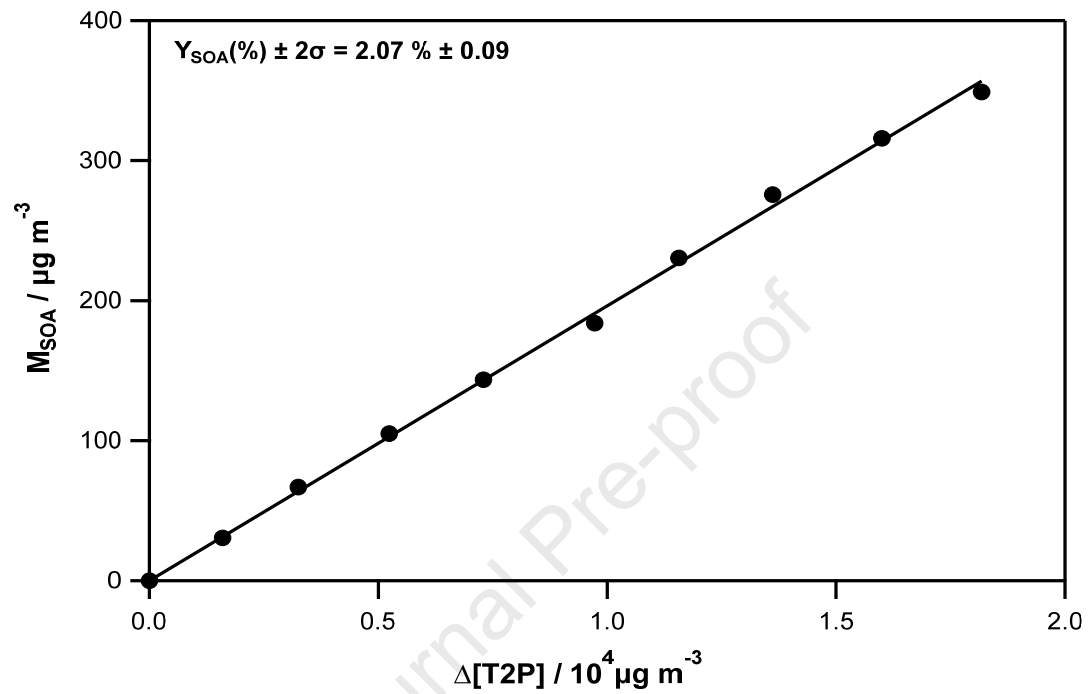
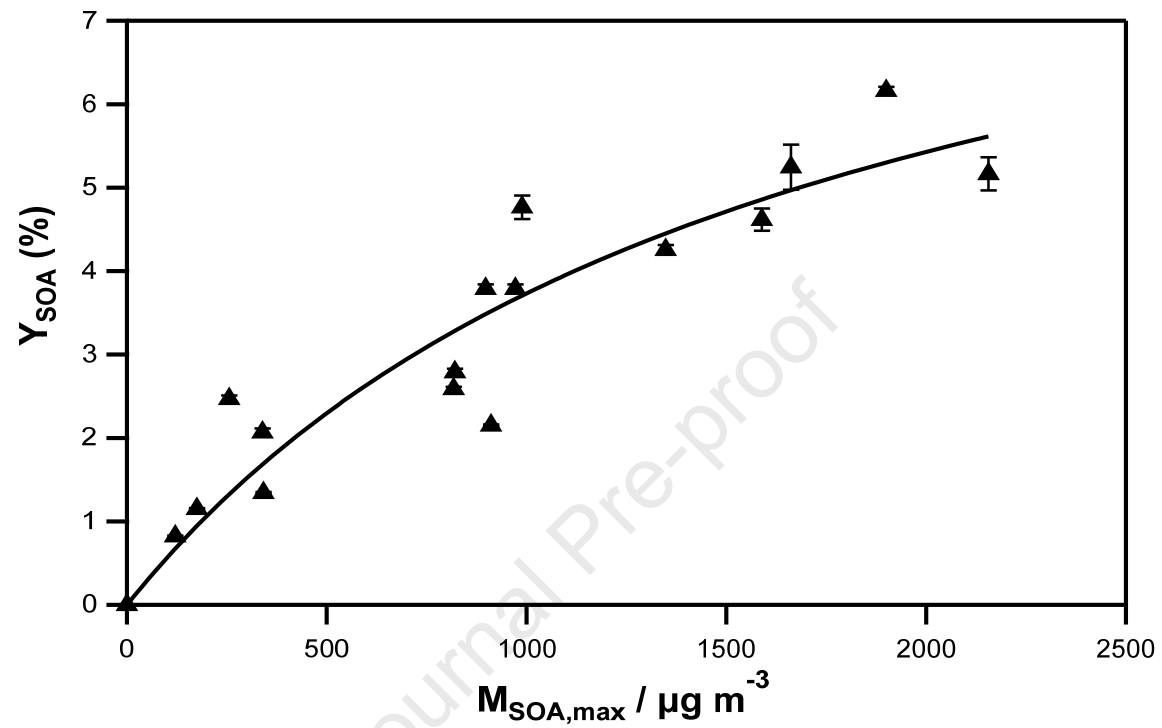


