Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)

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Abstract

The chemical composition of organic aerosols influences their impacts on human health and the climate system. Aerosol formation from gas-to-particle conversion and in-particle reaction was studied for the oxidation of limonene in a new facility, the Cambridge Atmospheric Simulation Chamber (CASC). Health-relevant oxidising organic species produced during SOA formation were quantified in real-time using an Online Particle-bound Reactive Oxygen Species Instrument (OPROSI). Two categories of reactive oxygen species (ROS) were identified based on time series analysis: a short-lived component produced during precursor ozonolysis with a lifetime on the order of minutes, and a stable component which was long-lived on the experiment timescale (~ 4 hours). Individual organic species were monitored continuously over this time using Extractive Electrospray Ionisation (EESI) Mass Spectrometry (MS) for the particle phase and Proton Transfer Reaction (PTR) MS for the gas phase. Many first generation oxidation products are unsaturated, and we observed multiphase aging via further ozonolysis reactions. Volatile products such as $C_9H_{14}O$ (limonaketone) and $C_{10}H_{16}O_2$ (limonaldehyde) were observed in the gas phase early in the experiment, before reacting again with ozone. Loss of $C_{10}H_{16}O_4$ (7-hydroxy limononic acid) from the particle phase was surprisingly slow. A combination of reduced C=C reactivity and viscous particle formation (relative to other SOA systems) may explain this, and both scenarios were tested in the Pretty Good Aerosol Model (PG-AM). A range of characterisation measurements were also carried out to benchmark the chamber against existing facilities. This work demonstrates the utility of the CASC chamber, particularly for understanding the reactivity and health-relevant properties of organic aerosols using novel, highly time-resolved techniques.

1 Introduction

Organic aerosols make an important but poorly understood contribution to the climate system (Boucher et al., 2013). Airborne particles are also closely linked to the negative health effects of air pollution (Pope et al., 2009). Their atmospheric properties, including their interaction with trace gases and ability to act as cloud condensation nuclei, are closely linked to their chemical composition (Abbatt et al., 2012; Hallquist et al., 2009). Detailed chemical speciation is an important step towards understanding the formation and properties of aerosols. In particular, specific compound classes may dominate in certain processes. For example, water-soluble carbonyls may be responsible for a large fraction of aqueous secondary organic aerosol (SOA) formation (Ervens et al., 2011; McNeill et al., 2012). Similarly,~~ organic reactive oxygen species (ROS)~~ species including hydrogen peroxide and oxygen-centred radicals and ions can cause biological stress and damage (Anglada et al., 2015; Apel and Hirt, 2004).~~,~~ Related organic compounds including ~~organic ~~peroxides have been shown to be major SOA components (Camredon et al., 2007; Docherty et al., 2005). Together, these reactive oxygen species (ROS)~~and oxygen-centred radicals, ~~ are thought to be associated with the observed negative health effects of airborne particles (Verma et al., 2009).

SOA formation is an inherently multiphase process involving both gas-to-particle conversion and heterogeneous and in-particle chemistry (Kroll and Seinfeld, 2008). Atmospheric chambers constitute an invaluable tool for studying these processes under controlled conditions and relevant timescales. A variety of environmental chambers are in use globally, e.g. (Cocker et al., 2001; Hildebrandt et al., 2009; Klotz et al., 1998; Paulsen et al., 2005; Rohrer et al., 2004; Wang et al., 2014) to understand different aspects of atmospheric chemistry, air pollution and chemistry-climate interactions. Previous chamber studies have led to the discovery of important SOA formation and aging processes (Ehn et al., 2014; Kalberer et al., 2004; Odum et al., 1997; Shiraiwa et al., 2013).

The largest global source of SOA is from the oxidation of biogenic volatile organic compounds (BVOCs) (Hallquist et al., 2009). Limonene is one of the most abundant BVOCs in the troposphere, with an estimated biogenic emission rate of 11 Tg yr^{-1} (Guenther et al., 2012)~~a BVOC emitted in significant quantities (Guenther et al., 2000) in the biosphere~~. Its widespread use in industrial processes and household cleaning and fragrance products also results in elevated indoor concentrations with contingent impacts on indoor air quality (Wainman et al., 2000; Waring, 2016; Weschler and Shields, 1999).

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Limonene contains two reactive C=C double bonds which results in multiple generations of oxidation products (Bateman et al., 2009; Kundu et al., 2012; Walser et al., 2008) containing a range of functional groups including carboxylic acids, carbonyls, peroxides and alcohols. ~~and high aerosol yields relative to other terpenes (Hoffmann et al., 1997; Zhang et al., 2006).~~ Previous studies have mainly focused on the reaction of limonene with ozone (Kundu et al., 2012; Zhang et al., 2006), with relatively few OH-aging experiments reported, particularly with respect to chemical characterisation (Zhao et al., 2015). Ozone is a major sink for limonene under a range of atmospheric conditions (Atkinson and Arey, 2003) and will dominate in indoor scenarios which may be most relevant for the health effects of limonene SOA (Waring, 2016). The endo C=C of limonene is more susceptible to ozonolysis by a factor of 10-50 (Zhang et al., 2006) and some of the first-generation ring opening products are condensable (Figure 1). Subsequent oxidation of the remaining double bond may therefore occur in either the gas or condensed phases depending on the properties of the initial products and the aerosol loading.

The ability of limonene to form multifunctional products via successive oxidation steps results in high aerosol yields relative to other terpenes (Hoffmann et al., 1997; Zhang et al., 2006). Aside from ozonolysis, other condensed-phase reactions further modify the composition of limonene SOA. Kundu et al., (~~Kundu et al.,~~ 2012) report the reactive uptake of carbonyls to form oligomeric products, while the formation of light-absorbing "brown carbon" via uptake and reaction of ammonia and amines appears to be particularly efficient for limonene SOA compared to other precursors (Bones et al., 2010; Updyke et al., 2012).

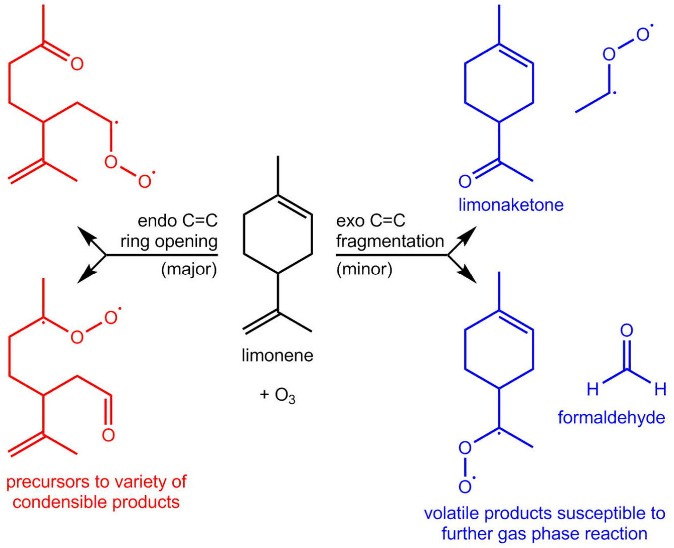

Figure 1: Initial products of limonene ozonolysis following reaction with the cyclic endo C=C (red channel) and terminal exo C=C (blue channel). The Criegee intermediates produced in these reactions can proceed to form a variety of multifunctional products observed both in the gas and particle phases.

The multiphase ozone-initiated oxidation of limonene to form SOA was~~is~~ studied in a new, state-of-the-art facility: The Cambridge Atmospheric Simulation Chamber (CASC). CASC is a 5.4 m^3 Teflon~~FEP~~ chamber which is coupled to a range of unique online chemical characterisation instruments. An Extractive Electrospray Ionisation Mass Spectrometer (EESI-MS) provides real-time measurements of particle-phase molecular composition (Gallimore and Kalberer, 2013)~~ (Gallimore et al., submitted)~~. EESI retains the key advantage of "soft" electrospray ionisation MS techniques, namely that quasi-molecular ions are produced from aerosol analytes with minimal fragmentation. Individual molecular species can be identified and relative intensity changes monitored over time as a measure of concentration changes with particles (Gallimore et al., 2017). Gas-phase VOC components are monitored using Proton Transfer Reaction Time of Flight (PTR-ToF) MS. Together these complementary techniques produce a detailed, highly time-resolved picture of the evolving organic components in the chamber on a molecular level. In parallel, an Online Particle-bound Reactive Oxygen Species Instrument (OPROSI) (Wragg et al., 2016) allows the health-relevant oxidising capacity of organic species to be quantified with high time resolution.

