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Abstract

The ozone reaction of γ-terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene), a monoterperne emitted by Elm, Cypress, Waterhickory and Maple trees, has been investigated at 294 ± 2 K, atmospheric pressure and under dry conditions (relative humidity, RH < 2 %) in two simulation chambers of the LPCA laboratory in Dunkerque (France): CHARME (CHamber for the Atmospheric Reactivity and the Metrology of the Environment) a 9.2 m^3 evacuable cylinder in stainless steel electropolished and LPCA-ONE a 8 m^3 cubic reactor in PMMA. Cyclohexane was used to scavenge the hydroxyl radicals formed from the rearrangement of the Criegee biradicals. The concentrations of the organic compounds were monitored versus the time with a PTR-ToF-MS and a TD-GC-FID. The rate coefficient for the γ-terpinene reaction with ozone has been determined using the pseudo first-order and the relative-rate methods. The values obtained with both methods are in a very good agreement and give an average value of $(2.10 \pm 0.11) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} which leads to an atmospheric lifetime of 32 minutes for γ-terpinene with respect to its ozonolysis reaction. The

main oxidation products observed and their respective molar yields (in %) include formic acid (7 - 11), glyoxal and/or acetone (4 - 9), 3-oxobutanal (6 - 8), 4-methyl-3-oxopentanal (5 - 8), acetic acid (5 - 9), acetaldehyde (3 - 6), formaldehyde (3 - 6), 3-oxopropanoic acid (2 - 4) and an unidentified compound with m/z 73.0 (2 - 3). The kinetic data are compared with the literature, and the reaction mechanism is discussed. To our knowledge this work represents the first mechanistic study for the ozonolysis reaction of γ-terpinene.

Keywords: simulation chamber, γ-terpinene ozonolysis, rate coefficient, mechanistic study.

1. Introduction

Volatile Organic Compounds (VOCs) are emitted into the atmosphere from both natural and anthropogenic sources. On a global scale, the emissions of natural VOCs exceed anthropogenic ones by a factor of about 10 (Lamb et al., 1987; Guenther et al., 1995). Biogenic volatile organic compounds (BVOCs) are mainly emitted from vegetation (Guenther et al., 1995), and they consist of isoprene (44 %) and monoterpenes (11 %). The emission fluxes of these BVOCs depend on the cover and type of vegetation, temperature, irradiation, ambient concentration of carbon dioxide and soil humidity (Peñuelas and Staudt, 2010). BVOCs are key compounds for the physical and chemical properties of the atmosphere and climate (Calfapietra et al., 2013). They influence the oxidative capacity of the atmosphere and impact the tropospheric ozone budget. They also contribute to the formation of secondary organic aerosols (SOAs), and hence affect the gas phase and the heterogeneous chemistry of the troposphere (Hoffmann et al., 1997; Mackenzie-Rae et al., 2017a). BVOCs are oxidized in the atmosphere and these atmospheric degradation processes are initiated in the gas phase by the attack of hydroxyl radical during daytime and by nitrate radicals during the night

(Finlayson-Pitts and Pitts Jr, 1999). BVOCs also react with ozone, during both night and day and the ozonolysis reactions of these unsaturated compounds are known to represent a significant source of OH radicals (Johnson and Marston, 2008). Among the different classes of BVOCs, monoterpenes ($C_{10}H_{16}$), whose structures are built up from two isoprene (C_5H_8) units, are considered to be of great importance in the atmosphere. They are very reactive and their atmospheric chemical lifetime ranges from minutes to hours. The most abundant monoterpenes are α-pinene and β-pinene (Guenther et al., 1995). γ-terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene) is a monoterpene emitted into the atmosphere from Elm, Cypress, Waterhickory and Maple trees (Khalil and Rasmussen, 1992; Rasmussen, 2012); its volumes ratios in the atmosphere are about a few pptv (Bouvier-Brown et al., 2009).

It is identified as an antioxidant in various essential oils like cumin oil and is used in fragrances and flavors. The presence of two endocyclic C=C double bonds makes γ-terpinene a reactive VOC and gives it the possibility to be oxidized into various products in the gas phase.

Previous works on the ozonolysis reaction of γ-terpinene have been performed. Grimsrud, et al. (1974) and Atkinson et al. (1990) have determined the rate coefficient using the absolute and relative-rate method, respectively, however the values they obtained disagree with a relative discrepancy of ≈ 50%.

The aim of this work was to study in a simulation chamber the atmospheric reactivity of γ-terpinene with ozone. The rate coefficient was determined using the pseudo-first-order and the relative-rate methods and the obtained value was compared with literature data. In addition, the oxidation products formed in the gas phase were characterized and quantified and the mechanism leading to the main degradation products is proposed. To our knowledge this work represents the first mechanistic study for the ozonolysis reaction of γ-terpinene in the atmosphere.

2. Material and methods

The experiments were performed in the dark, at 294 ± 2K, atmospheric pressure, and dry conditions (RH < 2 %) in two atmospheric simulation reactors: CHARME (CHamber for the Atmospheric Reactivity and the Metrology of the Environment) and LPCA-ONE. CHARME is a new reaction chamber designed in the LPCA (Laboratoire de Physico-Chimie de l'Atmosphere) laboratory in Dunkerque (France). It is a 9.2 m^3 (length of ≈4 m, diameter of ≈1.7 m and surface to volume ratio of ≈3.5 m^{-1}) evacuable cylinder in electro-polished stainless steel (304 L). Four stainless steel fans positioned at the bottom of the chamber allow the homogenization of the gaseous mixtures. The temperature and relative humidity were controlled using a combined T / RH probe (HMT334 series transmitters, VAISALA). The CHARME chamber was pumped down to 0.4 mbar with a vacuum pump (Cobra NC0100-0300B) and was then filled till the atmospheric pressure with purified and dried air using a generator (Parker Zander KA-MT 1-8). The LPCA-ONE chamber is described in detail in Lauraguais et al. (2012). Briefly, it consists of a 8 m^3 cubic reactor in PPMA (PolyMethyl Methacrylate) equipped with a fan to ensure homogeneous mixing of the reactants. Prior to each experiment, the reaction chamber was flushed with purified air for about 12 h (air generator; Dominick Hunter LGCAD 140). The ozonolysis reactions were performed in the presence of an excess of cyclohexane to scavenge the hydroxyl radicals produced from the rearrangement of the Criegee biradicals (Henry and Donahue, 2011). The cyclohexane concentrations were calculated in order to scavenge more than 95% of the OH radicals formed (i.e. $k_{(cyclohexane+OH)} \times [cyclohexane] / k_{(\gamma\text{-terpinene}+OH)} \times [\gamma\text{-terpinene}] \geq 10$).