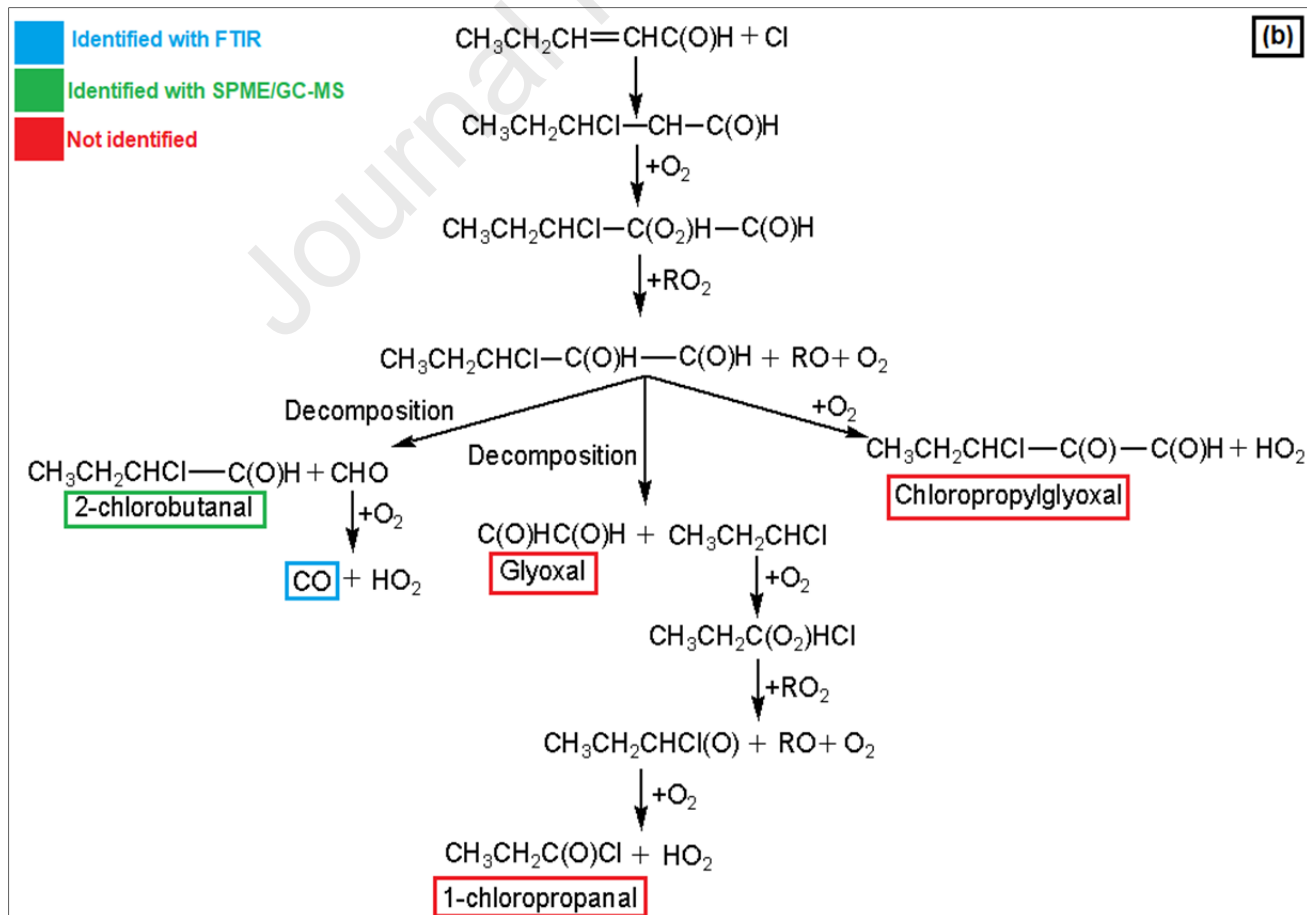
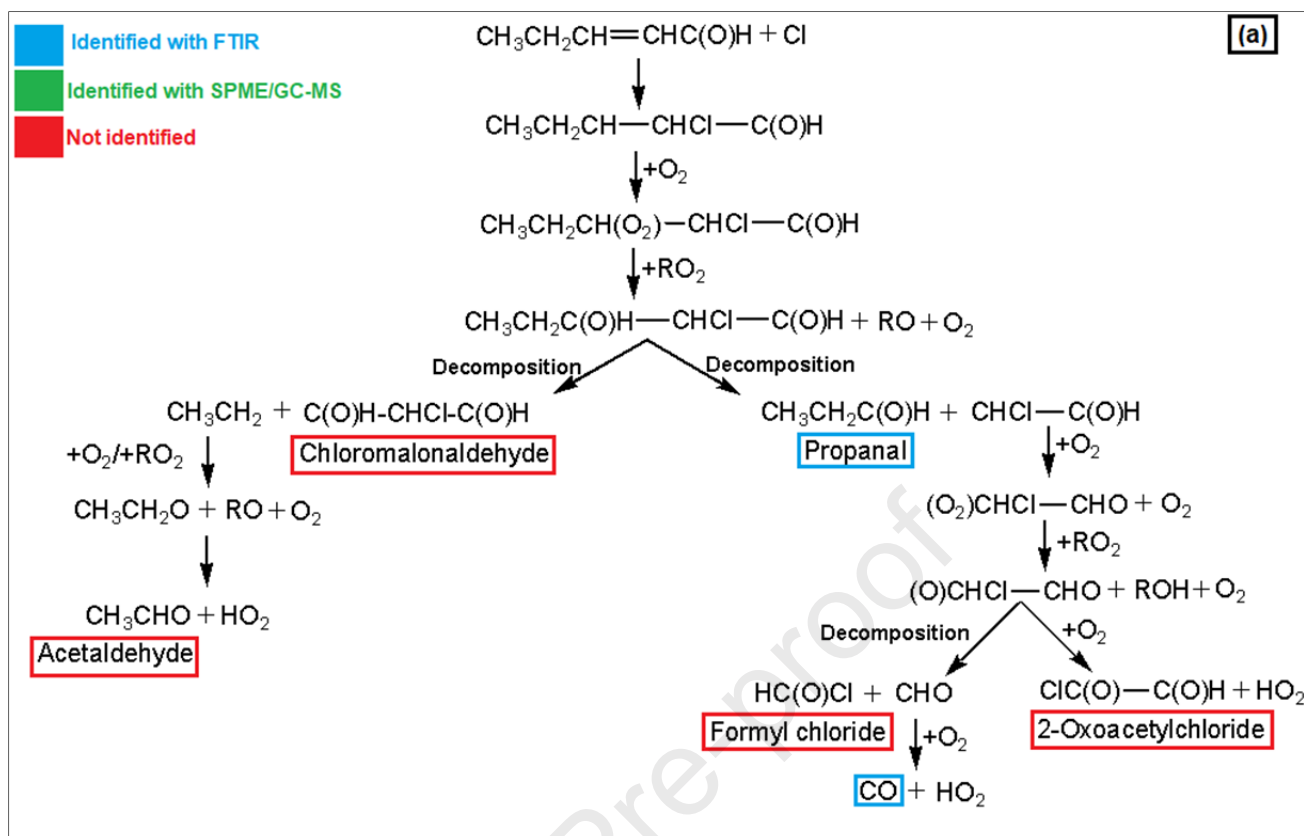
Figure 3. Product yields for  $\text{HC(O)OH}$  and propanal.