In our limonene ozonolysis experiments, we observe several reaction pathways using these instruments which contribute to SOA formation. These include: further oxidation of volatile unsaturated products in the gas phase, heterogeneous reaction of ozone with condensed double bonds, and reactive uptake of carbonyls to form accretion products. Most of the reactive chemistry is complete once the limonene has been consumed, but heterogeneous reaction and decomposition of ROS appear to continue on longer timescales. We develop model test cases and find that such apparently "slow" rates of change may be explained by a combination of inhibited diffusion within viscous particles and reduced reactivity compared to other SOA systems. Compared to the widely used SOA surrogate, oleic acid aerosol, limonene SOA exhibits a longer ROS lifetime and higher overall ROS yield which we rationalise in terms of their respective chemical characteristics.

2 Methodology

2.1 Chamber construction and operation

A schematic of the Cambridge Atmospheric Simulation Chamber (CASC) is given in Figure 2. The design is based on a 5.4 m^3 (1.5 × 1.8 × 2.0 m) collapsible bag made from 125 µm DuPont Teflon fluorocarbon film (FEP type 500A, Foiltec GmbH, Germany). The panels are heat sealed and bonded with Teflon tape (Polyflon Technology Ltd, UK) at the edges and corners of the chamber. The bag is suspended in an aluminium frame (Rexroth, Bosch, Germany) and entirely enclosed by aluminium sheeting and Perspex panels covered with aluminium tape to reflect light. Stainless steel ports containing ¼" and ½" stainless steel bulkheads (Swagelok, UK) are attached to each end of the chamber to enable introduction and sampling of air from the chamber. An initial application of the chamber is described in Kourtchev et al. (2016).

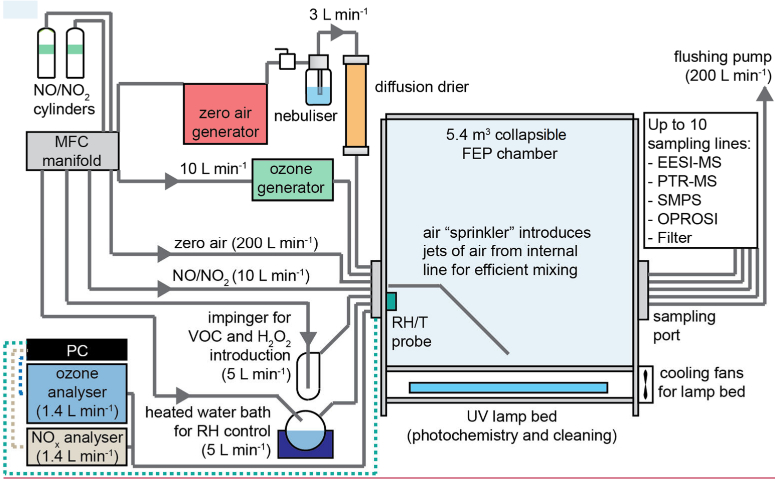

Figure 2: Schematic of the Cambridge Atmospheric Smog Chamber (CASC). The facility consists of a 5.4 m^3 collapsible FEP Teflon chamber with stainless steel ports at each end for introduction of gases and sampling of chamber air by a suite of instrumentation. Gas sampling lines are solid grey, data connections are dashed.

The temperature of the room which houses the chamber is controlled using a 7.1 kW air conditioning unit (Daikin, UK) and 10 fans are situated underneath one end of the chamber to circulate air from the room through the chamber enclosure. Light sources are situated under the bag and consist of twenty 160_W UV tanning lamps (Philips Body Tone, > 300 nm) for use during photochemical aging experiments and four 75_W “hard” UV lamps (Philips TUV75, 242 nm) for cleaning the chamber. The temperature in the chamber is typically 20 ± 1 ºC for “dark” experiments and 24 ± 2 ºC for photochemical aging experiments. Temperature is monitored along with relative humidity (RH) using a probe (Sensirion SHT75, UK) close to the inlet port of the chamber.

The chamber is filled with air from a zero air generator (KA-MT2, Parker Hannifin, UK) which uses a molecular sieve, an activated charcoal bed and filters to remove water, VOCs and particulates respectively. NO and NO_2 are supplied from cylinders (each 100 ppm, C grade, BOC, UK). Flow into the chamber is controlled through a series of mass flow controllers (MFCs) (MKS, UK). Water vapour is introduced by bubbling an air stream through a heated 0.5 L round-bottomed flask containing water (HPLC, Rathbones, UK) which is replaced at least each week. ~~This process does not introduce detectable levels of particles or VOCs~~We monitored changes in particle and VOC concentrations during water introduction and found particle formation to be negligible, but observed up to ~ 10 ppb acetone and lesser quantities (< 2 ppb) of C_1-C_2 aldehydes and acids. Ozone is generated by flowing air through either an enclosed mercury UV lamp (Appleton Woods, UK) or a commercial ozone generator (LABOZONE09, ESCO International Ltd, UK). VOCs and aqueous H_2O_2 (if used) are introduced into separate glass impingers and evaporated using an air stream and heating from a heat gun (PHG 2, Bosch, Germany). Seed particles can be optionally introduced from an atomiser (Model 3076, TSI, UK) and are dried using a silica diffusion drier and neutralised with a Kr-85 source (Model 3077, TSI, UK) prior to introduction into the chamber.

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A 200 L min^{-1} diaphragm pump (ET200, Charles Austen, UK) is used in combination with 200 L min^{-1} clean air introduction to flush the chamber. Flushing is carried out for at least 24 hours prior to the start of an experiment and may be accompanied by use of the "hard" UV lamps, ozone (~ 10 ppm) and water vapour to remove residual species from the chamber walls. The chamber is typically operated in a batch mode, where reactants are introduced into the chamber at the start of the experiment and allowed to evolve over a period of several hours. Typically a maximum of 1.5 m^3 air was removed during a batch experiment, and guide rails on the chamber frame allow the bag to inflate and deflate at ambient pressure. Up to ~ 60 % of the chamber volume could be sampled using this system if required. In principle ~~it~~ the chamber could also be operated in a flow-through mode, where continuous introduction of reactants produce steady state conditions in the chamber according to a characteristic mixing time.

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2.2 Chamber instrumentation

A series of instruments used to monitor physical and chemical parameters of the chamber are listed in Table 1. In addition to a suite of commercially available instrumentation, we also monitor the chemical evolution of the gas-phase and aerosols formed in the chamber using unique instruments developed in-house.

Instrument	Measures	Range	Uncertainty	Time resolution
EESI-MS (Gallimore and Kalberer, 2013)	Particle-phase chemical composition	0.2-600 µg/m^3		4-6 minutes
OPROSI (Wragg et al., 2016)	Particle-bound reactive oxygen species (ROS)	0-2000 nmol [H_2O_2] equiv m^{-3}	2-4 nmol [H_2O_2] equiv m^{-3}	4 minutes
Ionicon PTR-ToF 8000 MS	Gas-phase VOCs			As low as 100 ms, typically 1 minute
TSI 3086 SMPS	Particle size distribution	14-700 nm		< 2.5 minutes
Thermo 49C ozone analyser	[O_3]	0-200 ppm	± 1 ppb up to 1 ppm	1 minute
Teledyne 200E NOx analyser	[NO], [NO2], [NOx]	0-1000 ppb	± 1 ppb	1 minute
Sensirion SHT75	RH, T	0-100% (RH), -40 – 120°C (T)	± 1.8% (RH), ± 0.3°C (T)	1 second

Table 1: Overview of CASC instrumentation. EESI-MS and OPROSI are unique instruments developed in-house.