In CHARME, the organic compounds were first injected into the chamber using a glass impinger and their concentrations were continuously recorded using a proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS 1000, IONICON Analytik, Innsbruck,

Austria). The PTR-ToF-MS allows the detection of any chemical compounds that have a proton affinity higher than that of water. It uses hydronium ions (H_3O^+) to chemically ionize compounds through a proton transfer reaction and then identify them by their mass to charge ratio (m/z). The detailed principle of operation for the PTR is mentioned in Blake et al., (2009). The analytes were sampled by an inlet PEEK capillary line of 100 cm heated at 333 K to reduce the loss of the VOCs during their sampling and then ionized in the drift tube (E = 600 $V.cm^{-1}$; E/N=136 Td) which operates at 2.2 mbar and 333 K. To monitor the reactant concentrations, the ion at m/z 137.2, corresponding to its parent $[M+H]^+$ ion, was recorded for γ-terpinene and the one at 71.1 for the reference compounds, cis-2-pentene and 2-methyl-2-butene (both compounds have the same molecular formula, C_5H_{10}). In the PTR-ToF-MS, γ-terpinene is fragmented in two peaks at m/z 81.0 (≈65%) and m/z 137.2 (≈35%). As the main peak interferes with some products formed during the ozonolysis reaction, it was not selected to follow the γ-terpinene concentrations.

In LPCA-ONE, known volumes of VOCs were injected through a heated injector, sampled on stainless steel tubes filled with Tenax TA (60-80 mesh) and then thermodesorbed and analyzed with a ThermoDesorber - Gas Chromatograph - Flame Ionization Detector (TD-GC-FID; Autosystem XL, Perkin Elmer). The organics were separated onto a 30 m DB-5 capillary column held at 353 K during 5 min and then programmed to 523 at 5 K min^{-1}. Due to overlapping peak with y-terpinene at m/z 137.2 in the PTR-ToF-MS, the TD-GC-FID method was used for kinetic studies using α-pinene as reference compound.

Preliminary tests were performed for each organic compound to control the linearity of the PTR-MS and the GC-FID with respect to the injected VOC concentrations and also to verify the absence of interferences between γ-terpinene or the references and their oxidation products. The wall losses of organic compounds were also investigated in both chambers. They were determined in the dark from the decay of their concentrations before the ozone

127 introduction and were considered as negligible for γ-terpinene, α-pinene, cis-2-pentene and 2-
128 methyl-2-butene (for these 4 VOCs, $k_{wall\ loss}$ = (7 - 9) × 10^{-6} s^{-1}). Ozone was introduced into
129 the chambers using an ozone generator (Air Tree Ozone Technology C-L010-DTI) that
130 converts pure oxygen to ozone with a high voltage corona discharge and its concentrations
131 were monitored by an UV photometric ozone analyzer (Thermo Scientific 49i). The initial
132 mixing ratios used ranged from 43 to 800 ppbv for organic compounds and from 200 to 5300
133 ppbv for ozone. Acetonitrile (2.5 μL) was injected in all the experiments as a dilution tracer.
134 Oxidation products were analyzed in the gas-phase with the PTR-ToF-MS. For formaldehyde
135 (m/z = 31.0), formic acid (m/z = 47.0), acetone (m/z = 59.0), acetic acid (m/z = 61.0) and γ-
136 terpinene (m/z = 137.2) the instrument was calibrated from injection of known volumes of
137 standards into the chamber. However, for most of the oxidation products, the volume ratios
138 were determined using a generic H_3O^+ rate coefficient for their protonation reaction of 2 × 10^{-9}
139 cm^3 $molecule^{-1}$ s^{-1}. Certain compounds are subject to fragmentation. This is the case for
140 example for glyoxal which fragments into an ion at m/z 31 (Stonner et al., 2017) and then
141 interferes with the formaldehyde parent ion and for acetic acid (Haase et al. (2012);
142 Baasandori et al. (2015)). So, the uncertainties on the determination of the concentrations of
143 VOCs having low masses can be important and it has been estimated that the uncertainties on
144 the formation yields of these oxidation products are around 50 %.
145 The compounds used in this work, their manufacturer, and stated purity were as follows: γ-
146 terpinene (ACROS ORGANICS, 97%), α-pinene (ACROS ORGANICS, 98.0%),
147 cyclohexane (CHEM-LAB, ≥ 99.5%), cis-2-pentene (SIGMA-ALDRICH, 98.0%), 2-methyl-
148 2-butene (SIGMA-ALDRICH > 99.0 %), acetone (VERBIESE, 99.5%), acetonitrile (SIGMA-
149 ALDRICH, ≥ 99.5%), acetic acid (SIGMA-ALDRICH ≥ 99.5%), formic acid (Fisher
150 Scientific, 98%), formaldehyde (J.T.Baker, 37% stabilized with methanol 10-15%), and

151 oxygen (PRAXAIR 99.9999%). Pure dry air was supplied by a compressed air adsorption
152 dryer Zander KA-MT 1-8 (Parker).
153
154 **3. Results and Discussion**
155 **3.1. Rate constant determination**
156 The rate constant for the reaction of γ-terpinene and ozone was determined through two
157 different kinetic methods, the pseudo-first-order and the relative-rate method.
158
159 ***3.1.1. Pseudo-first-order kinetics***
160 A set of eleven experiments was performed under pseudo-first-order conditions with an
161 excess of ozone. The initial concentrations ranged from 43 to 497 ppbv for γ-terpinene and
162 from 450 to 5300 ppbv for ozone. To ensure that pseudo-first-order conditions prevailed, the
163 initial ozone concentrations were at least ten times higher than those of γ-terpinene.
164
165 The γ-terpinene decay due to its reaction with O_3 is described as followed:
166
167 γ-terpinene + O_3 → products ($k_{\gamma\text{-t}}$) (1)

168 $$-\frac{d[\gamma\text{-terpinene}]}{dt} = k_{\gamma\text{-t}} \times [O_3] \times [\gamma\text{-terpinene}] \quad \text{(I)}$$

169 By replacing $k_{\gamma\text{-t}} \times [O_3]$ by the pseudo-first-order rate coefficient $k'_{\gamma\text{-t}}$ (in s^{-1}), equation (I) can be
170 simplified into:

171 $$-\frac{d[\gamma\text{-terpinene}]}{dt} = k'_{\gamma\text{-t}} \times [\gamma\text{-terpinene}] \quad \text{(II)}$$

172 The integration of equation (II) leads to the following relationship:

173 $$\frac{\ln[\gamma\text{-terpinene}]_0}{\ln[\gamma\text{-terpinene}]_t} = k'_{\gamma\text{-t}} \times t \quad \text{(III)}$$

where $k_{\gamma t}$ is the rate coefficient for the reaction of γ-terpinene with ozone (reaction 1), and the subscripts *0* and *t* indicate concentrations at the start of the reaction and at a time *t*, respectively.

The rate coefficient $k'_{\gamma\text{-}t}$ are deduced from the straight lines of the plots of $\ln([\gamma\text{-terpinene}]_0/[\gamma\text{-terpinene}]_t$ versus the time according to equation (III) (see Fig. S1. Supporting Information). The uncertainties on the measurement of $k'_{\gamma\text{-}t}$ are twice the standard deviation arising from the linear regression analyses of the slopes of $\ln([\gamma\text{-terpinene}]_0/[\gamma\text{-terpinene}]_t$ as a function of time; they are in the range 0.02-0.04%. $k_{\gamma\text{-}t}$ is determined from the plot of the obtained $k'_{\gamma\text{-}t}$ values versus the initial ozone concentrations as shown in Fig. 1. Indicated error on the measurement of $k_{\gamma\text{-}t}$ include both the relative uncertainties on the determination of $k'_{\gamma\text{-}t}$ and that on the measurement of the O_3 concentration (relative uncertainty = 5%).The rate coefficient determined using this method is $k_{\gamma\text{-}t} = (2.03 \pm 0.10) \times 10^{-16}$ cm^3 molecule s^{-1} (see table 1). The indicated errors (in the range 0.03-0.07 %) are twice the standard deviation arising from the linear regression analysis of the data.

