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Development and validation of a thermally regulated atmospheric simulation chamber (THALAMOS): A versatile tool to simulate atmospheric processes 3

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11

12

Abstract

13 Atmospheric simulation chambers, are unique tools for investigating atmospheric processes in the gas and heterogeneous phases. They can provide a controlled yet realistic environment that simulates 14 atmospheric conditions. In the current study, a Teflon atmospheric simulation chamber of 600 L, 15 16 named THALAMOS (thermally regulated atmospheric simulation chamber) has been developed and 17 cross-validated. THALAMOS can be operated over the temperature range 233 to 373 K under both 18 static and flow conditions. It is equipped with state of the art instrumentation (selective ion flow tube 19 mass spectrometry (SIFT-MS), long path Fourier transform infrared spectroscopy (FTIR), gas 20 chromatography mass spectrometry (GC-MS), various analyzers) for the inline monitoring of both 21 reactants and products. THALAMOS was validated by measuring the rate coefficients of well 22 documented reactions, i.e. the reaction of ethanol with OH radicals and the reaction of dichloromethane with Cl atoms, in a wide temperature range. Two different detection techniques were 23 used in parallel, FTIR and SIFT-MS, to internally cross-validate the obtained results. The measured 24 25 rate coefficients are in excellent agreement both between each other and with the literature recommended values. Furthermore, the gas phase oxidation of toluene by Cl atoms (kinetics and 26 product yields) was studied in the temperature range of 253 to 333 K. To the best of our knowledge, 27 28 THALAMOS is a unique facility on national level and among a few smog chambers internationally 29 that can be operated in such a wide temperature range providing the scientific community with a 30 versatile tool to simulate both outdoor and indoor physicochemical processes.

- 31 Keywords:
- 32 Thermostated simulation chamber
- 33 Gas phase kinetics
- 34 Cl initiated degradation of toluene
- 35 Benzaldehyde
- 36 -----
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Introduction

40 41

Air pollution is one of the major concerns of our society nowadays. The intense anthropogenic 42 activities related to combustion, industrialization, agriculture and livestock, release a wide variety of 43 44 pollutants in the atmosphere affecting air quality. Furthermore, in the context of climate change and 45 the anticipated global temperature change, as well as the increasing urbanization rate observed within the last 70 years (in 2015 around 80% of the population was living in urban areas in developed 46 47 countries (United Nations, 2018)), the effects on air quality have been a top priority issue in the 48 agenda of many countries. Therefore, a strong effort has been made by the atmospheric science 49 community through multidisciplinary actions involving laboratory, field and modeling studies aiming 50 to elucidate the important processes that lead to air pollution, to propose solutions and to make 51 predictions regarding the future Earth's climate.

52 Hence, the thorough study of chemical processes occurring during night time or daytime in the 53 atmosphere, is of great importance in order to (i) elucidate the fate of pollutants and investigate their 54 impact to the physicochemical properties of the atmosphere, e.g., formation of organic aerosols and 55 tropospheric O₃, stratospheric ozone depletion as well as to (ii) determine the lifetimes of pollutants and thus their impact on the future climate. However, the atmosphere is an open chemical reactor and 56 thus the direct control or isolation of chemical processes is challenging. Alternatively, in laboratory 57 scale the investigation of key atmospheric phenomena can occur inside Atmospheric Simulation 58 Chambers (ASC). ASC provide a controlled, yet realistic environment, aiming to simulating 59 60 atmospheric conditions without any meteorological or emissive influences that occur in real 61 atmosphere. Since the first ASC development (Akimoto et al., 1979; Leone et al., 1985) in the mid-62 1980s, several small to large-scale facilities have been developed worldwide aiming to study (i) gas phase reactions between the major atmospheric oxidants and both anthropogenic and biogenic volatile 63 64 organic compounds (VOCs), (ii) secondary organic aerosol (SOA) formation and (iii) nucleation 65 phenomena, and/or processes related with air-quality and climate. In Europe, most of these facilities 66 are integrated in the Eurochamp-2020 project and are accessible to the scientific community (Huang et 67 al., 2012).

Generally, there are two types of simulation chambers: indoor and outdoor. They are also present in a wide range of volumes and forms, and can be constructed by several materials including Teflon, Pyrex glass, stainless steel etc. However, till today, the majority of simulation chambers studies, especially the ones related to gas-phase chemistry, have been conducted close to ambient temperature and sea level pressure conditions. Atmospheric pressure and temperature though vary with the altitude. Particularly, temperature variation can strongly affect physicochemical phenomena (i.e. kinetics, reaction mechanism, nucleation processes, etc.) and plays a key role in several atmospheric studies.

75 Therefore, the objective of this study was to develop and validate an atmospheric simulation chamber, 76 named THALAMOS (thermally regulated atmospheric simulation chamber), that can be used as a 77 reference tool for temperature dependent studies simulating both outdoor and indoor environment. In 78 this paper, we introduce THALAMOS to the scientific community presenting a detailed description of 79 chambers' characteristics and capabilities. To the best of our knowledge, THALAMOS is the first ASC, in national level that allows temperature dependent studies, and one of very few facilities 80 globally, with such a wide accessible temperature range, 233 – 373 K that fully covers relevant to the 81 troposphere temperature range and can also be operated at higher temperatures either to study extreme 82 indoor conditions or to investigate reaction mechanism. Within this framework, a series of results that 83 84 demonstrate both THALAMOS validity as a versatile tool for temperature dependent kinetics and endproducts determination as well as the extent of its capabilities are presented herein. First, 85 THALAMOS was validated by measuring the kinetics of the well documented gas phase reactions of 86 87 OH radicals and Cl atoms with ethanol and dichloromethane (DCM), over a wide temperature range. Next, the Cl atoms rate coefficients for the gas phase reaction of Cl atoms with toluene were measured 88 89 and the reaction mechanism was investigated, as a function of temperature. Finally, the obtained results are discussed. Toluene is an aromatic compound mainly emitted by anthropogenic activities 90 91 and concentrations that can reach up to several hundreds of ppbV in outdoor (Hazrati et al., 2016) or 92 working indoor environments (Can et al., 2015).

93 1. Materials and methods

94 1.1 THALAMOS description and characteristics

95 THALAMOS is an indoor, atmospheric simulation chamber with a volume of 0.6 m³ (Fig. 1) that 96 consists of three main parts, (i) a climatic thermostatic cage (VT-4100, Vötsch industrietechnik, 97 Germany), (ii) a Teflon chamber of cuboid shape attached on an aluminum frame (see Fig. 1) and (iii) 98 multiple inline complementary detection techniques, such as Fourier transform infrared spectroscopy 99 (FTIR), selective ion flow tube mass spectrometry (SIFT-MS), and gas chromatography mass 100 spectrometry (GC-MS) that they are assembled externally to the Teflon-chamber. The thermostatic 101 cage (or climatic box) has an effective volume of 1200 L and the temperature can be regulated 102 between 231 and 453 K. The climatic box is equipped with a platinum temperature sensor (PT-100, 103 Pico technology, France) to measure the temperature and two fans to transfer and homogenize the 104 heated/cooled air in the thermostatic cage (Fig. 1). Fig. 2 displays the temperature change rate inside the climatic box illustrating the facility efficiency to achieve extreme cold or hot conditions in a 105 106 relatively short time window and to adequately simulate the relevant to the Troposphere conditions, in 107 a very well-controlled environment inside the Teflon-chamber.

108 The Teflon chamber volume was experimentally determined via absolute concentration measurement 109 of ethylbenzene by employing Beer-Lambert low and using in-line infrared spectroscopy. Particularly, 110 multiple titrated volumes of liquid ethyl-benzene ($C_6H_5CH_2CH_3$) were introduced via micro-syringe into the chamber, i.e., 0.1 - 0.5 mL, and the infrared (IR) spectra were recorded using 1 cm⁻¹ 111 resolution and 128 co-added scans. IR spectra were integrated between 2493 and 3492 cm⁻¹. Using an 112 integrated band strength of 3.36×10^{-17} cm²/(molecule cm), and a density of 0.8626 g/cm³ for ethyl-113 114 benzene, chamber volume was determined to be $601 \pm 6 L$ (Lide, 2005). A temperature and pressure 115 sensor were assorted in the center and back side of the Teflon chamber (see Fig. 1) and the gas mixture temperature/pressure were monitored in real-time. Both measurements were digitized and 116 117 recorded and stored in a lab computer for further analysis.

118 The Teflon chamber is also equipped with four fans to ensure (i) the temperature homogeneity of the 119 gas mixture and (ii) the efficient mixing of reagents. Particularly, the two fans are placed at the front and bottom-right side of the chamber, right after the inlet port and installed with a 45 degrees angle allowing the efficient transport of the injected compounds to the main body of the chamber. Two more fans are placed at the back and up-left side (**Fig. 1**). The temperature inside the thermostatic cage and the Teflon chamber were measured via two thermocouples and the readings comparison over a wide range are comparatively depicted in Appendix A **Fig. S1**. An excellent agreement - differences are lower than 1% in Kelvin scale, validating that the gas mixture in the Teflon chamber is effectively thermally-equilibrated throughout the reactor volume.