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2.2.1 Extractive Electrospray Ionisation Mass Spectrometry

Extractive Electrospray Ionisation Mass Spectrometery (EESI-MS) is an online particle analysis technique and the design and optimisation of our EESI source is described in Gallimore and Kalberer (2013). It contains a commercial electrospray probe (Thermo

Scientific HESI-II) with a custom-built aerosol injector and manifold. The primary electrospray was operated at a voltage of –3.0 kV and a N_2 sheath flow rate of 0.8 L min^{-1}. A water−methanol 1:1 mixture (Optima LC-MS grade solvents; Fisher Scientific) containing 0.05% formic acid (90%, Breckland Scientific) was infused into the ESI probe at 10 µL min^{-1}. Chamber air was delivered into the source at 1 L min^{-1}. Collision and extraction of the SOA particles by primary electrospray droplets occurs in an off-axis configuration with respect to the MS inlet, to minimise source contamination and memory effects through particle deposition. The EESI source was coupled to an ion-trap mass spectrometer (Thermo Scientific LTQ Velos). Spectra were acquired in the negative ionisation mode over the range *m/z* 50-500, with a mass resolution ~ 2000 (full width at half maximum, FWHM) at *m/z* 400.

Gallimore and Kalberer (~~Gallimore and Kalberer,~~ 2013) demonstrated that the relative EESI-MS ion intensity correlated with the mass concentration of tartaric acid particles delivered into the source, suggesting that the entire particle bulk is extracted for analysis. More recently, Gallimore et al., (~~Gallimore et al.,~~ 2017) showed that the kinetics of particle-phase reactions could be monitored; loss rates derived from EESI-MS measurements compared well with other studies, and spectra were compared to Liquid Chromatography (LC) MS to confirm that the EESI-MS assignments were present in the aerosol rather than formed as artefacts in the ion source.

~~It retains the key advantage of "soft" electrospray ionisation MS techniques, namely that quasi-molecular ions are produced from aerosol analytes with minimal fragmentation, and hence individual molecular species can be identified. It is also particularly suited to chamber measurements because time-resolved information is obtained and relative intensity changes can be linked to concentration changes in the particle Gallimore et al., (submitted).~~

2.2.2 Proton Transfer Reaction Mass Spectrometry

The gas phase VOC composition of the chamber is monitored using Proton Transfer Reaction MS (Blake et al., 2009). The PTR-MS (PTR-ToF 8000, Ionicon, Innsbruck, Austria) measures VOCs with a proton affinity higher than water in the *m/z* range 10-500, with a typical mass resolution of 5000 (~~full width at half maximum~~FWHM) at the mass of

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protonated acetone, and a typical time resolution of 1 s. Typical detection limits are in the order of 1-2 ppb at 1 s time resolution and ~30 ppt at 1 min time resolution (Blake et al., 2009; de Gouw and Warneke, 2007). For these experiments, source settings were: drift tube voltage of 600 V, drift tube pressure at ~ 2.20 mbar, drift tube temperature at 60ºC, resulting in an E/N of ca. 135 Td (1 Td = 10^{-17} V cm^2). $k = 2.54 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} was used for limonene quantification (Zhao and Zhang, 2004) and a default rate constant (k) of 2×10^{-9} cm^3 $molecule^{-1}$ s^{-1} was used for the other ions.

2.2.3 Online Particle-bound Reactive Oxygen Species Instrument

Reactive Oxygen Species (ROS) can be~~are~~ associated with the negative health impacts of aerosols (den Hartigh et al., 2010; Steenhof et al., 2011). A new Online Particle-bound Reactive Oxygen Species Instrument (OPROSI), described in Wragg et al. (2016) is used to continuously monitor this health relevant property of aerosols from the chamber. The continuous sample inflow (5 L min^{-1}) passes through a $PM_{2.5}$ cyclone (URG-2000-30E-5-2.5-S) and charcoal denuder prior to entering into a particle-into-liquid sampler (PILS). Particles are collected into a 1 mL min^{-1} spray containing horseradish peroxidase (HRP) (TypeVI, 1 unit mL^{-1} in 10% phosphate buffer solution (PBS), Sigma Aldrich) which reacts with ROS present in the particles. This is combined with a 1mL min^{-1} aqueous 2’7’-dichlorofluorescein (DCFH) solution (10μM, 10% PBS, Sigma Aldrich), which is oxidised to a fluorescent product (DCF) by the ROS-HRP solution. After a 10 minute reaction time at 40 ºC the concentration of DCF is quantified via fluorescence spectroscopy. The fluorescence response is calibrated with H_2O_2 and quantitative ROS concentrations are reported as “[H_2O_2] equivalents”. The assay also responds to organic peroxides. It is likely sensitive to HO_x radicals and ions such as superoxide but we are unable to obtain suitable standards to test this directly. OPROSI has a time resolution of 4 minutes (e-folding time during online particle collection tests) and is thus able to capture most time-dependant processes observed during SOA formation and evolution. This instrument is especially sensitive to short-lived ROS components, which react within seconds-minutes after sampling (Wragg et al., 2016)~~(see Wragg et al. (2016) for more details).~~

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EESI-MS, PTR-MS and OPROSI are all placed in a laboratory just next the room that houses the chamber. Stainless steel tubing (ca. 3 m length) connects the chamber with EESI-MS and OPROSI. The PTR-MS is connected via a 1mm inner diameter PTFE tube kept at room temperature.

2.3 Chamber photochemical characterisation

The tanning lamps used during photochemical aging experiments emit primarily in the range 300-400 nm (Figure S1(a)). Emissions below 300 nm, which in the atmosphere are attenuated before reaching the troposphere, are absent. This measured spectrum also overlaps with the absorption cross sections of NO_2 ($\lambda < 400$ nm) and to a small extent with O_3 ($\lambda < 310$ nm). Photolysis of these species drives photochemistry in the troposphere. By contrast, "black lamps", which are commonly employed in chamber studies, emit over a narrower range, 350-400 nm, where ozone photolysis will not occur. Transmission of light through the FEP film used for the bag was tested over the range 200-800 nm (Figure S1(b)). Transmission of light > 300 nm, used in aging experiments, was higher than 80 %. Transmission of "hard" UV from the cleaning lamps is also acceptable at > 60%.

The photolysis characteristics of the chamber were assessed by quantifying the photolysis frequency of NO_2, J_{NO2}. Following four NO_2 irradiation experiments in which the steady state concentrations of NO, NO_2 and O_3 were measured, $J_{NO2} = 0.49 \pm 0.09$ min^{-1} was calculated (Table S1). This is within the range of values determined for other chambers and is comparable to ambient values in Pasadena, California (0.5 min^{-1}) (Cocker et al., 2001) and the outdoor EUPHORE chamber (0.44-0.56 min^{-1}) (Martın-Reviejo and Wirtz, 2005).

2.4 Mixing and wall losses

The chamber air volume is mixed using an "air sprinkler" system. High pressure air is introduced from a PTFE tube (4 mm inner diameter) which extends from the introduction port across the entire the length of the chamber. Periodic holes along the tube allow "jets" of air to escape and mix the chamber volume. This approach avoids the use of mixing fans which may produce unwanted vapours or particles during operation. Mixing with and without use of the air sprinkler was assessed by evaporating α-pinene into the chamber and monitoring its concentration from the opposite port with the PTR-MS (Figure S2). With 3 × 10 s bursts from the air sprinkler over the course of a minute, the observed α-pinene concentration sampled at the far end of the chamber was seen to stabilise rapidly and reaches 90 % of its steady state value within 4 minutes of mixing. Without active mixing, the α-pinene concentration took around 30-40 minutes to reach a stable value. This efficient mixing procedure (adding ca. additional 100 L clean air into the chamber) is usually applied during the introduction of oxidants (for a “dark” experiment) or after the addition of all components, before initiating photochemistry (for photochemical aging experiments).

The loss of ~~oxidants and VOCs~~ozone to the walls of the chamber was tested~~ using ozone and α-pinene as representative test species~~. Ozone was lost from the clean chamber at an average rate of 5.9 × 10^{-5} min^{-1} over 9 hours. This compares to a loss rate of 1.31 × 10^{-4} min^{-1} for a similar facility, described by Wang et al. (2014). ~~During the α-pinene wall loss experiment, an average loss rate of 1.6 × 10^{-5} min^{-1} was observed over 14 hours.~~

Particle deposition to the chamber walls was also determined, assuming deposition to be a first order process (Cocker et al., 2001). Ten experiments involving the introduction of ammonium sulfate particles to the clean chamber were performed. Characteristic first-order coefficients for the rate of change of particle number and mass were found to be $\beta_N = 0.201 \pm 0.025\ h^{-1}$ and $\beta_M = 0.166 \pm 0.020\ h^{-1}$ respectively, as detailed in the supporting information. This corresponds to aerosol lifetimes of 5-6 hours, comparable to other chambers as illustrated in Table S2. The potential impact of changes in chamber volume during sampling (maximum ~30 %) on wall loss rates was not considered.