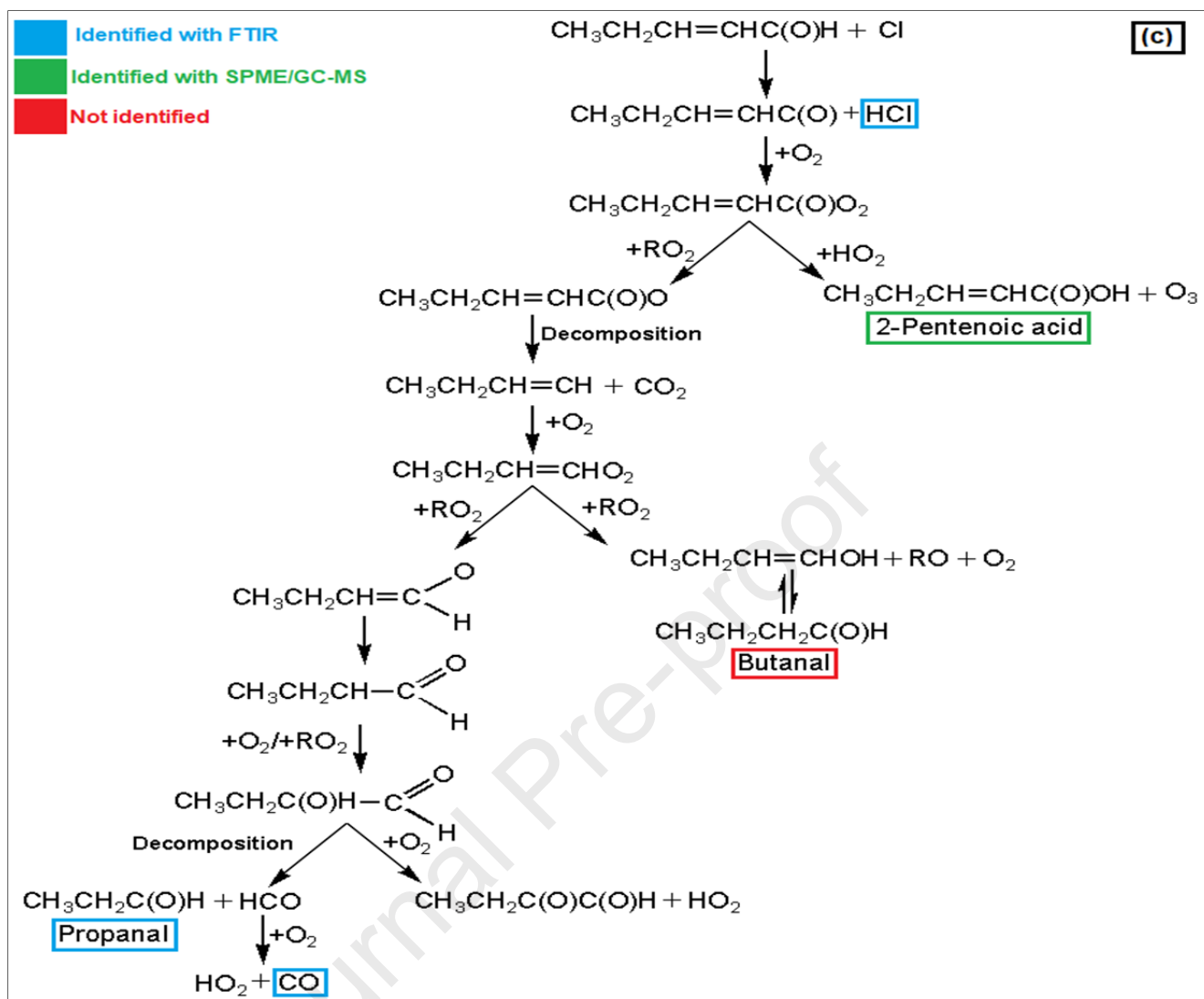
**Figure 4.** SOA mass concentration  $M_{SOA}$  produced from the T2P+Cl reaction as a function of the consumed T2P with an initial concentration of  $4.03 \times 10^{14}$  molecule. $\text{cm}^{-3}$  for T2P and  $6.72 \times 10^{14}$  molecule. $\text{cm}^{-3}$  for  $\text{Cl}_2$ . The SOA yield  $Y_{SOA}$  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:  $\alpha$ -addition (a),  $\beta$ -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  $\beta$ -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:

Journal Pre-proof