127 1.1.1 Admission and mixing of compounds

A multi-inlet port placed in the front and bottom-right side of the chamber was used for compounds
introduction (Fig. 1). Depending on the physical state and volatility of compounds, different injection
methods were applied.

131 (i) Injection of gas phase compounds

Gases are introduced in the chamber either using gas syringes or via controlled flow through massflow controllers.

134 (ii) Injection of liquid phase compounds

For the injection of liquid phase compounds two different methods were applied. In the first method, 135 136 liquid compounds were injected inside the chamber via a septum inlet using syringes, under a stream of zero-air. To facilitate the evaporation of the liquid, the introduction line was heated at 323 K by 137 138 using heating taped inlets to control the temperature. Nevertheless, to ensure complete vaporization of 139 the injected compounds, inlet-line's temperature can be increased up to 423 K, when needed, in the case of very low-volatile compounds. In the second method, gas mixtures of known concentrations 140 141 were prepared in zero air and injected using mass flow controllers. In particular, compounds in the liquid phase were transferred to a glass tube that could be thermostated. Then using gas handling 142 system equipped with Baratron pressure gauges compounds' were either collected in 10 L glass bulb 143 or to a 6 L Silonite canister (both were previously evacuated to a pressure of 10⁻³ mbar) and further 144 145 diluted to a total pressure of 1300 mbar for the glass bulb and 2070 mbar for Silonite canister using zero air as bath gas. The manometrically prepared mixtures were injected in the chamber using massflow controllers under zero air stream.

148 (iii) Mixing of compounds

Gas mixture homogenization inside THALAMOS, at 296 K, is achieved within ~1 min, but in general, it is also dependent on compound volatility, potent adsorption, hydrolysis or condensation onto chamber's surface and THALAMOS temperature. To ensure steady-state concentrations for all the species in the chamber, gas mixture was fan-mixed for, at least, 20 min before reaction's initiation, and the gas phase concentrations of the organic compounds were continuously monitored to warrant steady-state using the analytical instrumentation described below.

155 1.1.2 Bath gas and Teflon chamber cleaning

In the majority of the THALAMOS runs, zero air is being used as bath gas, generated from an oil-free 156 air-compressor, coupled with an inline water removal system. Then, zero air could be further purified 157 and is provided to the chamber under a regulated constant flow. Depending on the purification 158 process, two different zero air flows can be used. In the first case, the air produced is driven through a 159 zero air generator (AZ-2020, Claind, Italy) operated at 673 K to catalytically convert the organics 160 present in the air flow to CO₂. The exact relative humidity (RH) in the gas flow at room temperature, 161 162 293 K, was determined to be 2% using a temperature and relative humidity probe (HQ 210, Kimo, France) with an accuracy $\pm 1\%$ as stated by the manufacturer. Alternatively, the air flow from the 163 compressor is sent to a high purification system (zero-air generator equipped with a pressure swing 164 165 adsorption (PSA) device), where volatile organic compounds (VOCs), CO₂, CO and H₂O are removed. 166 The remaining impurity levels in the air stream are always lower than the analytical system detection limits: VOCs < 0.1 ppbV, CO₂ < 10 ppbV, CO < 80 ppbV and H₂O ~ 2 ppmV at 293 K. We estimate 167 that NOx and O₃ concentration levels in the chamber are below 50 and 500 pptV respectively 168 (detection limits of NO_x analyzer (T200 UP, Teledyne, USA) and ozone analyzer (APOA 370, Horiba, 169 170 France)). In addition, it is important to mention that when measurements in the presence of NO_x are carried out in THALAMOS, right after their completion the Teflon film of the chamber, the tubing's 171

and even the diaphragm in the Teflon pump are replaced to ensure that our system is clean and free ofany memory effects in the future experiments.

Prior to each experiment, THALAMOS is flushed-out for at least 2 hours, using a constant flow of zero-air, i.e., 20 L/min and a similar pumped-out rate. The cleaning process is necessary in order to avoid any side reaction or accumulation of different reactants inside the chamber or dead-volumes, eliminating memory effects during sequential experiments.

178 1.1.3 Light sources and radicals/atoms precursors and production

In order to induce photo-oxidation reactions, the thermostatic cage has been equipped with a light 179 irradiation system capable to host 20 lamps. More specifically, the attached broad-band emission light 180 181 sources are (i) 10 ultraviolet (UV) lamps emitting in the A region of electromagnetic spectrum, i.e. UV-A lamps (PL-L 24W/10/4P, Philips, Netherlands) with a maximum wavelength (λ_{max}) at 365 nm, 182 and (ii) 10 mercury lamps (HNS-L 24W 2G11, Osram, UK) emitting UV radiation in the C region of 183 the electromagnetic spectrum, i.e. UV-C lamps, with a λ_{max} at 254 nm. Therefore, THALAMOS can 184 be used to study any induced processes in the gas phase (e.g. photolysis of compounds of interest, or 185 cross section measurements) or involving heterogeneous phase (e.g., TiO_2 photocatalysis). It should be 186 noted that the heat released from the lamps (when switched on) does not impact the temperature inside 187 188 THALAMOS. In particular, the response of the climatic box to temperature variations has been settled 189 to a minimum of ± 1 K, which is feasible due to the high performance of our heating/cooling system. 190 Gas mixture temperature inside THALAMOS is maintained stable (±1 K) and any variations are 191 continuously monitored, both inside and outside the Teflon chamber, during the course of all the 192 photochemical experiments.

- 193 In the current study, UV-A lamps were used to generate Cl atoms via Cl₂ photolysis:
- 194 $Cl_2 + hv \rightarrow 2 Cl$
- 195 Similarly, the UV-C lamps were used to photolyze H₂O₂ and produce OH radicals via the reaction:
- 196 $H_2O_2 + hv \rightarrow 2 \bullet OH$ (2)
- 197 where *hv* corresponds to the light source photon-energy.

8

(1)

198 1.1.4 Reaction mixture sampling and detection techniques

A Restek Sulfinert-treated stainless steel tube was placed in the center and back-side of the chamber, 199 200 allowing the reaction mixture sampling off the chamber. Stable reactants and products were continuously monitored via coupling the chamber in series with several detection methods and 201 202 sensors, with the main ones to be (i) a SIFT-MS (Voice 200 ultra, Syft Technologies, New Zealand), (ii) a multipath FTIR (Antaris IGS, Thermo Scientific, France) with an optical path of 10 m and (iii) a 203 204 thermal desorption GC-MS (7890A, Agilent Technologies, France). The complementary detection 205 techniques provides with the advantage to identify a great variety of chemical species with high sensitivity and via cross-validation allow to minimize intrinsic uncertainties in temporal loss and 206 207 formation profiles measurements for reactants and products, respectively. Sample-out rate was adjusted in a case by case experiment, according to the analytical methods employed at each 208 209 measurement. Particularly, a recycling Teflon diaphragm pump, 4 L/min, is used to create a closed-210 loop between the chamber and the analytical instruments. In the case that solely SIFT-MS is used, reaction mixture was continuously sampled-out with a flow rate of 5 to 25 mL/min. Given that 211 212 experiments duration was less than two hours, a negligible gas-mixture volume was lost <0.5%, taking into account experimental uncertainties. FTIR optical cell is part of the closed-loop and thus does not 213 214 alter the gas volume. Finally, although it was not used in the present study, it is worth to note that GC-215 MS could be also used simultaneously in THALAMOS, since the amount of the required reaction 216 mixture for the analysis is insignificant (~200 mL/min), compared to THALAMOS volume. It is also 217 worth mentioning that in all cases results were cross-validated using simultaneously at least two 218 independent detection methods, and the required sampling did not result in any measurable alteration 219 of reactants concentrations, within the precision of the measurements.