2.5 Aerosol numerical modelling

Illustrative model simulations were performed using the Pretty Good Aerosol Model (PG-AM). PG-AM is described in detail in Griffiths et al., (2009) and Gallimore et al., (~~Gallimore et al.,~~ 2017)~~ Gallimore et al., (submitted)~~. ~~In brief, t~~The model treats the following processes in a kinetic framework: chemical reaction in both the gas and particle phases, gas-particle exchange via uptake and evaporation, and diffusion within the particle. Fluxes between the gas and particle phases depend on the aerosol surface area as well as each species' accommodation coefficient (α, dimensionless) and partitioning coefficient (K, M atm^{-1}). Diffusion is parameterised according to Griffiths et al., (2009); the particle is treated as a series of nested shells, with the rate of transport of each species between shells determined by its diffusion coefficient (D, cm^2 s^{-1}). The differential equations governing reaction and diffusion are integrated forwards in time using Mathematica (v11, Wolfram).

-In this study, ~~loss~~ reaction of unsaturated $C_{10}H_{16}O_4$ ~~from the particle by reaction~~ with ozone was simulated for a single particle of characteristic radius $r_{\mathrm{eff}} = 3V_t/S_t = 84$ nm based on the measured total particle volume (V_t) and surface area (S_t). $C_{10}H_{16}O_4$ was assumed to be 7-hydroxy limononic acid for vapour pressure calculations and formation of a corresponding carbonyl oxidation product, $C_9H_{14}O_5$, was represented in the model mechanism (Figure S3). The vapour pressures of $C_{10}H_{16}O_4$ and $C_9H_{14}O_5$ were estimated at ~2.8 × 10^{-5} Pa and ~2.2 × 10^{-6} Pa using the online model EVAPORATION (Compernolle et al., 2011) which performed well in our tests for a species with known vapour pressure, pinic acid. The resulting partitioning coefficients calculated from these vapour pressures, $K \sim 2 \times 10^{10}$ M atm^{-1} and ~ 2 × 10^{11} M atm^{-1} means that both species are almost entirely condensed (> 99 %) under the experimental conditions.

The accommodation coefficient for organic species was fixed at $\alpha_{\mathrm{org}} = 0.1$. Ozone ~~solubility~~ partitioning ($K_{\cancel{\mathrm{H,}}\mathrm{O3}} = 0.1$ M atm^{-1}) (Morris et al., 2002) and accommodation ($\alpha_{\mathrm{O3}} = 10^{-3}$) (Gallimore et al., 2017)~~(Gallimore et al., submitted)~~ were fixed based on the literature for oleic acid particles. The ~~bulk~~ particle phase bimolecular rate constant for ozonolysis (k_p^{II}~~k^{II}~~) and the ozone and organic diffusion coefficients (D_{O3} and D_{org}) were varied as described in the results. A fixed gas-phase rate constant for exo double bond ozonolysis, $k_g^{\mathrm{II}} = 7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} (Zhang et al., 2006) was also included. However, gas-phase loss was not competitive with particle phase oxidation due to this relatively small rate constant and the low vapour pressure of $C_{10}H_{16}O_4$. The carbonyl product $C_9H_{14}O_5$ was formed with a yield of 0.4, based on the branching of exo-C=C ozonolysis products for β-pinene (Jenkin, 2004). We did not attempt to account for the fate of the other reaction branch featuring a C_9 Criegee intermediate due to the wide range of possible Criegee intermediate products in the

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condensed phase including peroxides, carbonyls and secondary ozonides (Lee et al., 2012; Maksymiuk et al., 2009).

3. Limonene SOA formation and characterisation

Insight into the chemical and health-relevant properties of limonene-derived SOA is provided by the online characterisation techniques coupled to CASC. We focus on ozonolysis in order to compare the results from CASC with a range of previous studies which measure SOA chemical composition (Bateman et al., 2009; Kundu et al., 2012; Maksymiuk et al., 2009; Walser et al., 2008). In addition, from a human health perspective, exposure to limonene SOA is most likely to occur indoors, where ozone is the dominant sink of limonene.

Before the introduction of reactants, the concentrations of O_3, NO_x and particles in the clean chamber were below the detection limits of the respective instruments in Table 1. The relative humidity of the chamber air was adjusted to 40 % and 6 µL limonene (> 99%, Sigma) was added and mixed to produce a starting concentration of ~190 ppb based on PTR-MS quantification. Ozone was introduced into the chamber over a 20 minute period, during which time the chamber air was regularly mixed; a maximum concentration of ~450 ppb was achieved (Figure 3). This corresponds to a stoichiometric excess of ozone with respect to the number of double bonds present in the limonene precursor. Ozonolysis was performed under dark conditions without the addition of NO_x.

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SOA was produced rapidly following the introduction of ozone to the chamber (Figure 3). Particles grew via homogeneous nucleation into a single mode with diameter ~160 nm and standard deviation $\sigma=0.21$. The measured SMPS data (black curve) were corrected for particle wall losses (red curve) using a procedure similar to Rollins et al., (2009) which is described in the supplementary information. Over 85% of the loss-corrected mass was formed within the first 30 minutes of ozone introduction, with slower additional growth over the next ~ 3 hours of the experiment.

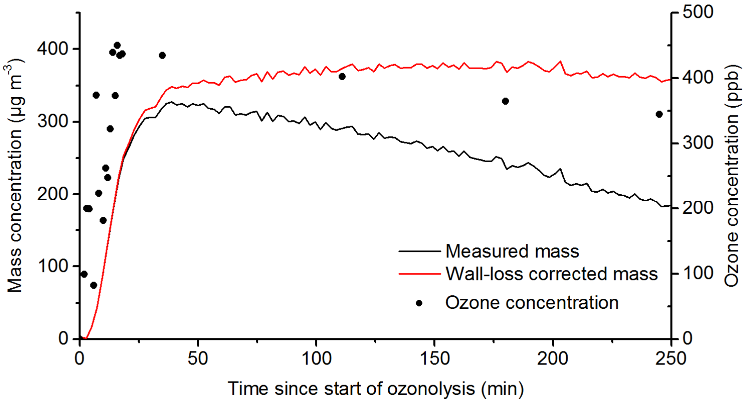

Figure 3: Time series showing evolution of SOA mass (primary y-axis) and ozone concentration (secondary y-axis) in the chamber. ~~the total SOA mass in the chamber (black curve).~~ The measured SOA concentration (red curve) was corrected to account for particle deposition to the chamber walls (black curve).

3.1 Gas and particle molecular composition changes during ozonolysis

3.1.1 CASC measurements: PTR-MS and EESI-MS

Limonene was lost from the chamber over a period of 30 minutes, due to reaction with ozone~~The characteristic time for limonene loss due to reaction with ozone was also 30 minutes~~ (Figure 4). Limonene was quantified using the PTR~~-ToF~~-MS from the sum of signals at *m/z* 137 ($[M + H]^+$) and *m/z* 81 (major fragment). We detect a number of gas-phase products, noting that structural isomers of the species described here cannot be distinguished in our analysis. These were mostly assigned as $[M + H]^+$ and agree well with previous studies of limonene and other terpene ozonolysis (Ishizuka et al., 2010; Lee et al., 2006). The largest yields are for ubiquitous small acids and carbonyls such as formic acid (*m/z* 47, Figure 4), formaldehyde (*m/z* 31, Figure 4), acetic acid, acetaldehyde and acetone. *m/z* 75 reported by Lee et al., (2006) is present here, with an ~~and based on our~~ assigned neutral formula ($C_3H_6O_2$). Plausible structures require secondary OH-mediated fragmentation of the limonene backbone ~~could plausibly be~~and could include known atmospheric consituents such as propanoic acid

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(Chebbi and Carlier, 1996), hydroxyacetone (Zhou et al., 2009) or methyl acetate (Christensen et al., 2000).