3.1.2. Relative-Rate Method

The rate constant of the ozonolysis of γ-terpinene was also obtained with the relative-rate kinetic method. Three references compounds were used and a minimum of three experiments were performed for each of them. The references used in this study and their rate coefficients with ozone (in units of cm^3 $molecule^{-1}$ s^{-1}) were 2-methyl-2-butene ($k_{(2\text{-methyl-2-butene})} = (4.1 \pm 0.5) \times 10^{-16}$; Witter et al., 2002), cis-2-pentene ($k_{(cis\text{-}2\text{-}pentene)} = (1.32 \pm 0.04) \times 10^{-16}$; Avzianova and Ariya, 2002) and α-pinene ($k_{(\alpha\text{-pinene})} = (9.6 \pm 0.15) \times 10^{-16}$; IUPAC current recommendation). These experiments were performed with an OH scavenger (cyclohexane).

The rate coefficient with ozone was determined by comparing the decay rate of γ-terpinene relative to that of the references.

199 γ-terpinene + O_3 → products ($k_{\gamma\text{-t}}$) (1)

200 reference + O_3 → products (k_{ref}) (2)

201

202 Kinetic treatment of reactions 1-2 leads to the following relationship:

203 $$\ln\frac{[\gamma\text{-terpinene}]_0}{[\gamma\text{-terpinene}]_t} = \frac{k_{\gamma\text{-t}}}{k_{ref}} \times \ln\frac{[\text{reference}]_0}{[\text{reference}]_t} \quad \text{(IV)}$$

204 where $k_{\gamma\text{-}t}$ and k_{ref} are the rate coefficients for the reactions of γ-terpinene and the references
205 with ozone (reactions 1 and 2), respectively, and the subscripts *0* and *t* indicate concentrations
206 at the start of the reaction and at a time *t*, respectively.
207 The VOC concentrations measured versus the reaction time were plotted in the form of
208 equation IV and the obtained plots show a good linearity with near zero intercept (Fig. 2). The
209 slopes ($k_{\gamma\text{-}t}/k_{ref}$) derived from the plots and the calculated ozone rate coefficients ($k_{\gamma\text{-}t}$) are
210 displayed in table 1. The indicated errors are twice the standard deviations arising from the
211 least squares linear regression of the data and do not include the uncertainties in the reference
212 rate coefficients.

213

214 Rather than calculating an average rate coefficient for the γ-terpinene using the different
215 reference compounds, a more representative values for $k_{\gamma\text{-t}}$ was obtained by combining the
216 data recorded for the three references into one plot represented by eq V. This plot is also
217 linear with near-zero intercept (see Fig. S2. Supporting Information).

218 $$k_{ref} \times \ln\frac{[\gamma\text{-terpinene}]_0}{[\gamma\text{-terpinene}]_t} = k_{\gamma\text{-t}} \times \ln\frac{[\text{reference}]_0}{[\text{reference}]_t} \quad \text{(V)}$$

219

220 The rate coefficients for the reaction of γ-terpinene with ozone determined with the relative-
221 rate method using the three references are in accordance (relative discrepancy lower than 5 %)
222 and lead to an average value of $k_{(\gamma\text{-terpinene})} = (2.17 \pm 0.11) \times 10^{-16}$ cm^3 molecule s^{-1}). This

value is also in good agreement with the rate coefficient measured with the pseudo-first-order method ($k_{(\gamma\text{-terpinene})}$ = (2.03 ± 0.10) × 10^{-16} cm^3 molecule s^{-1}), so this provides a good confidence in the data determined in the present work for the γ-terpinene reaction with ozone. So, based on these two methods, the mean rate coefficients for the reaction of γ-terpinene with ozone is $k_{(\gamma\text{-terpinene})}$ = (2.10 ± 0.11) × 10^{-16} cm^3 molecule s^{-1}. Indicated errors are twice the standard deviation arising from the linear regression analysis and do not include the uncertainty in the reference rate coefficients. This rate coefficient can be compared with literature data as well. Two previous determinations were reported as it is shown in table 1. The rate coefficient obtained by Atkinson et al. (1990) using the relative-rate method ($k_{(\gamma\text{-terpinene})}$ = (1.63 ± 0.12) × 10^{-16} cm^3 molecule s^{-1}; this value has been recalculated using the current recommended value for the reference compound, α-pinene (IUPAC)) is ≈ 22 % lower than the one obtained in the present work. As this difference is within an acceptable 20-25% error margin, both values can be considered to be in accordance. On the contrary, the rate coefficient reported by Grimsrud et al. (1974) with the absolute method ($k_{(\gamma\text{-terpinene})}$ = 2.84 × 10^{-16} cm^3 molecule s^{-1}) is ≈ 39 % higher and does not match with that determined in this study. In their study, Atkinson et al., (1990) determined consistently lower rate coefficients (from a factor of ≈ 2 to 6) for monoterpenes (e.g. β-pinene, α-pinene, α-phellandrene and γ-terpinene) than Grimsrud, et al. (1974). Atkinson et al., (1990) suggested that the highest values reported by Grimsrud, et al., (1974) were probably due to secondary reactions which occurred at atmospheric pressure in the slow flow system used to perform the experiments.

2. Gas-phase oxidation products

A total of five experiments were carried out in the dark using the CHARME chamber to characterize the products formed from the gas phase from the oxidation of γ-terpinene with ozone. PTR-ToF-MS analyses were continuously performed during the ozonolysis reaction to

monitor the concentration of the organics versus the time. The peaks which were detected along the course of the experiments are listed in table 2 and their typical time profiles are displayed in Fig. 3. The concentrations have been corrected for their backgrounds signals recorded before the ozone introduction.

γ-terpinene was first introduced into the chamber and followed throughout the experiment with the PTR-ToF-MS at m/z 137.2. Cyclohexane was then injected and theoretically as its proton affinity is lower than that of water, it should not be detected by the PTR-ToF-MS. However, a peak at m/z 85.1 was observed during/after its introduction, suggesting that it likely corresponds to cyclohexane. This peak was also detected by Lee et al., (2006) and Mackenzie-Rae et al. (2017) in similar investigations, and seems to result from termolecular reactions in the PTR-ToF-MS (Smith and Španěl, 2005). Acetonitrile was injected as a dilution tracer and followed throughout the experiment at m/z 42.0. Its signal remained constant indicating that dilution effects in the chamber are negligible.

As soon as ozone is introduced, γ-terpinene is rapidly oxidized (within a few minutes) to form a number of oxidation products whose concentrations continuously increase during the experiment and then reach a plateau when the γ-terpinene is totally consumed. Meanwhile, the ozone concentration displays a rapid initial consumption followed by a slow decrease in part due to wall losses ($k_{wall(O3)} \approx 3\times10^{-5}$ s^{-1}).

18 compounds were observed with the PTR-ToF-MS (see table 2 and Fig. 3) and 12 of them were identified using their m/z ratio as well as the proposed chemical mechanism (Fig. 6) leading to these chemical species.