The SIFT-MS is a tandem chemical ionization mass spectrometer based on the chemical ionization of the analytes. A microwave discharge is used for the simultaneous generation of three precursor ions, H_3O^+ , NO⁺ and O_2^+ , which are sequentially selected by a first quadrupole mass filter (Smith and Spanel, 2005; Spanel and Smith, 2013). Then, the precursor ions are injected inside a flow tube reactor operated at mTorr pressure using N₂, as carrier gas. At the same time, the sample is injected at the upstream-end of the reactor. The precursor ions react with the analytes along the flow tube to produce

new characteristic ionized molecules (Smith and Spanel, 2005; Spanel and Smith, 2013). It is worth 226 227 mentioning that both the sampling port and the flow tube of the instrument are heated to 393 K to 228 eliminate contaminations of the sampling line and wall reactions along the flow tube. Subsequently, 229 the gas flow passes through a pinhole orifice of 0.3 mm diameter, located at the downstream end of the flow tube reactor to create a molecular beam. The molecular beam enters a differentially-pumped high 230 231 vacuum chamber and both the precursor and reaction product-ions are focused, via electrostatic lenses, 232 into a second quadrupole mass spectrometer for mass analysis and ion counting for identification and 233 quantification, respectively. The mass spectrometer is internally calibrated on a daily basis, by flowing 234 a standard mixture of 9 compounds provided by the supplier. The internal calibration procedure and 235 the known reaction rate coefficients of the precursor ions with the analytes, allow estimating the 236 theoretical concentrations of any organic compound. Nevertheless, to obtain accurate concentration 237 measurements, the instrument was regularly calibrated by passing standards of the compounds of 238 interest. Although in kinetic measurements the absolute concentrations are not used, it is worth 239 mentioning that the difference between estimated theoretical concentrations and the ones determined 240 experimentally were in fairly reasonable agreement with the observed differences never being higher than 30%. Instrument's time resolution depends on the number of mass spectral peaks monitored, as 241 242 well as on the number of the averaging counts. For instance, the real time monitoring of 20 mass 243 spectral intensities with a limit of 10000 counts for each mass, time resolution was ca. 10 sec. Under 244 these conditions the detection limits for ethanol, dichloromethane and toluene were 1, 0.8, and 0.9 245 ppbV, respectively.

Complementary to the SIFT-MS, the reaction mixture was simultaneously analyzed employing an FTIR spectrometer equipped with a 10 m path length White-cell, with anti-reflected coated zinc selenide transmission windows. A liquid-N₂ cooled mercury cadmium telluride (MCT) detector was attached and 64 co-added IR spectra were recorded between 650 and 4000 cm⁻¹, with 1 cm⁻¹ resolution, using Result-3 software. Quantification and data processing was performed using a thermos scientific software, TQ-AnalystTM, and internally developed routines for kinetic analysis. The optical path was also experimentally calibrated using compounds with well-known IR cross-sections and it was determined to be 10 ± 0.1 m, that is in excellent agreement with manufacturer technical data. The detection limits for ethanol, dichloromethane and toluene were in the ppmV range (~ 1 ppmV).

255 Background IR spectra were collected before compounds injection in the chamber. Note that a Teflon 256 circulating pump was used in a closed loop to ensure gas phase mixture homogeneity between 257 chamber and FT-IR cell. After recording the background, reaction mixture was introduced in the 258 chamber left until it was well-mixed. Well-mixing was verified by recording sequential IR spectra. 259 The stabilization of the concentrations in the Teflon chamber was achieved after a few minutes and 260 was verified by observing stable. The reactants characteristic IR absorption bands reached a steady 261 absorbance (±1 %) within a few minutes and that was also cross-checked by monitoring the compounds concentration profiles using the SIFT-MS. 262

263 1.1.5 THALAMOS first-order losses

n-Pentane (C_5H_{12}) was used as probe molecule aiming to evaluate possible leaks of THALAMOS. In 264 265 this series of experiments, 30 ppmV of *n*-pentane was injected in the chamber and its temporal profile was monitored for several hours using the SIFT-MS. A typical plot, 293 K, is shown in Appendix A 266 Fig. S2. The first order loss of pentane was measured to be $\sim 10^{-6}$ sec⁻¹ and it is not expected to affect 267 the kinetic measurements. Similar tests were carried-out between 253 and 353 K leading to identical 268 269 results. However, since wall-loss and on surface hydrolysis is also an intrinsic variable of the compound used (volatility, functionality, chemical affinity, etc.), dark-loss tests were carried-out in a 270 case-by-case basis, before every experimental series runs. 271

272 1.2 Relative rate measurements

In this section THALAMOS validation approach is presented. Two well-studied gas phase reactions, i.e., OH radicals with ethanol (C_2H_5OH) and Cl atoms with dichloromethane (DCM, CH_2Cl_2), were studied between 253 and 363 K at 760 Torr, in the presence of zero air. Further, kinetics and endoxidation products for the reaction of Cl atoms with toluene (C_7H_8) were also determined. In all cases, the kinetic measurements were performed applying the relative rate method (RR).

In RR method the temporal loss of the under study compound (M) is measured relative to that of areference compound (REF) ensuring that the observed changes are solely due to their reaction with the

oxidant of interest X (X: OH, Cl, NO₃, O₃). RR method is a widely used method (Atkinson et al.,
2006; Burkholder et al., 2015) and the relative rate coefficient is derived by the expression (King,
2016):

283
$$\ln\left(\frac{[M]_0}{[M]_t}\right) = \frac{k_M}{k_{\text{REF}}} \ln\left(\frac{[\text{REF}]_0}{[\text{REF}]_t}\right)$$
(3)

where $[M]_0$, $[REF]_0$, $[M]_t$, and $[REF]_t$ are the initial concentrations of the compound of interest and that of the reference, at reaction time t = 0, and at discrete times (t) after reaction mixture irradiation and k_M and k_{REF} are the corresponding second order rate coefficients, respectively. A relative rate plot, $\ln([M]_0/[M]_t)$ versus $\ln([REF]_0/[REF]_t)$, should be linear, with a slope equal to rate coefficients ratio, k_M/k_{REF} , and a zero intercept. Therefore, the rate coefficient for the reaction of interest can be determined from the relative rate data fitting relative to the known rate coefficient of the reference reaction (k_{REF}) (King, 2016).

Dark loss and photolysis tests were always conducted before rate coefficient measurements to ensure that both reactants are only lost via the reaction with the reactive species, while reactants well-mixing was verified before irradiation. In all measurements presented herein, UV-A and UV-C lamps photolysis loss was negligible for all the compounds the study involves, within the time frame of the experiment, while no measurable dark loss were observed.

296

297 1.3 Experimental protocol

Prior to each relative rate experiment, the chamber was continuously flushed with zero air (cleaning 298 299 process). Next, the background concentrations of the compounds of interest were measured using all 300 the employed detection techniques. In kinetics determinations and at temperatures above 293 K, 301 reactants and radical precursors were introduced in the chamber once the desired chamber temperature 302 had been reached. At lower temperatures than 293 K the reaction mixture was introduced at room 303 temperature and then the desired temperature was set. Reactants concentration was monitored through the whole time until the final temperature adjustment of the chamber to ensure that no wall loss 304 processes were occurred. Two criteria need to be fulfilled before initiating the reaction: (i) the 305 306 temperature in the climatic box to be equal to ± 1 K with that of the gas mixture recorded inside the 307 Teflon chamber, and (ii) the concentration profiles of organic compounds to be stable. Then, the reaction is initiated by switching on the UV-A or UV-C lamps, which photolyzes the OH radicals or
Cl atoms precursors, respectively. Reactants consumption and products formation is then continuously
recorded, as a function of time.

311 1.4 Materials

All chemicals used in the current study are commercially available and listed in Appendix A **Table S1** along with their stated purities. The mass spectrometric ion peaks selected to monitor the concentration profiles of reference and target molecules are listed in **Table 1**.

315

316 2. Results and discussion

317 2.1 THALAMOS validation for kinetic measurements

In this section, OH radicals and Cl atoms kinetics for their reaction with ethanol and DCM, 318 respectively, are presented. There were multiple reasons for choosing the abovementioned reactions. 319 First, both reactions are of atmospheric interest; in particular, the study of atmospheric relevant 320 321 reactions initiated by OH radicals (the major tropospheric oxidant) and Cl atoms (important tropospheric oxidant in coastal and urban areas) is of significant importance in order to determine the 322 323 fate of pollutants in the atmosphere and thus their impact on air quality and climate change. Secondly, the rate coefficients of both reactions have been extensively studied and the kinetic data have been 324 evaluated by both International Union of Pure and Applied Chemistry (IUPAC) and the National 325 Aeronautics and Space Administration/Jet Propulsion Laboratory (NASA/JPL) Panels. Therefore, 326 327 these reactions were selected to evaluate THALAMOS reliability to measure relative rate coefficients 328 over a wide temperature range, 253 - 353 K and thus its capability to provide accurate kinetic data of 329 atmospheric relevant reactions.