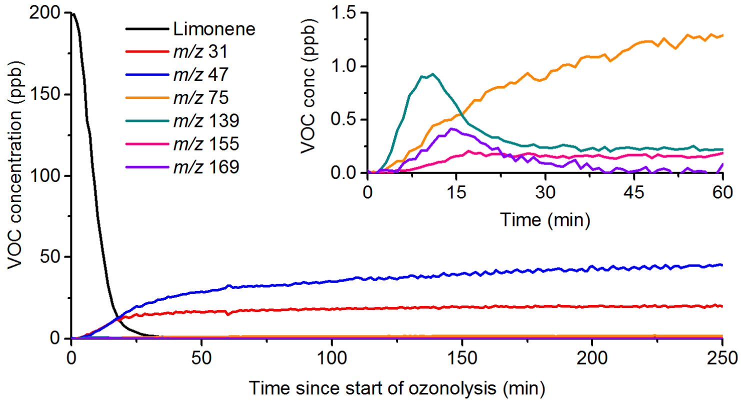

Figure 4: Concentrations of selected gas-phase VOCs including limonene, formaldehyde (*m/z* 31) and formic acid (*m/z* 47) detected using PTR-MS during limonene ozonolysis. The inset graph shows products formed in lower concentrations, including first-generation unsaturated species (*m/z* 139, limonaketone and *m/z* 169, limonaldehyde) which are removed by further ozonolysis.

Unsaturated gas-phase products corresponding to both reaction channels in Figure 1 can be detected at higher masses. In particular, limonaketone ($C_9H_{14}O$, *m/z* 139) is produced from the minor exo-double bond ozonolysis channel and is the most volatile unsaturated product (Donahue et al., 2007). It peaks in concentration at~~fter~~ 11~~2~~ minutes before being depleted, presumably by oxidation of the remaining double bond in the gas phase. Relatively few products from the ring-opening endo C=C channel can be quantified, but we note that limononaldehyde ($C_{10}H_{16}O_2$, *m/z* 169), the analogous ring-opening product to limona~~-~~ketone, exhibits a similar time dependence and peaks at 14 minutes. Other products of endo C=C ozonolysis are generally condensable since a double functionalization reaction occurs without fragmenting the carbon backbone. Small gas phase signals for such products including *m/z* 155 ($C_9H_{14}O_2$) (Lee et al., 2006) (Figure 4), *m/z* 187 ($C_9H_{14}O_4$, limonic acid) and *m/z* 201 ($C_{10}H_{16}O_4$, 7-hydroxy limononic acid) were detected close to the instrument background. The same peaks were observed in limonene ozonolysis experiments performed by Ishisuka et al., (~~Ishizuka et al.,~~ 2010).

We discuss these products further in the context of particle-phase composition measurements from EESI-MS, which is applied to long term (> 4 hour) SOA monitoring for the first time here. An EESI mass spectrum 50 minutes after the start of ozonolysis is shown in Figure 5(a). As for the PTR measurements, isobaric compounds may complicate interpretation of the spectrum. The ion source was operated in negative ionisation mode and the most abundant $[M - H]^-$ ions detected with EESI-MS compare well with major products identified in previous offline ESI-MS studies (Bateman et al., 2009; Kundu et al., 2012; Walser et al., 2008). We base potential assignments on previous literature. These include: *m/z* 185 (neutral formula $C_9H_{14}O_4$, limonic acid), *m/z* 171 ($C_8H_{12}O_4$, keto-limonalic acid), *m/z* 183 ($C_{10}H_{16}O_3$, limononic acid), *m/z* 199 ($C_{10}H_{16}O_4$, 7-hydroxy limononic acid). ~~and~~ *m/z* 245 ($C_{11}H_{18}O_6$), one of the most abundant products from Kundu et al., (~~Kundu et al.,~~ 2012) is observed here and is along with other C_{11}-C_{15} products is indicative of oligomerisation, specifically via the reactive uptake of gas-phase carbonyls to the particle phase.

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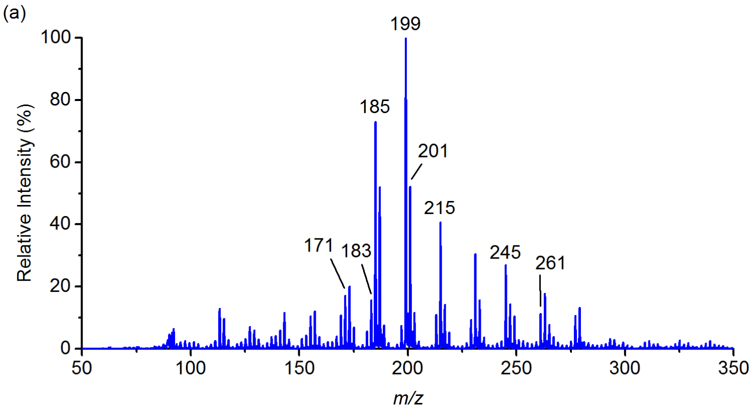
Larger $C_{>20}$ products described by Kundu et al., (2012) and Bateman et al., (2009) could not be identified here. Since most products described in Kundu et al., (2012) are unsaturated, they would ultimately be oxidised in the conditions used here. Reactions of stabilised Criegee intermediates with initial products could plausibly produce other high molecular weight species. ~~It is also~~However, these are not observed here and it is likely that the pre-concentration achieved by filter or impactor sampling in other~~these~~ studies leads to a greater sensitivity for species with very low concentrations compared to our online method.

We show time series for selected ions, along with the cumulative total ion current (TIC) across all ions, in Figure 5(b). The time resolution of the measurements is 4 minutes, which are shown as continuous lines for clarity. The EESI-MS ion source is stable over the > 4 hour time period of the experiment with respect both to the TIC and individual ion time series, demonstrating that the technique can operate continuously throughout long laboratory experiments.

As demonstrated in Gallimore and Kalberer (2013) and Gallimore et al., (~~Gallimore et al.,~~ 2017)~~(submitted)~~, relative intensity changes in EESI-MS can be used to infer relative concentration changes in the particle phase. Many individual time series scale approximately with the loss-corrected particle mass (Figure 3) as shown in Figure 5(b). Slightly different upward (e.g. *m/z* 201, $C_9H_{14}O_5$) or downward (e.g. *m/z* 215, $C_{10}H_{16}O_5$) trends can be observed as aging continues on longer timescales. This suggests a slow production or loss from multi-generational chemistry either in the gas or particle phases, and is investigated in more detail later for *m/z* 201.



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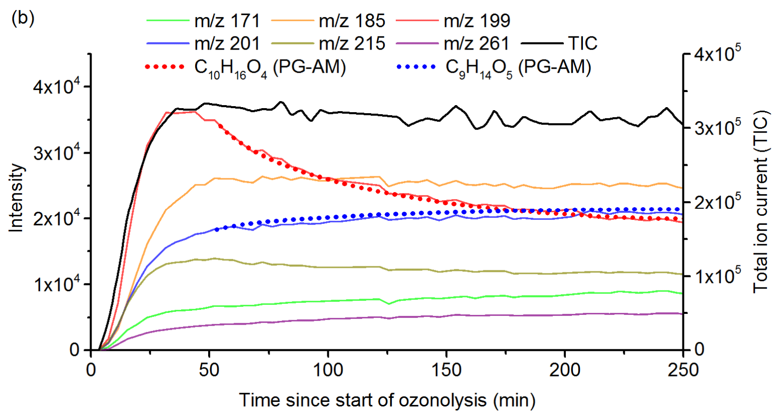

Figure 5: (a) EESI mass spectrum after 50 minutes. Some major peaks discussed in the text are labelled with their *m/z*. (b) Wall-loss corrected intensities for selected particle-phase ions detected using EESI-MS during limonene SOA formation. The total ion current (TIC) across the entire MS is shown on the secondary y-axis. The ~~dashed~~ dotted lines ~~is~~ are a PG-AM simulations for the ~~heterogeneous ozonolysis of unsaturated~~reaction of $C_{10}H_{16}O_4$ with ozone to form $C_9H_{14}O_5$, assuming semisolid SOA.

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A number of ions over a large molecular weight range (*m/z* 107-295) deviate significantly from the above trend and become depleted from the aerosol on longer timescales. We focus on the most abundant of these, *m/z* 199 (Figure 5(b)) which peaks after ~ 30 minutes and then decays notably over the remainder of the experiment. Other ions showing similar trends are discussed later in section 3.2.