For the 9 most abundant oxidation products, the formation yields were determined from the plot of their concentrations versus the amount of γ-terpinene consumed (Fig. 4). The yields obtained from the slope of the linear least-squares fit to the data are also shown in table 2.

The major oxidation products observed and their respective molar yields are (the indicated m/z include the addition of H^+): formic acid (m/z 47.0; 7 - 11 %), glyoxal and/or acetone (m/z 59.0; 4 - 9 %), 3-oxobutanal (m/z 87.0 ; 6 – 8%), 4-methyl-3-oxopentanal (m/z 115.1; 5 - 8 %), acetic acid (m/z 61.0; 5 - 9 %), acetaldehyde (m/z 45.0; 3 - 6 %), formaldehyde (m/z 31.0; 3 - 6 %), 3-oxopropanoic acid (m/z 89.0 ; 2 - 4) and an unidentified compound (m/z 73.0; 2 - 3 %).

9 minor compounds were also formed from the gas-phase reaction of ozone with γ-terpinene: 2-oxosuccinaldehyde (m/z 101.0; < 1%); γ-terpinonaldehyde (m/z 169.2; < 1%); $C_4H_6O_3H^+$(m/z 103.1 ; 1 - 2 %); $C_6H_{10}O_3H^+$(m/z 131.1 ; 1 - 2 %); $C_{10}H_{16}O_3H^+$(m/z 185.2 ; < 1%) and 4 unidentified (m/z 141.1, 155.2, 167.0 and 183.1; each < 1%).

The yields of formaldehyde (3 - 6 %) are in accordance with those reported by Lee et al. (2006) (4 ± 2 %) who studied the reaction of α-terpinene with ozone. Moreover, the sum of the yields of glyoxal and acetone (4 - 9 %) agrees with that of acetone (11%) obtained by Reissell et al. (1999) for the ozonolysis reaction of γ-terpinene.

The sum of the yields of the 12 oxidation products identified in the gas-phase leads to a mean value of ≈ 50 %, which suggest that about half of the reacted γ-terpinene is not detected by the PTR-MS. The missing products can be present in the gas phase but not measured by the PTR-MS (multifunctional organic compounds), be lost in the inlet PEEK tubing or on the chamber walls and/or partitioned to the condensed phase.

Mechanism

Several previous works (Atkinson, 1997; Calvert and Madronich, 1987; Herrmann et al., 2010, Lee et al., 2006; Leungsakul et al., 2005, Mackenzie-Rae et al., 2017, Zhang and Zhang, 2005) have been performed to study the gas phase reaction of monoterpenes with ozone. However, to our knowledge there are no literature data describing the oxidation

298 products and the chemical mechanism related to the ozonolysis of γ-terpinene. γ-terpinene
299 contains two endocyclic C=C double bonds so, mechanistic details were evolved from
300 experimental findings and literature data of monoterpenes having one or two endocyclic
301 double bonds. Research works that have investigated the ozone reaction of α-phellandrene
302 (Mackenzie-Rae et al., 2017), limonene (Leungsakul et al., 2005), α-pinene (Zhang and
303 Zhang, 2005) and α-terpinene (Herrmann et al., 2010) were useful guides for this study. As
304 there are similarities between the chemical structure of γ-terpinene and these monoterpenes,
305 comparable degradation pathways following the ozone oxidation can be expected.
306 The reaction mechanism of γ-terpinene with ozone leading to the products listed in table 2 is
307 proposed in Figs. 5 and 6 and Figs. S3-S5. As shown in Fig. 5, the ozonolysis reaction is
308 initiated by the addition of ozone on both endocyclic C=C double bonds resulting in the
309 formation of two primary ozonides POZ1 and POZ2. The rapid decomposition of both POZs
310 through homolytic cleavage of the C–C and O–O bonds leads to the formation of four Criegee
311 intermediates (CIs) named CI1, CI2, CI3 and CI4 (Johnson and Marston, 2008). The detailed
312 degradation mechanism of CI1 is displayed in Fig. 6. Comparable schematics for CI2, CI3
313 and CI4 are provided in the Supporting Information (Figs. S3-S5), they lead to similar
314 products as those formed from CI1.
315 The CIs contain excess of energy so they are either stabilized or decompose. Stabilization of
316 CIs is achieved through unimolecular or bimolecular reactions with available atmospheric
317 species and their decomposition is believed to occur via several reaction channels (Finlayson-
318 Pitts and Pitts Jr, 1999) including the “hydroperoxide” channel (HP) which is responsible for
319 the OH formation and the “ester” channel, leading to the formation of an ester that can further
320 decompose into different compounds.
321 Hydroperoxide channel is an important pathway for CIs decomposition and it generally
322 explains the OH formation during alkene ozonolysis. Through this degradation pathway, CI1

rearranges into vinyl hydroperoxide before it losses an OH and decomposes into a vinyloxyl radical. The latter is followed by addition of oxygen molecule to form peroxy radicals. These radicals further react with other peroxy radicals to form dicarbonyl compounds such as α-hydroxycarbonyls having the chemical formula $C_{10}H_{16}O_3$ (m/z 185.2). A set of isomeric species having the same molecular formula (same m/z value) are also suggested from the different reactive channels.

CI1 may also decompose through an ester channel to form dioxirane intermediate. The dissociation of the O–O bond of the dioxirane leads to the formation of diradical that rearranges to form two unsaturated esters. These esters can further react with ozone to form a variety of oxygenated compounds with short carbon chain.

In the proposed mechanism for CI1, an unsaturated keto-aldehyde of chemical formula $C_{10}H_{16}O_2$ (detected at m/z = 169.2 with the PTR-MS) probably known as γ-terpinonaldehyde analogous to pinonaldehyde from α-pinene or limonaldehyde from limonene may be formed from the oxygen-atom elimination channel. However as this unsaturated compound was detected at low concentration by the PTR-ToF-MS (< 0.5 ppbv) one can assume that it was decomposed through its reaction with ozone, may be lost on the inlet PEEK tubing of the PTR-ToF-MS or on the walls of the chamber and/or partition to the particle phase rather than stay in the gas phase.

4. Conclusion and atmospheric implications

Research works to study the gas-phase reaction of ozone with γ-terpinene, an important monoterpene containing two endo-cyclic double bond, have been carried out in atmospheric simulation chambers. The kinetic investigations and the mechanistic studies have been performed for the first time at 294 ± 2 K, atmospheric pressure and under dry conditions (RH < 2 %) and in the presence of cyclohexane as an OH scavenger. Two different methods, the

pseudo-first-order and the relative-rate method were used to determine the kinetic rate coefficient for the reaction between ozone and γ-terpinene. The values obtained with both methods are in good agreement and lead to a rate coefficient of $(2.10 \pm 0.11) \times 10^{-16}$ cm^3 molecule s^{-1} for the ozonolysis reaction of γ-terpinene. This average rate coefficient is also in accordance (within the uncertainties) with that determined by Atkinson et al. (1990) using the relative-rate method.