330 2.1.1 OH radical reaction rate coefficients with ethanol

The gas phase reaction of OH radicals with ethanol has been the subject of interest for more than 3
decades (Campbell et al., 1976; Dillon et al., 2005; Greenhill and Ogrady, 1986; Jiménez et al., 2003;
Kovács et al., 2005; Nelson et al., 1990; Oh and Andino, 2001; Orkin et al., 2011; Overend and
Paraskevopoulos, 1978; Picquet et al., 1998; Ravishankara and Davis, 1978; Sørensen et al., 2002;

Wallington and Kurylo, 1987; Wayne and Tully, 1988; Wu et al., 2003). For the determination of the 335 bimolecular rate coefficient, both absolute and relative rate methods have been employed. Early 336 published data were in large disagreement between each other (Campbell et al., 1976; Greenhill and 337 338 Ogrady, 1986; Overend and Paraskevopoulos, 1978; Wallington and Kurylo, 1987; Wayne and Tully, 1988) with the problem to become even more intense between the temperature dependent kinetic 339 studies (Greenhill and Ogrady, 1986; Wallington and Kurylo, 1987; Wayne and Tully, 1988). 340 Nevertheless, the latest temperature dependent studies by Jimenez et al. (2003), Dillon et al. (2005) 341 342 and Orkin et al. (2011) are in excellent agreement. It is worth mentioning that, to the best of our 343 knowledge, all the temperature dependent studies have been carried out using absolute rate methods and thus the present work is the first temperature dependent study using relative rate methods. 344 Literature data have been reviewed by both NASA/JPL and IUPAC kinetics panels (Atkinson et al., 345 2006; Burkholder et al., 2015). In particular, IUPAC panel has adopted two different expression 346 depending on the temperature region of interest: $k(210 - 300 \text{ K}) = 3.2 \times 10^{-12} \exp(\frac{20}{T})$ 347 cm³/(molecule·sec) and $k(216 - 599 K) = 6.7 \times 10^{-18} T^2 \exp(\frac{511}{T}) \text{ cm}^3$ /(molecule·sec) (Atkinson 348 349 et al., 2006). On the other hand, NASA/JPL panel preferred values are based on the comprehensive absolute rate coefficient measurements at sub-ambient temperatures by Jiménez et al. (2003), Dillon et 350 351 al. (2005) and Orkin et al (2011). Therefore, a temperature independent reaction rate coefficient $(k(210 - 298 K) = 3.35 \times 10^{-12} \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ (Burkholder et al., 2015)) is recommended 352 between 210 and 298 K. 353

In the current study, the kinetics of OH reaction with ethanol were studied in THALAMOS within the temperature range of 263 to 353 K, using OH + *n*-pentane as reference reaction. The SIFT-MS was employed for the real time monitoring of ethanol and the reference compound using the mass peaks 45 (C₂H₅O⁺) and 42 (C₃H₆⁺) employing NO⁺ and O₂⁺ precursor ions chemistry, respectively (see also **Table 1**). The temperature dependent rate coefficients for the reference reaction have been adopted from the recent review study from Morin et al. (2015) and was $k_{(OH+n-pentane)} = 9.0 \times 10^{-17} \times$ $T^{1.8} \exp(\frac{120}{r}) \text{ cm}^3/(\text{molecule} \cdot \text{sec})$. The initial concentrations of ethanol and reference compound were

between 3 - 4.5 ppmV, while H₂O₂ was ranged between 90-500 ppmV. The summary of the 361 experimental conditions and the rate coefficients values obtained are given in Table 2. Typical relative 362 rate kinetic profiles are shown in Fig. 3, the NO⁺ and O_2^+ precursor ions were selected to monitor the 363 364 concentrations of ethanol and pentane respectively. The lines are linear least-squares fits of the data and the fit results are given in Table 2. The rate coefficient values determined in the current study, 365 along with the recommended literature values from IUPAC and NASA/JPL are depicted in Fig. 4. One 366 can notice an excellent agreement between the measured rate coefficients and the IUPAC and 367 368 NASA/JPL recommended values (±3%) within the entire temperature range experiments performed. Therefore, it is evidenced that THAMALOS is capable of determining the rate coefficient of OH 369 370 initiated reactions as a function of temperature.

371 2.1.2 Cl atoms reaction rate coefficients with DCM.

372 The rate coefficient for the reaction of Cl atoms with DCM has been widely studied and kinetic data are very well-established (Beichert et al., 1995; Bryukov et al., 2003; Catoire et al., 1996; Clyne and 373 374 Walker, 1973; Davis et al., 1970; Niki et al., 1980; Orlando, 1999; Sarzyński et al., 2011; Tschuikow-375 Roux et al., 1988). Both absolute and relative rate measurements have been carried out to determine 376 the temperature dependent rate coefficient (see Fig. 5). The reported data have been reviewed by 377 IUPAC and NASA/JPL kinetics evaluation panels and the recommended expressions are k (220 – 300 K = $5.9 \times 10^{-12} \exp(-\frac{850}{T}) \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ (IUPAC) and $k (273 - 790 \text{ K}) = 7.4 \times 10^{-12} \exp(-\frac{850}{T})$ 378 $10^{-12} \exp(-\frac{910}{T}) \text{ cm}^3/(\text{molecule} \cdot \text{sec}) (\text{NASA/JPL})$. 379

380 In the current study, the rate coefficient for the gas phase reaction of Cl atoms with DCM was 381 measured as a function of temperature using two reference compounds, i.e., methane (CH₄) ($k_{\text{(methane + })}$ $_{\text{Cl}} = 7.1 \times 10^{-12} \exp(-1270/T) \text{ cm}^3/(\text{molecule} \cdot \text{sec}), \text{ NASA/JPL recommended over 181-1550 K})$ 382 and acetone (CH₃C(O)CH₃) ($k_{(acetone + Cl)} = 1.63 \times 10^{-11} \exp(-\frac{610}{T})$ cm³/(molecule·sec), 383 recommended by NASA/JPL panel (Burkholder et al., 2015)). Furthermore, a series of experiments 384 were carried out at room temperature using 2,2,2-trifluoroethanol (CF₃CH₂OH) as reference, an 385 average value of $k_{\text{(trifluoroethanol + Cl)}} = 6.85 \pm 0.8 \times 10^{-13} \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ was calculated from 386 literature studies at 298 K (Garzón et al., 2010; Papadimitriou et al., 2003; Sellevåg et al., 2004) to 387

cross validate the rate coefficients measured using SIFT-MS and FTIR as detection techniques. The 388 SIFT-MS mass peaks used to monitor the reactants are summarized Table 1. FTIR kinetics analysis 389 390 was carried out employing the subtraction method in which the recorded spectra during reactions progress were subtracted from scaled to the initial compounds concentration reference spectra 391 recorded, separately, for each compound. In all the cases, multiple bands for DCM and CH₃C(O)CH₃ 392 or CF₃CH₂OH were monitored and it was ensured that the selected peaks were zeroed. Products 393 394 contribution was either subtracted, where possible, or taken into account in cases where interference 395 was intense and hard to resolve. Experiments at which differential IR spectroscopy was employed 396 were also carried out. In that case products appeared as positive peaks, while reactants as negative. 397 Differential analysis also led to indiscernible results. The experimental conditions and the rate coefficient values determined are given in Table 2. Typical relative rate profiles are presented in 398 399 Appendix A Fig. S3 and rate coefficients are summarized in the Arrhenius plot (Fig. 5). Kinetic results from the present study are in excellent agreement with the corresponding recommended 400 literature data from both IUPAC and NASA/JPL kinetics evaluation panels within 4%. 401

To conclude, in this section has been evidenced that THALAMOS is capable of measuring accurate gas phase rate coefficients of atmospheric relevant reactions as a function of temperature. To the best of our knowledge, on European level there is no other simulation chamber that has been used for gas phase kinetic studies in such a wide temperature range. Therefore, THALAMOS appears to be an innovative reference tool for temperature dependent investigation of atmospheric relevant processes extending and completing the capabilities of ASCs. Finally, we also present the kinetic and mechanistic investigation of Cl atoms initiated reaction with toluene, as a function of temperature.

409 2.2 Cl atoms reaction rate coefficients with toluene

In this section, temperature dependent Cl kinetics and reaction products with toluene, a common anthropogenic pollutant, are presented. Besides kinetics, product yields of benzaldehyde and benzyl alcohol - primary oxidation products - as a function of temperature were also determined, and a detailed mechanistic scheme is proposed.