A few assignments exist for *m/z* 199 (neutral formula $C_{10}H_{16}O_4$), which has been observed as a major product in previous studies (Kundu et al., 2012; Walser et al., 2008). The most direct route to such an oxidised C_{10} species involves ring-opening by ozonolysis of the endo C=C and hence preservation of the intact carbon backbone. For instance, 7-hydroxy limononic acid is a compelling assignment which is functionalised at the former endo C=C and still contains an intact exo C=C. ~~Other less direct~~Secondary formation routes may include reacti~~ve uptake~~on of small carbonyls ~~with $C_{<10}$ products~~with initial $C_{<10}$ oxidation products

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in the particle phase, as discussed for *m/z* 245 above, or (unsaturated) hydroperoxide formation (Kundu et al., 2012).

We note that most plausible assignments for *m/z* 199 are unsaturated. The chemical loss of ~~these species~~*m/z* 199 will~~is~~ therefore ~~likely to~~ include ozonolysis reactions. In addition to SOA composition changes, oxidation at longer times is also indicated by a continuing decrease in ozone after limonene has been consumed (Figure 3). We propose that this is via heterogeneous reaction due to the low volatility of any possible $C_{10}H_{16}O_4$ product. The very low corresponding gas phase signal (*m/z* 201, $[M + H]^+$) and previous observations of products which form only in the condensed phase (Maksymiuk et al., 2009) ~~appears to confirm~~ support this. Assuming $C_{10}H_{16}O_4$ to be 7-hydroxy-limononic acid, a major ozonolysis product would be a carbonyl with formula $C_9H_{14}O_5$ (*m/z* 201, Figure S3). The *m/z* 201 time series in Figure 5(b) increases slowly during the period after 50 minutes when *m/z* 199 is depleted, consistent with this hypothesis. We explore this proposed reaction further using the PG-AM model below.

Zhang et al., (2006) point out that for uptake coefficients (~ 10^{-3}) typical of other model SOA systems such as oleic acid, the heterogeneous loss rate of ~~these~~ unsaturated species should be fast, and limited by their formation rate. By contrast, the ~~characteristic~~ time constant for loss of *m/z* 199 in this experiment is finite and relatively long, on the order of 1 hour. This is consistent with the study of Bateman et al., (2009), who found a ~ 30 minute lifetime for similar species (with higher ozone concentrations, ~ 1 ppm) using a time resolved analysis technique. Based on this slow loss, they estimated an effective ozonolysis rate coefficient of 10^3-10^4 M^{-1} s^{-1}, consistent with some rate constants measured in water (Hoigne and Bader, 1983) but 2-3 orders of magnitude lower than for a commonly used model SOA system, oleic acid (Lisitsyn et al., 2004).

We note here that other potentially unsaturated ions such as *m/z* 185 do not exhibit a decrease at longer times. Limonic acid is one likely assignment but Walser et al., (2008) have proposed saturated alternatives. It may be that the stable *m/z* 185 signal at longer times is a combination

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of loss of limonic acid and compensating production of other isobaric species, but we are unfortunately unable to investigate this further here.

3.1.2 PG-AM modelling of SOA composition changes

We investigate the~~is~~ time dependence of *m/z* 199 and 201 further, considering two possible scenarios: loss limited by bulk ozone-alkene reaction, and the formation of high viscosity particles which impede (an otherwise fast) bulk reaction. The latter of these has received substantial attention in recent years since the discovery that monoterpene-derived SOA can form an amorphous phase state (Virtanen et al., 2010). The characteristic time for bulk diffusion described in Shiraiwa et al., (2011) is on the order of minutes-hours for a semisolid accumulation mode particle, consistent with the 30-60 minutes estimated here and in Bateman et al., (2009).

The two scenarios were modelled by simulating reactive uptake of ozone to SOA containing unsaturated $C_{10}H_{16}O_4$ using the Pretty Good Aerosol Model (PG-AM, (Griffiths et al., 2009), (Gallimore et al., submitted)). The model was initialised to the experimental conditions 50 minutes after the introduction of ozone; an initial mole fraction of 0.05 was assumed for unsaturated $C_{10}H_{16}O_4$ based on the ion intensities in Figure 5(a) and further production was neglected. Physico-chemical model parameters were fixed (section 2.5), with the exception of the organic and oxidant diffusion coefficients, and condensed-phase ozonolysis rate constant, which were varied manually. Formation of the predicted carbonyl product of $C_{10}H_{16}O_4$ ozonolysis, $C_9H_{14}O_5$, was also simulated and the resulting reactant and product time series were compared to *m/z* 199 and 201 respectively in Figure 5(b).

In both scenarios, gas-phase loss of the reactant only made a very small contribution to the total loss rate, owing to its low vapour pressure and the relatively small gas-phase rate constant, k_g^{II}. In the bulk diffusion-limited scenario, a condensed-phase~~n~~ ozonolysis rate constant of k_p^{II}~~k^{II}~~ = 10^6 M^{-1} s^{-1}, comparable to oleic acid, was assumed. To reproduce our observations, diffusion coefficients representative of semisolid SOA were required. The model simulation overlaid on Figure 5(b) is for $D_{org} = 10^{-16}$ and $D_{O3} = 5 \times 10^{-9}$ cm^2 s^{-1}

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respectively. There is good correspondence between the model and measurements for both $C_{10}H_{16}O_4$ (*m/z* 199) and $C_9H_{14}O_5$ (*m/z* 201). This is consistent with the hypothesis that 7-hydroxy limononic acid and its carbonyl oxidation product make the dominant contribution to the measured *m/z* 199 and 201 signals. The model was found to be sensitive to both parameters and various combinations in the range $D_{\mathrm{org}} = 10^{-15}\text{-}10^{-17}$ and $D_{\mathrm{O3}} = 10^{-7}\text{-}10^{-9}$ cm^2 s^{-1} provide reasonable fits to the data.

For the bulk reaction-limited scenario, the modelled concentration was sensitive only to the slow bulk ozonolysis rate constant, k^{II}, for any representative liquid SOA diffusion coefficients ($D_{\mathrm{O3}} > 10^{-6}$ and $D_{\mathrm{org}} > 10^{-10}$ cm^2 s^{-1} respectively). $k^{\mathrm{II}} = 8 \times 10^3$ M^{-1} s^{-1} was found to give the best agreement with our measurements, in good agreement with the range (10^3-10^4 M^{-1} s^{-1}) estimated by Bateman et al., (2009). The modelled ~~decay profile~~time series were ~~was~~ very similar to the diffusion-limited case and so are~~is~~ omitted from Figure 5(b) for clarity.

The extent to which high particle viscosity influences reactivity is still an open question and we are not aware of any studies of the viscosity properties of limonene SOA. However, the diffusion coefficients used here are at the lower limit of what has been reported for monoterpene SOA at 40% RH (Renbaum-Wolff et al., 2013) ($D_{\mathrm{org}} \geq 10^{-16}$ cm^2 s^{-1}) and significantly lower than some other determinations in SOA, e.g. (Hosny et al., 2016) ($D_{\mathrm{org}} \sim 10^{-11}$ cm^2 s^{-1}). It therefore seems unlikely that the aerosol is sufficiently viscous to fully explain our data, but a combination of slow diffusion and reaction may well do, especially given further suggestions of inhibited reactivity discussed in the following section. A more detailed modelling investigation is out of the scope of this study given the lack of constraining experimental data (both here and in general for limonene SOA) and the assumptions made about the chemical identity of *m/z* 199 and 201. However, this prompts further study of the diffusion characteristics of limonene SOA, especially since the SOA yield is higher and the aerosol components more oxidised than for many other biogenic VOCs.

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3.2 Particle-bound Reactive Oxygen Species (ROS) quantification

3.2.1 CASC measurements: OPROSI

We also monitored the formation of particle-bound reactive oxygen species (ROS) during the chamber experiment. The raw ROS concentration data were wall loss corrected using the same procedure as for the particle mass, and the corrected data are presented in Figure 6. We report ROS quantities as an equivalent concentration of hydrogen peroxide per cubic metre of air which reflects the effective reactivity of the ROS present in the aerosol to the assay (red curve in Figure 6). The appearance of ROS is highly correlated in time with the formation of SOA mass in the chamber (Figure 3) within the first few minutes of ozone introduction. However, while the SOA mass concentration continues to increase slowly for a number of hours, the ROS signal reaches a small maximum after around 30 minutes. Both tend towards relatively stable values after the first hour of oxidative chemistry in the chamber, consistent with the relatively small composition changes in the aerosol (Figure 5(b)). To make this more explicit, we normalise this measured quantity to the mass of SOA present to give a relative in-particle concentration (blue curve in Figure 6). The mass-weighted ROS concentration is highest in the early stages of the reaction, before tending to a stable value of 0.42 ± 0.04 nmol [H_2O_2] µg^{-1} after the first hour of the experiment.