The oxidation products formed in the gas-phase were analyzed with a PTR-TOF-MS. 18 oxidation products were observed out of which 12 were identified and quantified. The molar yields determined for the most abundant ones are (in %): formic acid (7 - 11), glyoxal and/or acetone (4 - 9), 3-oxobutanal (6 - 8), 4-methyl-3-oxopentanal (5 - 8), acetic acid (5 - 9), acetaldehyde (3 - 6), formaldehyde (3 - 6), 3-oxopropanoic acid (2 - 4) and an unidentified compound with m/z 73.0 (2 - 3).

The rate coefficient determined in this study for the gas-phase ozonolysis of γ-terpinene allows the calculation of the atmospheric lifetimes of γ-terpinene with respect to its reaction with ozone. Assuming a 24-h average concentration of ozone of 100 ppbv (2.46×10^{12} molecule.cm^{-3}) for a polluted area (Lin et al., 2001), the estimated lifetime of γ-terpinene in the atmosphere is 32 min (see table 3). The rate coefficients of γ-terpinene with hydroxyl radical and nitrate radical (IUPAC, recommended values) were previously measured and the corresponding calculated lifetimes are also provided in table 3 for comparison. The reaction of γ-terpinene with OH and NO_3 leads to atmospheric lifetimes of about 49 min and 2 min, respectively, so the ozonolysis is also an important sink of this monoterpene in polluted areas. The mechanism proposed in this study can be integrated into atmospheric models such as the Master Chemical Mechanism (Saunders et al., 2003) to describe the chemistry of γ-terpinene and similar endocyclic monoterpenes. Future works on the reactivity of γ-terpinene with ozone should also include the identification and quantification of oxidation products formed in

373 the particle phase (secondary organic aerosol formation) under various atmospheric
374 conditions.
375
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383
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Fig. 1. Plot of the pseudo-first-order rate coefficients ($k'_{\gamma-t}$) for the reaction of O_3 with γ-terpinene as a function of the initial ozone concentration, obtained at 294 ± 2K, atmospheric pressure and in the presence of an ozone scavenger (cyclohexane). The error bars vary in the range 0.03-0.07 % and reflect the uncertainties on the measurements of $k'_{\gamma-t}$.

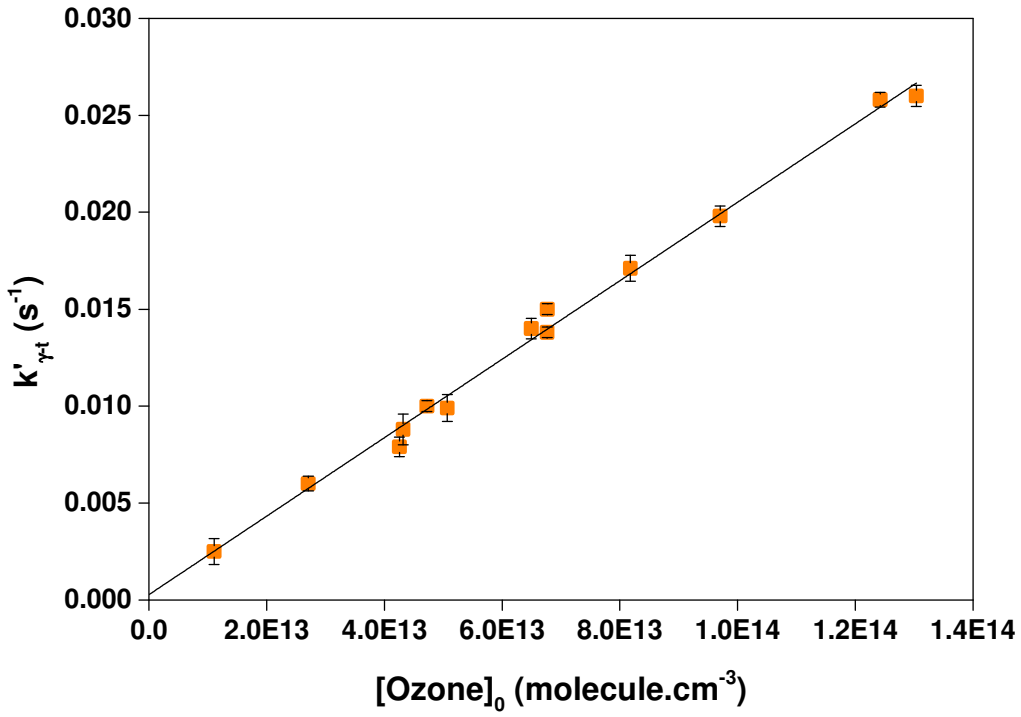


Fig. 2. Relative rate plots for the reaction of γ-terpinene with ozone obtained at 294 ± 2K, atmospheric pressure and in the presence of an ozone scavenger (cyclohexane). Three references were used: cis-2-pentene (red squares; PTR-ToF-MS analyses), 2-methyl-2-butene (blue triangle; PTR-ToF-MS analyses) and α-pinene (green circles; GC-MS analyses).

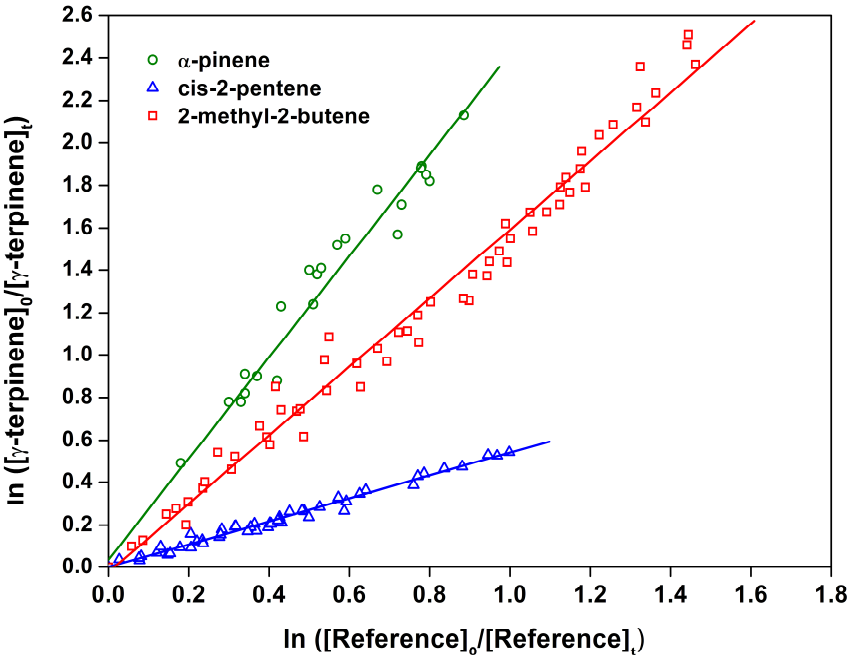


Fig. 3. Typical time profiles of chemical compounds detected by PTR-ToF-MS and ozone analyzer during the ozonolysis of γ-terpinene (initial concentrations: γ-terpinene 200 ppbv ; O_3 2780 ppbv). Note that m/z includes the addition of H^+. a) reactants (m/z): γ-terpinene (137.2), cyclohexane (ozone scavenger; 85.1) and acetonitrile (dilution tracer; 42.0); b) major oxidation products; c) minor oxidation products. The compounds corresponding to the m/z ratios are listed in table 2.