414 2.2.1 Rate coefficient measurements

415 To the best of our knowledge, there are only room temperature kinetics studies for the reaction of Cl atoms with toluene in the literature (Atkinson and Aschmann, 1985; Fantechi et al., 1998; Markert and 416 417 Pagsberg, 1993; Noziere et al., 1994; Shi and Bernhard, 1997; Wallington et al., 1988). In this work, 418 the rate coefficients of the Cl reaction with toluene were determined between 253 and 333 K, at 1 atm 419 (zero air) employing relative rate methods. Cl reaction with ethane, methanol, and butanone were used 420 as references, and their temperature dependent rate coefficients were taken from IUPAC kinetic database (Atkinson et al., 2006), i.e., $k_{\text{(ethane + Cl)}} = 7.05 \times 10^{-11} \exp(-\frac{60}{T}) \text{ cm}^3/(\text{molecule·sec})$ 421 recommended over 180-330 K; $k_{\text{(methanol + Cl)}} = 7.10 \times 10^{-11} \exp(-\frac{75}{T}) \text{ cm}^3/(\text{molecule}\cdot\text{sec})$ 422 recommended over 200-500 K; $k_{\text{(butanone + Cl)}} = 3.05 \times 10^{-11} \exp(\frac{80}{T}) \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ recommended 423 over 200-450 K, where $k_{(M + CI)}$ is the rate coefficient of the Cl reaction with the compound M. 424 425 Reactants loss and stable products formation were monitored via SIFT-MS. In particular, toluene, methanol and butanone, were monitored using all the three precursor ions of the MS, i.e. H₃O⁺, NO⁺ 426 and O_2^+ , and the characteristic mass intensities of each compound are given in **Table 1**. Consequently, 427 the relative rate ratios were determined for each pair of precursor ions for toluene $(k_{toluene}^{precursor ion})$ and 428 the reference compound $(k_{\text{reference}}^{\text{precursor ion}})$ i.e., $k_{\text{toluene}}^{\text{H}_3\text{O}^+}/k_{\text{reference}}^{\text{N}_3\text{O}^+}$, $k_{\text{toluene}}^{\text{N}_2\text{O}^+}/k_{\text{reference}}^{\text{N}_2\text{O}^+}$ and $k_{\text{toluene}}^{\text{O}_2^+}/k_{\text{reference}}^{\text{O}_2^+}$ 429 $k_{\text{reference}}^{O_2^+}$, respectively. The reported relative rate ratio represents the averaged value of the ions' 430 precursor ratio. However, in the cases that ethane was used as reference $(k_{ethane}^{precursor ion})$ and due to the 431 low proton transfer affinity of the H₃O⁺ and NO⁺ (low detection sensitivity), only O₂⁺ precursor ion 432 433 was selected to monitor its concentration. Therefore, the relative rate ratios are given by the expressions $k_{\text{toluene}}^{\text{H}_3\text{O}^+}/k_{\text{ethane}}^{\text{O}_2^+}$, $k_{\text{toluene}}^{\text{NO}^+}/k_{\text{ethane}}^{\text{O}_2^+}$ and $k_{\text{toluene}}^{\text{O}_2^+}/k_{\text{ethane}}^{\text{O}_2^+}$, while the mean relative rate 434 coefficients were obtained by averaging the values of the aforementioned fractions. Table 3 435 436 summarizes the conditions that experiments carried out, the relative rate ratios and the obtained rate 437 coefficients at each temperature. Typical relative rate kinetic profiles at 293 K are presented in Fig. 6. 438 The lines are linear least-squares fits of the data and the fit results are given in **Table 3**. It should be 439 pinpointed that as shown in Fig. 6 a slight deviation from straight line fitting was observed, when

butanone was used as reference compound. This trend is a model-example that demonstrates vulnerability of RR methods when compounds or references might be involved in secondary processes (e.g photolysis, on-surface or gas phase hydrolysis, polymerization etc.). Therefore, although the measurements, in which butanone was used as reference, lead to reasonable kinetic results, within the measurements uncertainties, the number of the experiments were limited.

445 The results from this study are comparatively given in Fig. 7, along with the existing literature data. It 446 is evident that our room temperature values are in excellent agreement with the ones in the literature. Averaged rate coefficient at 295 ± 3 K was measured to be $(5.82 \pm 0.19) \times 10^{-11}$ cm³/(molecule sec). In 447 448 addition, no temperature dependence of the reaction rate coefficient was measured for the reaction of Cl atoms with toluene between 253 and 333 K, leading to a value (5.85 \pm 0.12) \times 10⁻¹¹ 449 cm³/(molecule sec). The latter suggests a complex reaction mechanism that proceeds via adduct 450 451 formation. Although no temperature dependent experimental data exist in the literature Huang et al. (2012) have theoretically studied the reaction using ab-initio calculations reporting a strong positive 452 453 temperature dependence of the rate coefficient in the range 298 - 1000 K. However, there are no data available at lower temperatures. The authors propose that the reaction mainly proceeds through -H 454 atom abstraction from the methyl group of toluene (Huang et al., 2012). 455

456 2.2.2 Product Study and proposed reaction mechanism

The mechanistic investigation and product analysis of the Cl atoms reaction with toluene was carried 457 458 out in the temperature range 273 - 333 K using SIFT-MS as detection technique. Benzaldehyde and benzyl alcohol were identified as primary degradation products. Traces of benzyl hydroperoxide were 459 also observed. The precursor ions and the mass spectral intensities used for the products detection with 460 the MS are given in Table 1. All products were quantified using MS that was calibrated by (i) flowing 461 a standard reference gas mixture, e. g., known concentration for each compound (toluene, 462 benzaldehyde and benzyl alcohol) or (ii) by injecting known amount of the compounds (in the liquid 463 or gas phase as mixture diluted in air as discussed in section admission and mixing of compounds) 464 465 inside THALAMOS and following their concentration with SIFT-MS. The second calibration method was applied in order to account for the impact of temperature on the calibration factor of the 466

compounds. It should be noted that at sub-ambient temperatures, benzyl alcohol was not calibrated, 467 since it was very lossy on the wall surfaces due to the low vapor pressure (<0.2 Torr at 293 K and ca. 468 469 1.6 Torr at 333 K). Therefore, the calibration factor determined at room temperature was used to 470 estimate the corresponding product-yields. The estimated error to the concentration measurements was ~7% for toluene and benzaldehyde, and ~15% for benzyl alcohol due to its sticky nature. Benzyl 471 hydroperoxide was not available and the MS calibration was not feasible. Therefore, the theoretical 472 473 concentrations included in the instrument's software were used instead. In addition, separate photolysis tests for benzaldehyde and benzyl alcohol in the chamber were carried out leading to 474 negligible photolysis rates ($k_{\text{phot}} \sim 10^{-5} \text{ sec}^{-1}$) in the temperature range 273 – 333 K. 475

476 Typical temporal profiles for toluene consumption and benzaldehyde and benzyl alcohol formation are presented in Appendix A Fig. S4, at 333 K. It is worth to note that although benzaldehyde was rapidly 477 478 produced, benzyl alcohol was appeared to be formed at delayed times when substantial toluene 479 consumption took place. This delayed production of Benzyl alcohol suggests either that benzyl alcohol is a secondary reaction product or/and, less importantly, delayed mixing due to its low volatility. In 480 order to further look into benzyl alcohol formation, separate measurements carried out, in which the 481 reaction mixture was irradiated for ~ 10 min and then lights were off until benzyl alcohol reach a 482 483 steady state. The above cycle was repeated several times, until toluene consumption due to its reaction 484 with Cl atoms to be at least 50%.

485 Furthermore, to complement and cross validate the results obtained with the MS, an experiment was 486 carried out at room temperature coupling the FTIR to the chamber. The concentrations of toluene and 487 molecular chlorine used were rather high, in the range of 55 ppmV each. Benzaldehyde and benzyl alcohol were also identified by FTIR. HCl was also observed to be formed. The reference spectra of 488 489 toluene and the formed organics were recorded in separate experiments after introducing a known 490 concentration of each compound in the FTIR cell. Toluene and benzaldehyde concentrations were determined using the well-established cross section values at 739.8 and 1731 cm⁻¹ for toluene and 491 492 benzaldehyde, respectively. Although benzyl alcohol was observed FTIR detection sensitivity was not 493 adequate to accurately measure its concentration. Toluene total loss was approximately 45%. Typical 494 IR spectra recorded during the reaction, as well as reference spectra of toluene, benzaldehyde and495 benzyl alcohol are given in Appendix A Fig. S5.

496 **Table 4** summarizes the experimental conditions and the yields of the major products in the 497 temperature range 273 - 333 K. The yield of the detected products (Y_{DP}) was determined as the ratio of 498 the product concentration formed to the concentration of toluene consumed during the course of the 499 reaction:

500
$$Y_{\rm DP} = \Delta [\text{product}] / \Delta [\text{toluene}]$$
 (3)

501 where Δ [product] correspond to the concentration of the product formed and Δ [toluene] the consumed 502 concentration of toluene.

It should be noted that product yields determination was based on the initial data of the photo-503 oxidation experiment, where Cl atoms are principally consumed by toluene and side reactions of the 504 505 products formed with Cl atoms are negligible compared to formation rate, within the experimental 506 uncertainties. Benzaldehyde was found to be the major product formed. Typical plots displaying the 507 consumption of toluene and the formation of benzaldehyde with the SIFT-MS and the FTIR are given 508 in Fig. 8. The total yield of benzaldehyde was independent of temperature with an average value of 509 0.80 ± 0.05 (Fig. 8). The yield of benzyl alcohol was measured to be ~0.11 at 293 K (Appendix A Fig. S6). At 273 K the yield of benzyl alcohol was decreased by a factor of 2 compared to the room 510 temperature value, but this might be an artifact of the system due to the high sticky efficiency and the 511 512 significantly decreased vapor pressure of the compound at lower temperatures. Regarding benzyl 513 hydroperoxide, an upper limit of 0.001 can be given based on the theoretical concentrations measured 514 with SIFT-MS.