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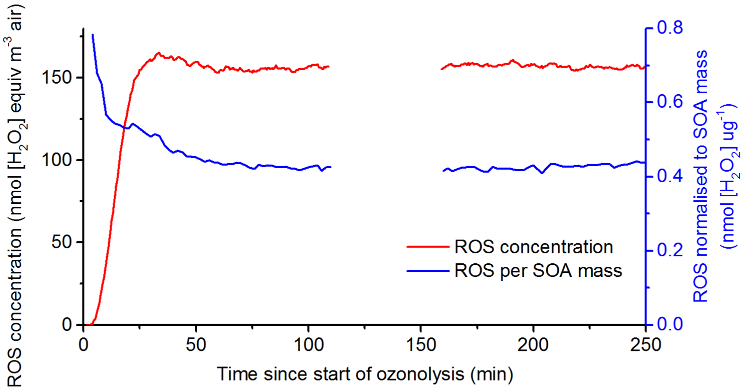

Figure 6: Wall loss corrected particle-bound ROS detected using OPROSI during limonene SOA formation. The procedural blank at 110-160 minutes has been removed for clarity. The secondary y-axis shows an effective ROS concentration per mass of aerosol, which is highest at the start of the experiment and reaches a stable value of 0.42 ± 0.04 nmol [H_2O_2] per µg SOA.

We present an analysis of the above time series which proposes that the total ROS signal can be ~~decomposed~~ split in to two components with different characteristic lifetimes:

$$[\boldsymbol{ROS_{total}}] = [\boldsymbol{ROS_{long}}] + [\boldsymbol{ROS_{short}}] \qquad \textbf{(1)}$$

We propose that ROS_{long} are a group of relatively stable long-lived products (such as hydrogen peroxide and organic peroxides) which constitute the stable ROS at the end of the experiment and which have been shown to be major products of monoterpene ozonolysis (Docherty et al., 2005; Wang et al., 2011).~~,~~ Meanwhile~~and~~ ROS_{short} are reactive species (possibly radicals or otherwise short-lived compounds such as reactive peroxides) ~~species~~ which are produced directly from ozonolysis or other early-generation reactions. Previous studies have concluded that a substantial fraction of ROS present in laboratory (Fuller et al., 2014) and ambient (Huang et al., 2016) aerosols is short lived.

If we assume that [ROS_{long}] scales with the total particle mass in proportion to the final mass-weighted ROS concentration (as do most individual aerosol components in Figure 5(b)), the net contribution of [ROS_{short}] to the total measured signal can be estimated:

$$[\boldsymbol{ROS_{total}}] = \boldsymbol{0.42} \times \boldsymbol{Mass_{SOA}} + [\boldsymbol{ROS_{short}}] \qquad \textbf{(2)}$$

Figure 7(a) shows the estimated contributions of long- and short-lived ROS to the total measured ROS signal using Equation 2. Based on this simple analysis, long-lived ROS makes the dominant contribution to the total ROS signal over the course of the experiment. As expected from the mass-weighted ROS curve in Figure 6, short-lived ROS is most important early in the reaction when reactive species are being produced by ozonolysis from the limonene precursor (Figure 4). If some ROS_{short} were converted to ROS_{long} during the early

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part of the experiment, Equation 2 could underestimate the ROS$_{short}$ contribution to [ROS$_{total}$] and correspondingly overestimate [ROS$_{long}$] early in the experiment.

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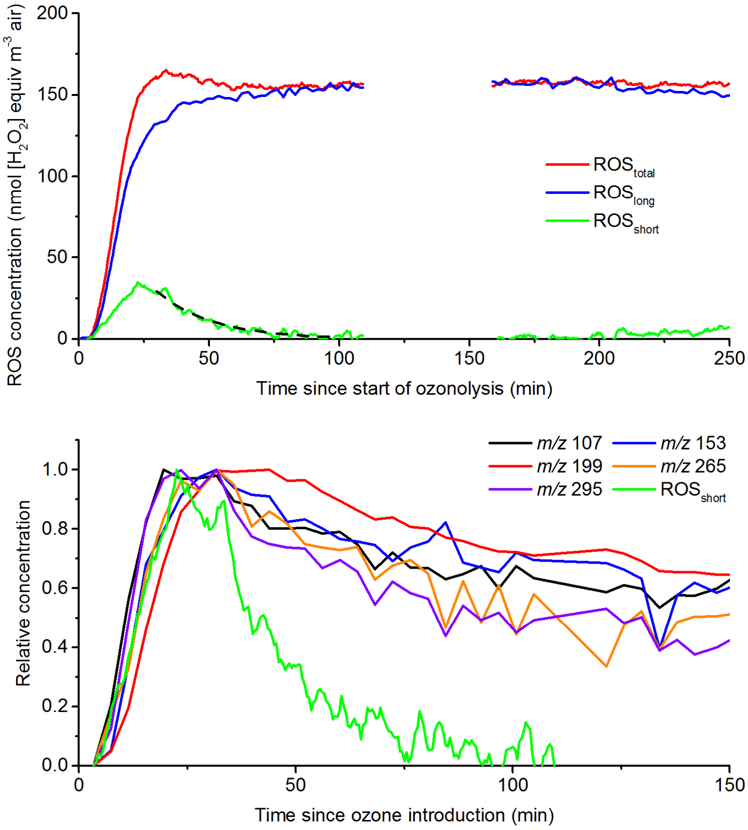

Figure 7: (a) Total particle-bound ROS decomposed into short-lived and long-lived components according to Equation 2. The black dashed line represents an exponential fit to ROS$_{short}$ with a characteristic lifetime of 17 minutes. (b) Relative abundance of a number of particle-phase ions which decay substantially over the course of the experiment. It is possible that some of these are tracers for ROS$_{short}$ (green curve) if isobaric species interfere with the measurements.

[ROS_{short}] reaches a maximum ~~around 20~~23 minutes into the experiment and tends towards zero at longer times. This reflects the competition between production and loss for short-lived species. The apparent production rate of ROS_{short} will depend on two factors. Firstly, chemical production (likely predominantly in the gas phase, but also via heterogeneous ozonolysis of later generation products), which will be fastest at the start of ozonolysis when precursor concentrations are at their highest. Secondly, gas-particle partitioning of reactive species, which will increasingly favour the particle phase as the mass loading in the chamber increases. A convolution of these factors is a plausible explanation for the maximum in [ROS_{short}] in Figure 7(a). At longer times, where the concentration of organic radical precursors (e.g. limonene) is reduced, chemical loss of ROS_{short} dominates and by definition in Equation 2 tends to zero at longer times.

We estimate the lifetime of particle-bound ROS_{short} by neglecting further production of short-lived species after 30 minutes, since the rate of change of chemical composition (Figures 4 and 5) and particle mass (Figure 3) has slowed by this point. We note that the 4 minute time resolution of the instrument (determined mainly by mixing times in the particle collector and fluorescence detector cell) will act as a lower limit on the apparent ROS_{short} lifetime in this analysis. The black dashed curve in Figure 7(a) represents an exponential fit to the data between 30 and 110 minutes and yields a characteristic time for pseudo first-order ROS_{short} loss of 17 minutes. This may be a overestimate if ROS_{short} production is not negligible during this time. Equation 2 also neglects any possible secondary chemistry involved in forming long-lived ROS.