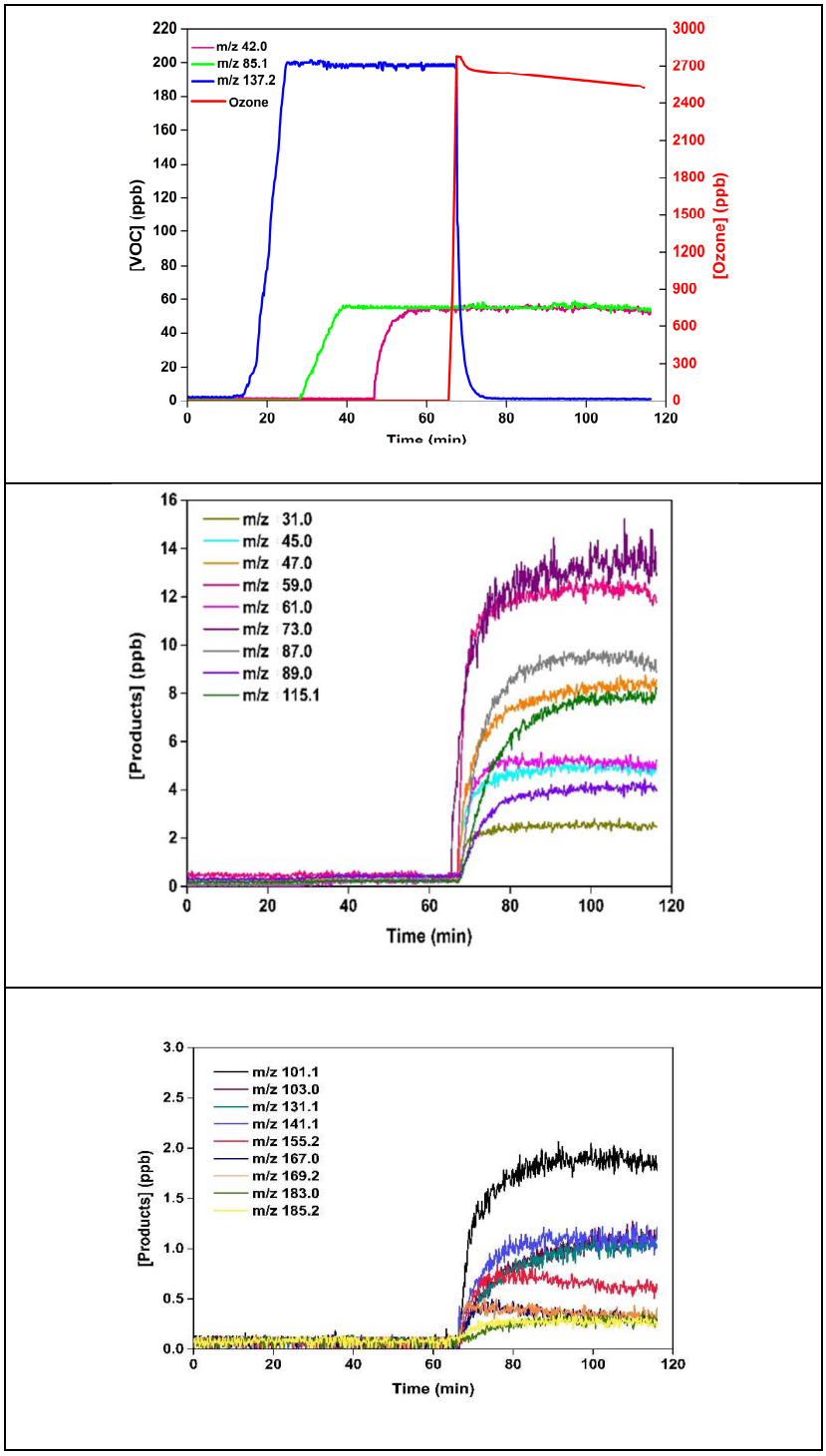


Fig. 4. Typical plot for the determination of the gas-phase product yields formed from the ozonolysis of γ-terpinene (initial concentrations: γ-terpinene 200 ppbv and O_3 2780 ppbv). Note that m/z includes the addition of H^+.

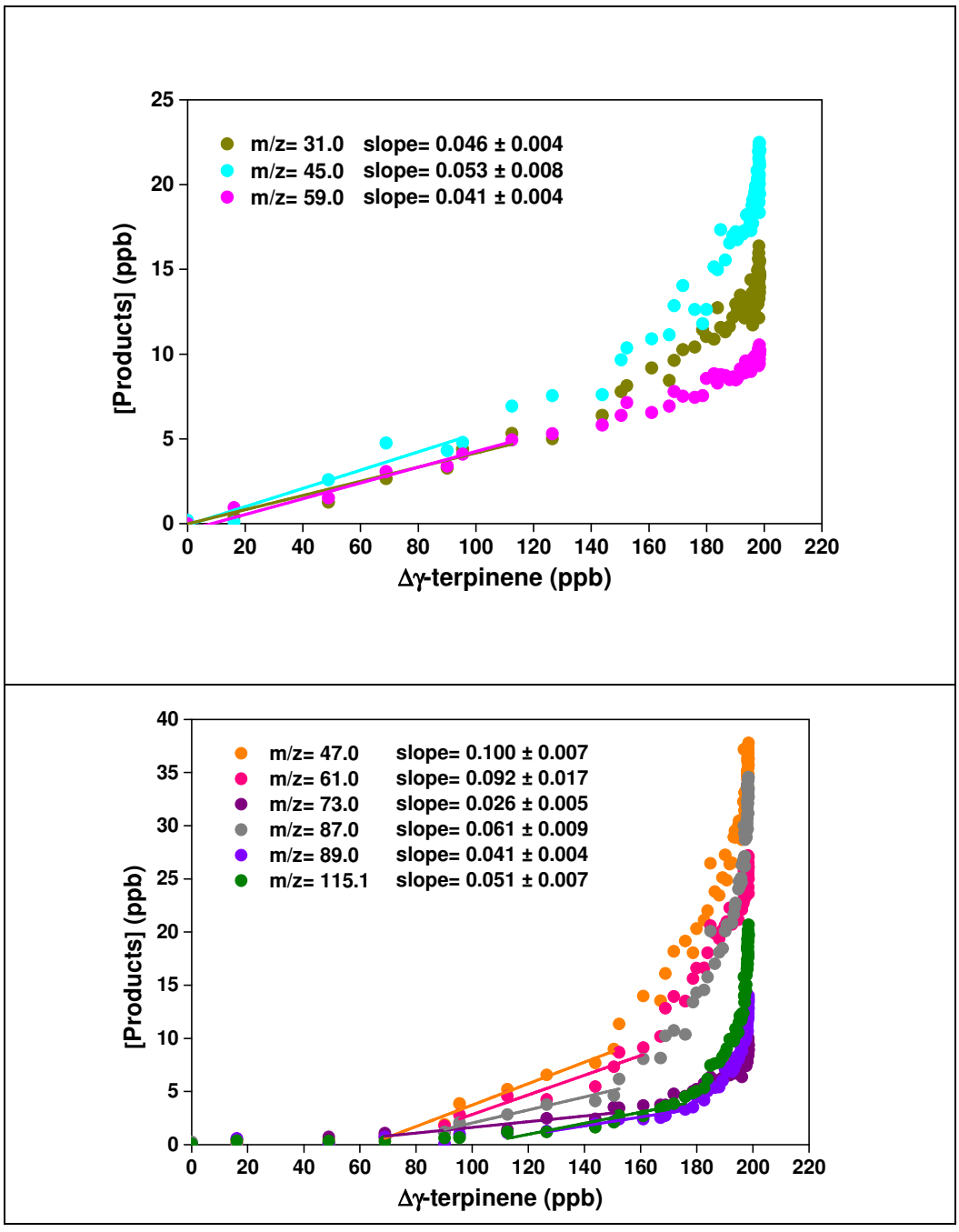


Fig. 5. Simplified mechanism for the formation of primary ozonides (POZs) and Criegee intermediates (CIs) from the reaction of γ-terpinene with ozone.