There is a large disagreement between literature studies regarding the absolute yield of the products formed from the Cl initiated oxidation of toluene. Nozière et al. (1994) conducted experiments in a 140 L Pyrex reactor using relatively high concentrations of toluene (6-33 ppmV) and Cl₂ (132 ppmV), and they observed benzaldehyde, as the major product, with a yield of 0.41 \pm 0.04. The formation of benzyl alcohol, and benzyl hydroperoxide was also reported with yields 0.15 \pm 0.03 and 0.18 \pm 0.04, 520 respectively (Noziere et al., 1994). On the contrary, Fantechi et al. (1998) did not detect either benzyl alcohol or benzyl hydroperoxide. According to these authors, the major end-oxidation product was 521 benzaldehyde with a yield of 0.62 ± 0.30 . Wang et al. (2005), recently, reported product-yields for 522 benzaldehyde and benzyl alcohol of 0.84 ± 0.07 and 0.11 ± 0.02 , respectively. The benzyl 523 hydroperoxide formation was not included in Wang et al.'s analysis (Wang et al., 2005). However, 524 under their experimental conditions (i.e. atmospheric pressure and 296 K) benzyl hydroperoxide 525 526 concentration is expected to be very low, especially since the total products yield is almost unity (0.95 \pm 0.08). The product yields measured in the current study at 293 K for benzaldehyde and benzyl 527 alcohol are in excellent agreement with those of Wang et al. (2005). In addition, no temperature 528 dependence of the yields was observed. although the upper limit for benzyl hydroperoxide (0.001) is 529 significantly lower than the reported value by Nozière et al. (1994), it is in agreement with the 530 531 observations from Fantechi et al. (1998) and Wang et al. (2005). Although Wang et al. (2005) suggested that dark reactions in Nozière et al.'s system (1994) might be responsible for the observed 532 533 discrepancy, there are no evidence and the issue is currently unresolved (due to high initial 534 concentrations of toluene and Cl₂ used).

Taking into account that the major products formed from the Cl initiated oxidation of toluene 535 536 preserved the aromatic structure and that no chlorinated organic compounds were observed, it seems 537 that reaction proceeds via direct or indirect -H atom abstraction and not by addition of Cl to the 538 aromatic ring. The formation of HCl observed in our FTIR experiment, as well as in other studies (Fantechi et al., 1998) provide with further indications that enhance the latter statement's validity. 539 Further, a comparison between benzene ($k = 1.3 \times 10^{-15} \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ at 295 K (Shi and 540 Bernhard, 1997) or $< 5.0 \times 10^{-16}$ (Noziere et al., 1994)) and toluene determined in this work (k = 5.82541 $\times 10^{-11}$ cm³/(molecule sec) at 298 K) was conducted, and reactivity towards Cl atoms reveals that 542 543 association mechanism is a highly unlikely reaction pathway and the replacement of one hydrogen 544 with a methyl group drastically increases toluene's reactivity, since -CH₃ hydrogen metathesis does 545 not affect ring's aromaticity. However, it is worth to mention that in order to further investigate if the hydrogen metathesis proceeds via adduct formation in a stepwise process or via direct abstraction 546

quantomechanical molecular calculations could be of use, although it was beyond the scope of the present study. Theoretical calculations performed by Huang et al. (2012) also support the experimental observations. In particular, it is proposed that the -H atom is mainly abstracted from the -CH₃ group of toluene, while the rest of the potent -H atom elimination sites, such as ortho, meta and para positions have a negligible contribution if any. The latter is also consistent with previously reported experimental studies (Fantechi et al., 1998; Markert and Pagsberg, 1993; Wang et al., 2005). Thus in **Fig. 9**, a mechanistic scheme is proposed for the oxidation of toluene from Cl atoms.

Assuming that toluene is mainly removed from the atmosphere via the gas phase reactions with OH radicals and Cl atoms, and reactions with O_3 and NO_3 are expected to be negligible, the atmospheric lifetime (τ_x , where x is the corresponding oxidant) can be estimated using the expressions:

557
$$\tau_{\rm OH} = \frac{1}{k_{\rm OH} \times [\rm OH]} \tag{4}$$

558 and

559
$$\tau_{\rm Cl} = \frac{1}{k_{\rm Cl} \times [\rm Cl]} \tag{5}$$

560 where k_{OH} and k_{Cl} are the bimolecular rate coefficients for the corresponding reactions of toluene with OH radicals (i.e. 6.12×10^{-12} cm³/(molecule sec) at 300 K) and Cl atoms (i.e. 5.82×10^{-11} 561 562 $cm^{3}/(molecule \cdot sec)$ at 295 ± 3 K average value of all studies) and [OH] and [CI] are the diurnally averaged concentrations of OH radicals and Cl atoms in the environment of reference. Assuming an 563 564 average tropospheric concentration of OH, i.e. 2×10^6 radical/cm³ and an average boundary layer concentration of Cl, i.e. 10⁴ atom/cm³ respectively, (Hein et al., 1997), OH radicals are expected to be 565 the dominant sink, leading to an estimated lifetime of about one day (1 day). In urban and coastal 566 areas though, where Cl atoms abundance is significant higher (Spicer et al., 1998), Cl chemistry will 567 568 substantially reduce the globally averaged lifetime of toluene, even locally, in the troposphere (Table 5), which might be important for such short-lived compounds. On the contrary, in indoor 569 environments where OH radical concentrations are significant lower, e.g., 10⁴ to 10⁵ molecule/cm³ 570

571 (Carslaw, 2007; Sarwar et al., 2002) and Cl levels substantially increased due to the use of Cl572 containing cleaning products and other indoor materials, Cl atoms might dominate over OH radicals.

573

574 3. Conclusions

575

576 In the current study, we present a recently designed and developed photochemical chamber, THALAMOS, with a wide temperature range thermostatic ability, 233 - 373 K. THALAMOS is 577 equipped with in-line FTIR, SIFT-MS and GC-MS complementary detection techniques that allow 578 internal cross-validation of various type of quantitative measurements, such as kinetics and product 579 580 yields studies. A detailed description of the facility, the instrumentation and the characterization of the 581 conditions has been realized. The first kinetic results employing relative rate methods obtained during 582 THALAMOS validation are also presented. Applying the relative rate method, and studying the 583 temperature dependence of two well documented reactions it was evident that THALAMOS is capable 584 of producing highly precise and accurate temperature kinetic data for atmospheric relevant OH and Cl 585 reactions. Furthermore, the kinetics and the mechanism for the Cl reaction with toluene was studied 586 within a wide temperature range. The kinetic measurements carried out in THALAMOS revealed that the degradation of toluene from Cl atoms is important in coastal areas and/or indoor environments. 587 Benzaldehyde and benzyl alcohol were identified as the major Cl initiated end-oxidation products and 588 589 the yields were measured to be 0.80 ± 0.05 and 0.11 ± 0.04 , respectively. The present results are in excellent agreement with the ones from Wang et al.⁴³ THALAMOS is oriented to be a unique tool for 590 591 temperature dependent studies in the gas or heterogeneous phases, targeted to elucidate the impact of 592 temperature to secondary organic aerosol formation, as well as to simulate extreme temperatures and 593 humidity conditions (i.e. $T > 25^{\circ}$ C, RH > 60%, typical for Southern countries). The latter aims to test 594 the efficiency of depolluting materials and to assist in sensors calibrations under extreme indoor or 595 outdoor conditions.

596

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Table 1 Mass spectral ions intensities selected to monitor the concentration profiles of the compounds used in the current study.

Compound	Product ions used monitored	Mass to charge ratio (<i>m/z</i>)	Precursor ion
Ethanol	$C_2H_5O^+$	45	NO ⁺
<i>n</i> -Pentane	$C_{3}H_{6}^{+}$	42	O_2^+
Dichloromethane (DCM)	CH(³⁵ Cl) (³⁵ Cl) ⁺	83	NO ⁺
Acetone	$C_3H_6O^+$	58	O_2^+
2,2,2-Trifluoroethanol	[CF ₃ CH ₂ OH]H ⁺	101	H ₃ O ⁺
Methane	$CH_3O_2^+$	47	O_2^+
	$C_7H_8H^+$	93	H_3O^+
Toluene	$C_7H_8^+$	92	NO^+
	$C_7H_8^+$	92	O_2^+
Ethane	$C_2H_4^+$	28	O_2^+
	CH ₅ O ⁺	33	H_3O^+
Methanol	NO ⁺ CH ₃ OH	62	NO ⁺
	CH ₃ O ⁺	31	O_2^+
	$C_4H_9O^+$	73	H_3O^+
Butanone	NO ⁺ C ₄ H ₈ O	102	NO ⁺
	$C_4H_8O^+$	72	O_2^+
	C ₇ H ₇ O ⁺	107	H ₃ O ⁺
Benzaldehyde	$C_7H_5O^+$	105	NO ⁺
	$C_7H_5O^+$	105	O_2^+
	C ₇ H ₇ +	91	H ₃ O ⁺
Benzyl alcohol	C ₇ H ₈ O ⁺	108	NO ⁺
	C ₇ H ₈ O ⁺	108	O ₂ +
	$C_7H_8O_2^+$	124	H ₃ O ⁺
Benzyl hydroperoxide	$NO^{+}C_{7}H_{8}O_{2}^{+}$	154	NO ⁺

$C_2H_5OH + OH$									
$T(\mathbf{K})$	[Ethanol] ₀	[Pentane] ₀ (ppmV)	$[H_2O_2]_0$	$k_{\rm ethanol}/k_{\rm pentane}^{\rm a}$	$k (\times 10^{-12})$				
	(ppmV)		(ppmV)		cm ³ /(molecul				
					$e \cdot sec))^b$				
263	3.1	3.0	300	1.04 ± 0.01	3.35±0.03				
278	3.2	3.0	90	0.97±0.01	3.37±0.03				
	3.5	3.4	250	0.93±0.01					
293	3.4	3.5	380	0.91±0.01	3.40±0.04				
	3.6	3.6	95	0.89±0.01					
313	3.7	3.7	90	0.85±0.01	3.48±0.04				
333	4.0	3.9	450	0.81±0.01	3.63±0.04				
353	4.2	4.1	500	0.77±0.01	3.75 ± 0.05				
		CH	$_{2}Cl_{2} + Cl$						
Reference: me 181-1550 K	ethane. $k_{(methane)}$	$_{+ Cl} = 7.1 \times 10^{-12} \exp($	(-1270/T)	$cm^3/(molecule \cdot sec)$, JPL recon	mmended over				
$T(\mathbf{K})$	$[DCM]_0$	[Methane] ₀ (ppmV)	$[Cl_2]_0$	$k_{\rm DCM}/k_{\rm methane}^{\rm a}$	<i>k</i> (×10 ⁻¹³				
	(ppmV)		(ppmV)		cm ³ /(molecul				
					$e \cdot sec))^b$				
258	2.8	21	80	4.16±0.05	2.15±0.03				
270	2.9	16.6	61	3.81±0.02	2.45±0.02				
208	3.8	18.1	36	3.48±0.02	2 40+0 02				
298	3.2	20.8	40	3.50±0.02	5.49±0.02				
323	3.4	20	48	3.16±0.02	4.36±0.03				
Reference: ad	cetone. $k_{(acetone + acetone + bcetone)}$	$_{\rm + Cl)} = 1.63 \times 10^{-11} \exp 210^{-11}$	(-610/ <i>T</i>))-440 K	cm ³ /(molecule⋅sec), JPL recor	nmended over				
$T(\mathbf{K})$	$[DCM]_0$	[Acetone] ₀ (ppmV)	$[Cl_2]_0$	$k_{\rm DCM}/k_{\rm acetone}^{\rm a}$	$k (\times 10^{-13})$				
	(ppmV)		(ppmV)		cm ³ /(molecul				
					$e \cdot sec))^b$				
253	2.7	1.0	56	0.15±0.01	2.22±0.14				
273	2.9	1.0	34	0.16±0.01	2.72±0.17				
298	3.2	1.1	6.3	0.18±0.01	3.79±0.21				
298	1.9	0.6	7.4	0.17±0.01	3.57±0.21				
323	3.4	1.2	8.0	0.19±0.01	4.68±0.24				
353	2.28	0.7	17	0.19±0.01	6.08±0.28				
Reference: 2,2,2-trifluoroethanol. $k_{\text{(trifluoroethanol + Cl)}} = (6.85 \pm 0.8) \times 10^{-13} \text{ cm}^3/(\text{molecule} \cdot \text{sec})$ at 298 K									
$T(\mathbf{K})$	$[DCM]_0$	[Trifluoroethanol] ₀	$[Cl_2]_0$	$k_{\rm DCM}/k_{\rm trifluoroethanol}^{\rm a}$	$k (10^{-13})^{b}$				
	(ppmV)	(ppmV)	(ppmV)						
298	2.1	1.1	6.0	0.52±0.01	3.56±0.07				
298	1.1	0.7	5.0	0.51±0.01	3.49±0.07				
298 (FTIR)	15	15	88	0.49±0.02	3.35±0.14				

Table 2 Experimental conditions and kinetics results for the gas phase reaction of OH radicals with ethanol and Cl atoms with DCM.

 $^{\rm a}$ Errors represent the 2σ precision from the least-squares fits and do not include systematic uncertainties.

 b Errors reflects the 2σ precision of the relative rate ratio measurements and do not include any systematic uncertainty.

[M]₀: initial concentration of the compound M; *T*: temperature; $k_{\text{ethanol}} / k_{\text{pentane}}$: the experimentally determined relative rate coefficient ratios of the ethanol and the reference compound; $k_{\text{DCM}} / k_{\text{methane}}$, $k_{\text{DCM}} / k_{\text{acetone}}$, and $k_{\text{DCM}} / k_{\text{trifluoroethanol}}$: the experimentally determined relative rate coefficient ratios of

DCM and the three reference compounds used (i.e. methane, acetone, trifluoroethanol), respectively; $k_{(methane + Cl)}$, $k_{(acetone + Cl)}$, and $k_{(trifluoroethanol + Cl)}$: the rate coefficients of methane, acetone and trifluoroethanol with Cl atoms as proposed in literature; k: is the final value of the rate coefficient of the compound of interest; NASA/JPL: National Aeronautics and Space Administration/Jet Propulsion Laboratory.

Refere	Reference: Ethane. $k_{\text{(ethane + CI)}} = 7.05 \times 10^{-11} \exp(-60/T)$, IUPAC recommended over 180-330 K								
<i>T</i> (K)	[Toluene] ₀ (ppmV)	[Ethane] ₀ (ppmV)	[Cl ₂] ₀ (ppmV)	$k_{ m toluene}^{ m H_3O^+}/k_{ m ethane}^{ m O_2^+}$ "	$k_{ m toluene}^{ m NO^+}/k_{ m ethane}^{ m O_2^+}$ a	$k_{ m toluene}^{ m O_2^+}/k_{ m ethane}^{ m O_2^+}$ a	Variation ^b	$k_{ m toluene}/k_{ m ethane}$ of all ions °	$k (\times 10^{-11} \text{ cm}^3/(\text{molecule} \cdot \text{sec}))^c$
253	3.3	3.3	22	1.14±0.08	1.16±0.08	1.19±0.04	4%	1.16±0.03	6.45±0.17
273	3.6	3.6	20	1.00 ± 0.01	1.00 ± 0.01	0.98±0.01	2%	0.99±0.01	5.60±0.06
293	3.8	3.8	15	1.02±0.02	1.01±0.01	1.03±0.01	2%	1.02±0.01	5 86+0 06
293	5.6	5.6	15	1.03±0.02	1.01±0.01	1.02±0.01	2%	1.02±0.01	5.80±0.00
313	4.1	4.1	11	0.98±0.02	1.00 ± 0.02	1.02±0.01	4%	1.00 ± 0.02	5.82±0.12
333	4.3	4.3	17	0.99±0.04	1.00 ± 0.04	0.99 ± 0.02	1%	1.00 ± 0.01	5.89±0.06
Refere	nce: Methanol	$k_{(\text{methanol} + \text{Cl})} = 7$	1.10×10^{-11}	$^{1} \exp(-75/T)$, IUPAC rec	ommended over 200-50	0 K			
<i>T</i> (K)	[Toluene] ₀ (ppmV)	[Methanol] ₀ (ppmV)	[Cl ₂] ₀ (ppmV)	$k_{ m toluene}^{ m H_3O^+}/k_{ m methanol}^{ m H_3O^+}$ "	$k_{ m toluene}^{ m NO^+}/k_{ m methanol}^{ m NO^+}$ ^a	$k_{\text{toluene}}^{\text{O}_2^+} / k_{\text{methanol}}^{\text{O}_2^+}$	Variation	k _{toluene} /k _{methanol} of all ions [°]	$k (\times 10^{-11} \text{ cm}^3/(\text{molecule} \cdot \text{sec}))^{\circ}$
253	3.4	3.4	33	1.02±0.01	0.97±0.01	1.08 ± 0.02	10%	1.02±0.06	5.38±0.32
268	3.3	4.1	17	1.20±0.01	1.07 ± 0.02	1.18±0.01	11%	1.15±0.07	6.17±0.38
278	1.7	1.8	10	1.11±0.01	0.97±0.02	1.12±0.01	13%	1.07 ± 0.08	5 80+0 43
278	3.5	4.5	20	1.06±0.01	1.04±0.02	1.10±0.01	5%	1.07±0.03	5.80±0.43
293	1.9	2.0	11	1.08 ± 0.01	0.96 ± 0.02	1.07 ± 0.01	11%	1.04 ± 0.07	5.72±0.38
333	2.1	2.2	12	0.99±0.01	0.95±0.02	1.05 ± 0.01	10%	1.00 ± 0.05	5.68±0.28
Refere	nce: Butanone	$k_{(butanone + Cl)} = 3$	$.05 \times 10^{-11}$	exp(80/T), IUPAC reco	ommended over 200-450	K			
<i>T</i> (K)	[Toluene] ₀ (ppmV)	[Butanone] ₀ (ppmV)	[Cl ₂] ₀ (ppmV)	$k_{\text{toluene}}^{\text{H}_3\text{O}^+}/k_{\text{butanone}}^{\text{H}_3\text{O}^+}$ ^a	$k_{ m toluene}^{ m NO^+}/k_{ m butanone}^{ m NO^+}$ ^a	$k_{ m toluene}^{ m O_2^+}/ \ k_{ m butanone}^{ m O_2^+}$ "	Variation	$k_{ m toluene}/k_{ m butanone}$ of all ions °	$k (\times 10^{-11} \text{ cm}^3/(\text{molecule} \cdot \text{sec}))^c$
293	1.9	1.8	11	1.58±0.10	1.45 ± 0.06	1.46 ± 0.08	8%	1.50 ± 0.07	6 22±0 21
293	1.9	1.8	11	1.72±0.06	1.60±0.04	1.51±0.04	12%	1.61±0.10	0.22±0.31
313	1.8	1.9	7.0	1.52±0.02	1.51±0.04	1.27 ± 0.02	16%	1.43±0.14	5.63±0.55
Average $k (\pm 2\sigma)$ over the temperature range 258-333 K								5.85 ± 0.15^{d}	

Table 3 Summary of the experimental conditions and rate coefficients obtained in this work for the gas phase reaction of toluene with Cl atoms.