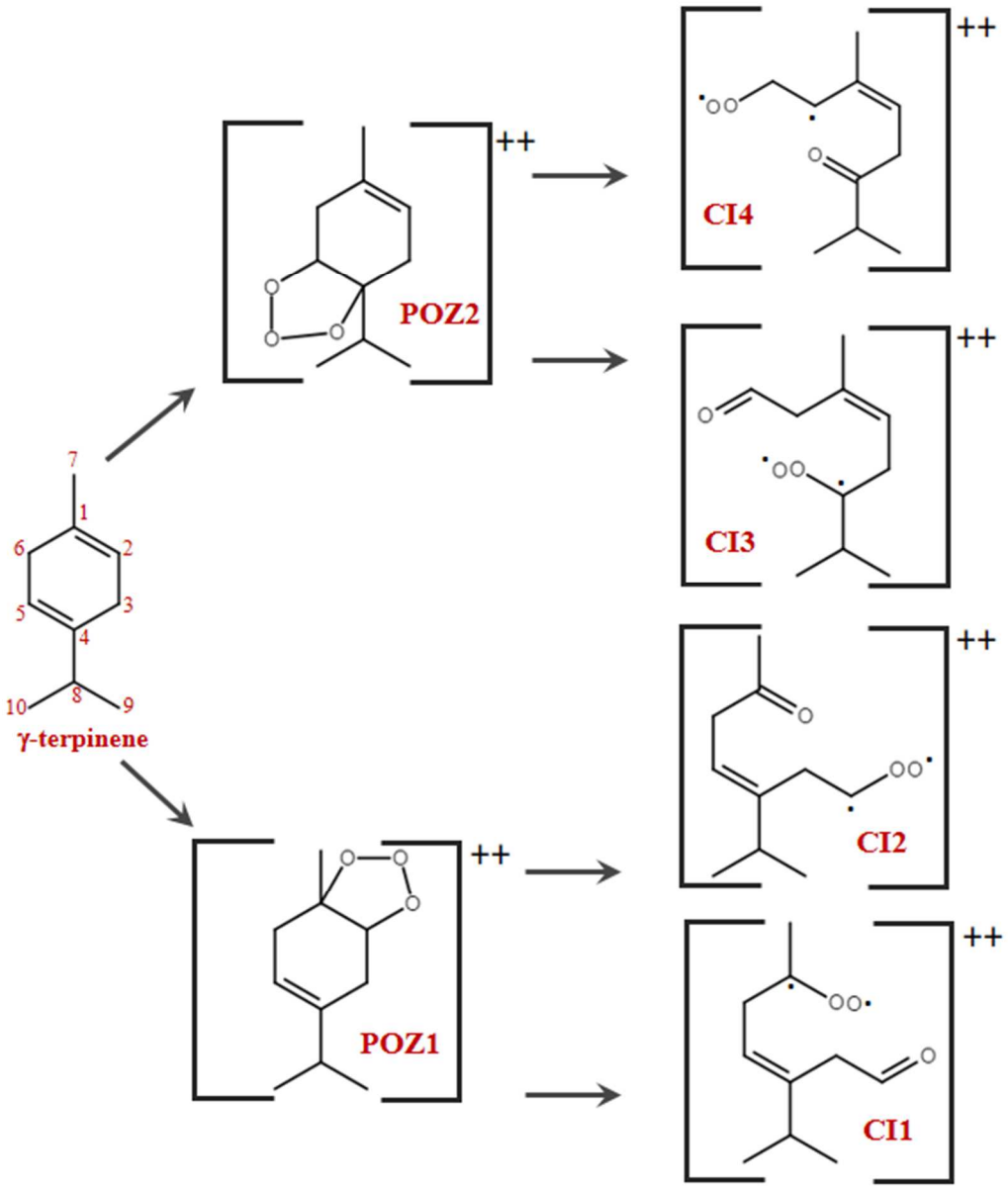


Fig. 6. The mechanism for the ozonolysis of γ-terpinene starting from CI1, and yielding different products detected by the PTR-ToF-MS. Comparable schematics for the remaining CIs are provided in the Supporting Information (Fig. S3-S5).

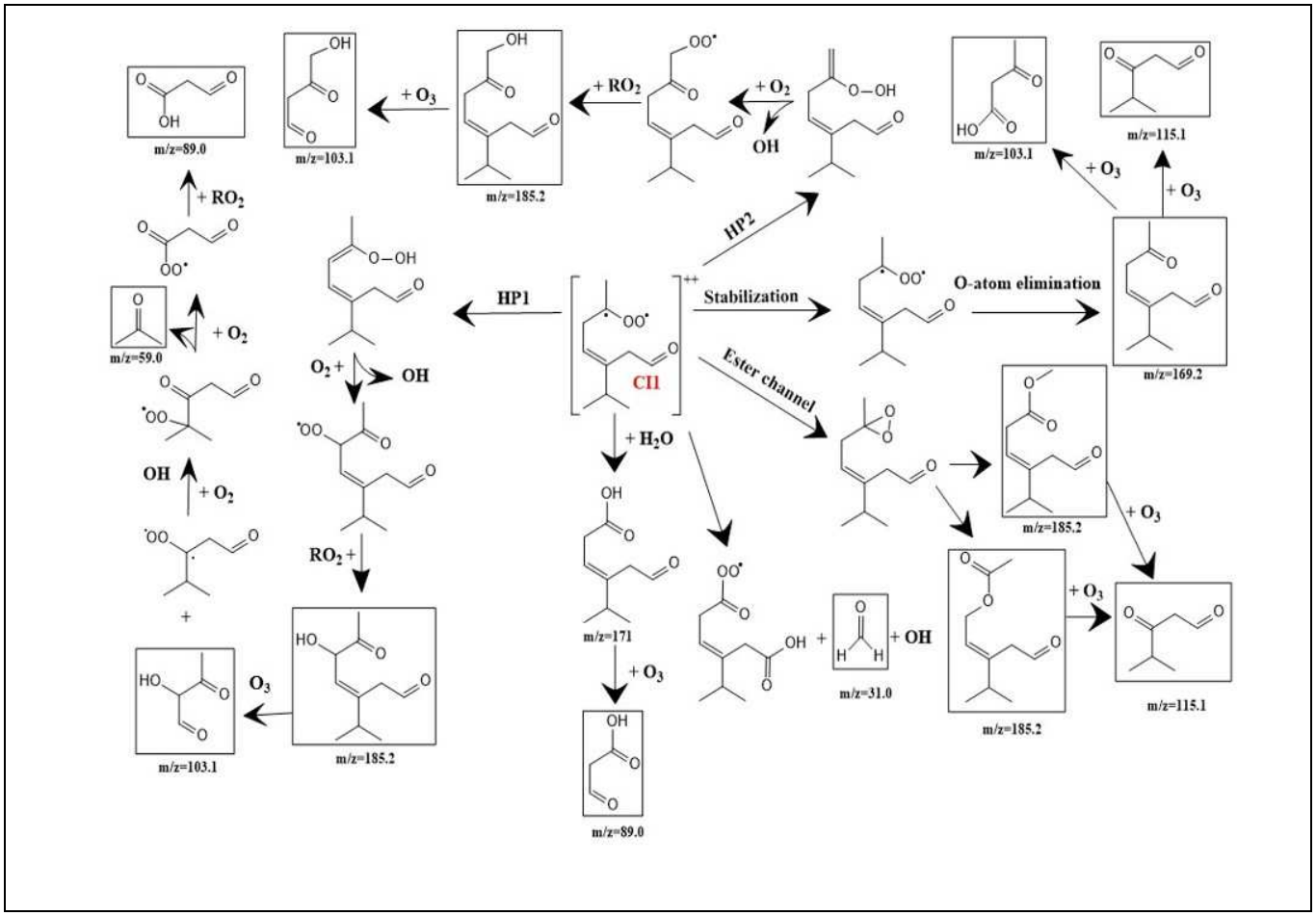
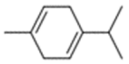