^a Errors represent the 2σ fit precision and do not include systematic uncertainties ^b Variation denotes the difference between the highest and the lowest relative rate ratios of the compound of interest and the reference, $k_{\text{toluene}}/k_{\text{reference}}$, values between the different precursor ions.

 $^{\circ}$ Uncertainties quoted to the mean values are the 2σ standard deviations.

^d Quoted uncertainty is the 2 σ precision of the average value obtained from the linear fit of all measurements (see **Fig. 7**). The relative rate ratios determined for each pair of precursor ions (H₃O⁺, NO⁺ and O₂⁺) for toluene ($k_{\text{toluene}}^{\text{precursor ion}}$) and the reference compound ($k_{\text{reference}}^{\text{precursor ion}}$) are given in the table as $k_{\text{toluene}}^{\text{H}_3\text{O}^+}/k_{\text{reference}}^{\text{NO}^+}$, $k_{\text{toluene}}^{\text{NO}^+}/k_{\text{reference}}^{\text{NO}^+}$, and $k_{\text{toluene}}^{O_2^+}/k_{\text{reference}}^{O_2^+}$. The reported relative rate ratio represents the averaged value of the ions' precursor ratio.

			Benzaldehyde				Benzyl alcohol				
<i>T</i> (K)	[Toluene] ₀ (ppmV)	(ppmV)	$\begin{array}{c} \text{Yield}^{\text{H}_3\text{O}^+}\\ (\%)^{\text{a}} \end{array}$	Yield ^{NO+} (%) ^a	$\begin{array}{c} \text{Yield}^{O_2^+} \\ (\%)^{a} \end{array}$	Average yield of all ions (%)	Yield FTIR (%) ^a	$\begin{array}{c} \text{Yield}^{\text{H}_3\text{O}^+} \\ (\%)^{\text{a}} \end{array}$	Yield ^{NO+} (%) ^a	Yield ^{O⁺₂} (%) ^a	Average yield of all ions (%) ^b
273	4.0	10.0	82±8	72 ± 7	80±8	78±5	nd ^b	5±1	4±1	6±1	5±1
293	4.0	10.0	88±9	90±9	84±8	87±3	nd	9±2	9±2	10±2	10±2
293	4.0	7.0	78±8	73±7	83±8	78±5	nu	11±2	11 ± 2	13±3	12±3
293	12.0	22.0	72±7	70±7	75±8	72±3		nd	nd	nd	nd
293	52.0	55.0	85±8	82±8	92±9	86±5	75±7	17±3	17±3	12±2	16±3
333	3.0	11.0	85±8	74±7	86±8	82±7	nd	13±3	11 ± 2	14±3	13±2
333	3.0	9.0	90±9	85±8	82±8	86±4		10±2	12 ± 2	14±3	12 ± 2
Total yield (independent on <i>T</i>)				80±	5 ^b				11±4 ^b		

Table 4 Summary of experimental conditions and product yields for the gas phase reaction of toluene with Cl atoms.

^a Errors represent the 2σ fit precision and includes the uncertainty to concentrations determination

^b Uncertainties quoted to the mean values are the standard deviation.

nd: not determined; Yield^{H₃O⁺}, Yield^{NO⁺} and Yield^{O⁺₂}: the yield of the products formed deploying selective ion flow tube mass spectrometry (SIFT-MS) for each of the precursor ions H₃O⁺, NO⁺ and O₂⁺; Average yield of all ions: the average yield of each product formation using SIFT-MS; Yield FTIR: the yield of benzaldehyde demined deploying Fourier transformed infrared spectroscopy (FTIR).

Table 5 Toluene atmospheric lifetime include both OH and Cl initiated tropospheric oxidation.

	Scenario 1		Scenario 2			
τ _{OH}	τ_{Cl} (hours)	$\tau_{eff} (hours)$	τ_{OH} (hours)	τ_{Cl} (hours)	$\tau_{eff} (hours)$	
(hours)						
22.7	955	22.2	22.7	47.7	15.4	

Two different scenarios with regard the globally averaged diurnal OH radicals and Cl atoms concentrations have been employed. OH levels remained stable in both cases [OH] 2×10^6 radical/cm³, while the extremes of diurnally averaged Cl concentration levels were used to include both free troposphere (Scenario 1: [Cl] 5×10^3 atom/cm³) and local characteristics of urban and/or coastal environment (Scenario 2: [Cl] 1×10^5 atom/cm³).

 τ_{OH} , and τ_{CI} : toluene atmospheric lifetime due to its degradation by OH radicals and Cl atoms respectively; τ_{eff} : the effective lifetime of toluene.

Figures



Fig. 1 General description of THALAMOS (thermally regulated atmospheric simulation chamber) facility. UV: ultraviolet; FTIR: Fourier transformed infrared spectroscopy; GC-MS: gas chromatography mass spectrometry; SIFT-MS: selective ion flow tube mass spectrometry.





Fig. 2 Temperature (T) dynamic in the climatic box determined under heating and cooling experiments. The arrows placed at the beginning of each curve aim to display the corresponding process followed to determine the temperature change rate. t: time.





Fig. 3 Relative rate data for the reaction of OH + ethanol using pentane as reference molecule at 263, 293, 333 and 353 K respectively. For clarity, the experimental measurements are shifted up on the *y* axis by 0.4 for 293 K, 0.8 for 333 K and 1.2 for 353 K. [ethanol]₀, [pentane]₀, [ethanol]*t*, [pentane]_t are the initial concentrations of the compound of interest (ethanol) and that of the reference (pentane), with no OH radicals present (light-sources off), at t = 0 and at discrete reaction times *t*, respectively.

Fig. 4.

T (K)



Fig. 4 Arrhenius plot for the OH + ethanol reaction. In comparison with the measurements of the current study, are displayed the literature results determined with absolute methods (AR) and relative rate methods (RR) as well as the International Union of Pure and Applied Chemistry (IUPAC) and the National Aeronautics and Space Administration/Jet Propulsion Laboratory (NASA/JPL) recommended values. For clarity purposes, the uncertainties on literature results are not given; only the 2σ precision of the measurements (<2%) of the current study are displayed.





Fig. 5 Arrhenius plot for the reaction of Cl atoms with DCM. For clarity purposes the NASA/JPL recommended values above 400 K are not displayed.





Fig. 6 Example of relative rate plots for the Cl + toluene reaction obtained at 293 K using the reference compounds labeled on the graph. For the relative rate data displayed, the H_3O^+ precursor ion of the SIFT-MS was selected to monitor in real time the concentrations of toluene and the reference. For clarity the measurements have been displaced vertically by 0.5 for methanol and 1 for butanone. [toluene]₀, [ref]₀, [toluene]_t, [ref]_t are the initial concentrations of the compound of interest and that of the reference, with no OH radicals present (light-sources off), at t = 0 and at discrete reaction times t, respectively.





Fig. 7 Temperature dependent data for the reaction of Cl atoms with toluene. The error bars quoted in our measurements correspond to the standard deviation of the mean values determined for the different precursor ions. The solid line corresponds to the average value of all measurements performed in the range of 253 to 353 K.





Fig. 8 Typical concentration plots of benzaldehyde formed versus toluene consumed at 293 K with (a) the SIFT-MS using the H_3O^+ precursor ion to monitor the corresponding compounds and (b) the FTIR. Error bars reflects the uncertainty to the determination of compounds concentrations. The lines are the

linear fit of experimental results (not forced to pass through the origin). The slope corresponds to the product yield of benzaldehyde ($\pm 2\sigma$ precision).



Fig. 9

Fig. 9 Proposed reaction mechanism for the oxidation of toluene from Cl atoms. The dash arrow is used to indicate the possible formation of a secondary product.