Table 1. Rate coefficient determined for the reaction of γ-terpinene with ozone at 294 ± 2K, atmospheric pressure and literature data.

Compound	Method	Reference	$k_{\gamma\text{-}t}/k_{ref}$[a]	$k_{\gamma\text{-}t}$[b] ($\times 10^{-16}$)	$k_{\gamma\text{-}t}$[b,c] ($\times 10^{-16}$)	$k_{\gamma\text{-}t}$[b,d] (average) ($\times 10^{-16}$)	Literature
γ-terpinene $C_{10}H_{16}$ 	Pseudo first order	-	-	2.03 ± 0.11[h]	2.17 ± 0.11	2.10 ± 0.11	This study
	Relative	2-methyl-2-butene[e]	0.53 ± 0.02	2.17 ± 0.08[a]			
		cis-2-pentene[f]	1.61 ± 0.06	2.13 ± 0.13[a]			
		α-pinene[g]	2.29 ± 0.14	2.23 ± 0.13[a]			
	Absolute	-	-	2.84	-	-	(Grimsrud, et al., 1974)
	Relative	α-pinene	-	1.63 ± 0.12[i]	-	-	(Atkinson et al., 1990)

[a] Indicated errors are twice the standard deviation arising from the linear regression analysis and do not include the uncertainty in the reference rate coefficients.

[b] Expressed in cm^3 $molecule^{-1}$ s^{-1}.

[c] Determined using plots based on eq V (see the text).

[d] Average rate coefficient for both methods.

[e] $k_{(2\text{-methyl-2-butene + O3})} = (4.1 \pm 0.5) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} (Witter et al. 2002).

[f] $k_{(cis\text{-}2\text{-pentene + O3})} = (1.32 \pm 0.04) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} (Avzianova and Ariya 2002) .

[g] $k_{(\alpha\text{-pinene + O3})} = (9.6 \pm 0.15) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, recommended value).

[h] Indicated errors include both the relative uncertainties on the determination of $k'_{\gamma\text{-}t}$ (twice the standard deviation arising from the linear regression analysis) and that on the measurement of the O_3 concentration (relative uncertainty = 5%).

[i] Recalculated using the current recommended value (IUPAC) for the α-pinene rate coefficient.

Table 2. Ions detected by the PTR-ToF-MS during the gas-phase reaction of γ-terpinene with ozone (m/z masses include the addition of H^+). Identification of the oxidation products and formation yields (the indicated ranges correspond to the values obtained from all experiments).

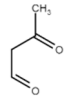
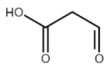
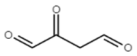
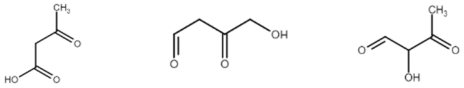
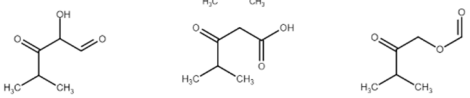
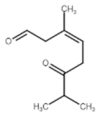
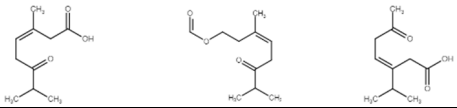
m/z	Formula	Name	Structure	Yield range (%)
31.0	CH_2OH^+	Formaldehyde		3 - 6
45.0	$C_2H_4OH^+$	Acetaldehyde		3 - 6
47.0	$CH_2O_2H^+$	Formic acid		7 - 11
59.0	$C_2H_2O_2H^+$	Glyoxal		4 - 9
	$C_3H_6OH^+$	Acetone		
61.0	$C_2H_4O_2H^+$	Acetic acid		5 - 9
73.0	$C_3H_4O_2H^+$	Unidentified		2 - 3
87.0	$C_4H_6O_2H^+$	3-oxobutanal		6 - 8
89.0	$C_3H_4O_3H^+$	3-oxopropanoic acid		2 - 4
101.0	$C_4H_4O_3H^+$	2-Oxosuccinaldehyde		< 1
103.1	$C_4H_6O_3H^+$	-		1 - 2
115.1	$C_6H_{10}O_2H^+$	4-methyl-3-oxo-pentanal		5 - 8
131.1	$C_6H_{10}O_3H^+$	-		1 - 2
141.1	Unidentified	-		< 1
155.2	Unidentified	-		< 1
167.0	Unidentified	-		< 1
169.2	$C_{10}H_{16}O_2H^+$	γ-terpinonaldehyde		< 1
183.0	Unidentified	-		< 1
185.2	$C_{10}H_{16}O_3H^+$	-		< 1

Table 3: Atmospheric life-time of γ-terpinene with different oxidants.

$\tau(OH)^a$	$\tau(NO_3)^b$	$\tau(O_3)^c$
49 min	2 min	32 min

[a]Assumed OH radical concentration: 2.0×10^6 molecules.cm^{-3}, 12-h daytime average (Atkinson and Arey, 2003) and calculated with $k_{(\gamma\text{-terpinene + OH})} = 1.7 \times 10^{-10}$ cm^3. molecule^{-1}.s^{-1} (IUPAC recommended value).

[b]Assumed NO_3 radical concentration: 2.5×10^8 molecules.cm^{-3}, 12-h nighttime average (Atkinson and Arey, 2003) and calculated with $k_{(\gamma\text{-terpinene + NO3})} = 2.9 \times 10^{-11}$ cm^3. molecule^{-1}.s^{-1} (IUPAC recommended value).

[c]Assumed O_3 concentration: 2.46×10^{12} molecules.cm^{-3} (100 ppbv), polluted atmosphere (Lin et al., 2001) and calculated with $k_{(\gamma\text{-terpinene + O3})} = (2.10 \pm 0.11) \times 10^{-16}$ cm^3. molecule^{-1}.s^{-1} (this study).