We have interrogated the EESI-MS data for species which may act as tracers for ROS_{short} based on their time dependence. As mentioned above, in addition to *m/z* 199, a number of other ions (over the range *m/z* 107-295) show a characteristic maximum at early times in the reaction followed by notable decay over the remainder of the experiment (Figure 7(b)). All of these ions could contain enough oxygen atoms to possess ROS-active functional groups, although we do not obtain definitive molecular formulae with low resolution EESI-MS and a lack of previous literature assignments. While none of these ions map perfectly onto the ROS_{short} time series, several species may be present for each low resolution peak such that the loss of some ROS compounds is obscured by others with different time dependences. An alternative explanation is that, like *m/z* 199, at least a partial contribution to the signals may be unsaturated and therefore oxidised over time. Despite the general difficulty of detecting peroxides and other related ROS species via MS, recent progress has been made in this area (Steimer et al., 2017). More definitive detection of ROS and its precursors (e.g. condensed unsaturated species) via EESI-MS is a direction for future work.

3.2.2 Comparison to other studies of ROS formation in SOA

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Chen and Hopke (~~Chen and Hopke,~~ 2010), Chen et al., (~~Chen et al.,~~ 2011) and Chen et al., (~~Chen et al.,~~ 2017) studied ROS formation from the ozonolysis of limonene using a similar chemical assay with an offline filter sampling and sonication and filter extraction method. Like the current study, both short-lived and long-lived ROS are reported. However, ROS_{long} yields reported by Chen and Hopke (~~Chen and Hopke,~~ 2010) and Chen et al., (~~Chen et al.,~~ 2017) (0.15-0.19 nmol [H_2O_2] µg^{-1}) were lower than those determined here (0.42 nmol [H_2O_2] µg^{-1}). A number of experimental differences may be important. The three other studies employed dry conditions, compared to 40% RH here. The presence of water may influence the gas-phase fate of initial products and promote ROS formation (for instance, hydroperoxides from reaction of stabilised Criegee intermediates with water (Docherty et al., 2005)) as well as potentially modifying Henry's law partitioning of species such as hydrogen peroxide, and facilitating oligomerisation and hydrolysis reactions in the condensed phase (Gallimore et al., 2011). The higher mass loading here (375 µg m^{-3}) compared to these previous studies (30-160 µg m^{-3}) may be an important parameter through its influence on gas-particle partitioning and subsequent particle-phase reaction.

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Chen et al., (~~Chen et al.,~~ 2011) reported a correlation between $[O_3]$/[VOC] and $[\mathrm{ROS}_{long}]$ for a range of VOCs, and found higher ROS yields when ozone was in excess, presumably as a result of increased formation of oxygenated products such as peroxides. This is consistent with the higher $[\mathrm{ROS}_{long}]$ reported here ($[O_3]_{max}/[\mathrm{limonene}]_0 = 2.4$) compared to Chen et al.,

(~~Chen et al.,~~ 2017) ($[O_3]_0$/[limonene]$_0$ = 0.45). Furthermore, we proposed above that oxidation of the second (exo) double bond is partly occurring in the particle phase; this direct ROS formation in the particle may result in higher measured yields than gas phase only routes. These findings contrast with Chen and Hopke (~~Chen and Hopke,~~ 2010) who do not see a systematic trend in [ROS_{long}] with varying [O_3]/[limonene].

Qualitatively, the ROS observations in the current study compare well with Fuller et al., (2014) who noted that oxidised oleic acid aerosols contained both short- and long-lived ROS components using the same assay. The quantitative differences are summarised in Table 2. In summary, limonene ROS was formed in overall higher yield and the short-lived components were in general longer lived. These differences can be rationalised by considering the molecular properties of oleic acid and limonene.

	Limonene SOA (this study)	Oleic acid SOA (Fuller et al., 2014)
ROS_{long} yield (nmol [H_2O_2] µg^{-1})	0.42	0.14
Maximum fraction of ROS_{short} (%)	25-40	75
ROS_{short} lifetime (mins)	17	a few

Table 2: Quantitative differences in ROS formation between the current study (limonene SOA) and Fuller et al., (2014) (oleic acid SOA). More long-lived ROS is formed for limonene, but short-lived ROS appears more important for oleic acid.

The majority (~75 %) of ROS detected for freshly oxidised oleic acid particles was short-lived in nature, compared to a relatively smaller fraction for limonene SOA in the current study. Oleic acid is of low volatility and subject only to heterogeneous ozonolysis in the particle, so ROS production will be in-situ in the particle phase. As discussed above, the oxidation of limonene is a more complex multiphase process, and at least initially a large fraction of organic intermediates will be produced in the gas-phase. Since such species have short gas-phase lifetimes, many will go on to react further (e.g. to make long-lived ROS by reaction with water as discussed above (Docherty et al., 2005)) before entering the particle phase, leading to an overall different ratio of short- and long-lived ROS in the oleic acid and limonene-SOA particles.

The overall yield of ROS_{long} is higher for limonene by a factor of 3. Limonene contains two C=C, and therefore more potential to form highly oxygenated products including ROS than oleic acid with a single C=C. The fates of initial products may also be different as a result both of the reaction phase (purely particle phase vs multiphase) and the presence of water vapour in the current experiments which favours hydroperoxide formation (Docherty et al., 2005).

Finally, the ROS_{short} lifetime in Fuller et al., (2014) was shorter (a few minutes) than that reported here (17 minutes). We note that the oleic acid aerosol samples~~data~~ were collected onto filters, stored at room temperature for different lengths of time and extracted into solution for offline analysis, ~~in an offline manner~~ which decoupled ROS_{short} production and loss. This is not possible for online sampling and as discussed above this could result in an overestimated ROS_{short} lifetime for limonene SOA. Particle viscosity may also play a role: oleic acid remains liquid throughout ozonolysis (Hosny et al., 2016) and so in-particle reactions which consume ROS_{short} should not be inhibited. If limonene SOA were viscous, as considered above, this could extend the effective lifetime of short lived species.

The very recent study of Tuet et al., (2017) also found that the oxidative potential of SOA, quantified using a different assay, depends on the hydrocarbon precursor. Particularly high redox activity was found for naphthalene-derived SOA. However, comparing directly between different assays is challenging because the relative sensitivity towards different organic components (e.g. peroxides, quinones, radicals, polyaromatic hydrocarbons) is not well established (Fang et al., 2015).

4 Conclusions

The new 5.4 m^3 Cambridge Atmospheric Simulation Chamber (CASC) facility enables atmospheric chemical processes to be studied in the laboratory under relevant conditions with a high degree of time and chemical resolution. The characteristics of the chamber in terms of lights, mixing and wall losses have been thoroughly characterised as an important benchmark for current and future studies. The multiphase oxidation of limonene was studied using a range of continuous time-resolved particle and gas-phase measurements. The merits of highly time resolved measurements of particle composition and reactive oxygen species (ROS) were demonstrated and the links between the two explored for limonene SOA.

The majority of particle bound ROS detected in limonene SOA is long lived on the experiment timescale (4 hours) suggesting an important role for such health-relevant species in ambient particles. The overall yield of ROS was also significantly higher than for another SOA model system studied with the same methodology, oleic acid. This may have important implications for indoor air quality in particular given the abundance of limonene in cleaning and "air freshening" products. Even for relatively simple model SOA systems, the time-dependent characteristics of ROS are variable and reflect the underlying chemistry of the gas and particle phases in terms of reactivity, partitioning and viscosity.

The apparently slow loss of unsaturated species via heterogeneous ozonolysis, and the relatively long decay time of $\mathrm{ROS_{short}}$, both provide indirect evidence of a role for viscous particle formation in limonene SOA. We note that substantial uncertainties remain associated with in-particle diffusion and gas-particle exchange in viscous organic aerosols. However, if particle viscosity is impeding chemical reactivity, these particles are in essence a reservoir for reactive organics (both unsaturated and health-relevant). Such reactive carbon may therefore enjoy an extended lifetime in the atmosphere before reacting in more humid regions, or in particular the elevated RH and temperature conditions of the human airways. The potential atmospheric and health implications of this hypothesis merit further study for limonene SOA and other aerosol systems.

Supplementary information

Chamber characterisation data relating to the spectra of the light sources, the mixing of VOCs, and particle wall loss rates are provided. A proposed reaction scheme for particle-phase oxidation of unsaturated species is also included.

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Data access

Data presented in this study can be obtained by contacting the corresponding author.

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Supplementary material for **“Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)”** by P.J. Gallimore et al.

Spectra of chamber light sources

The spectrum of the tanning lamps used for photochemistry and transmission characteristics of the FEP used for the chamber walls is presented in Figure S1.

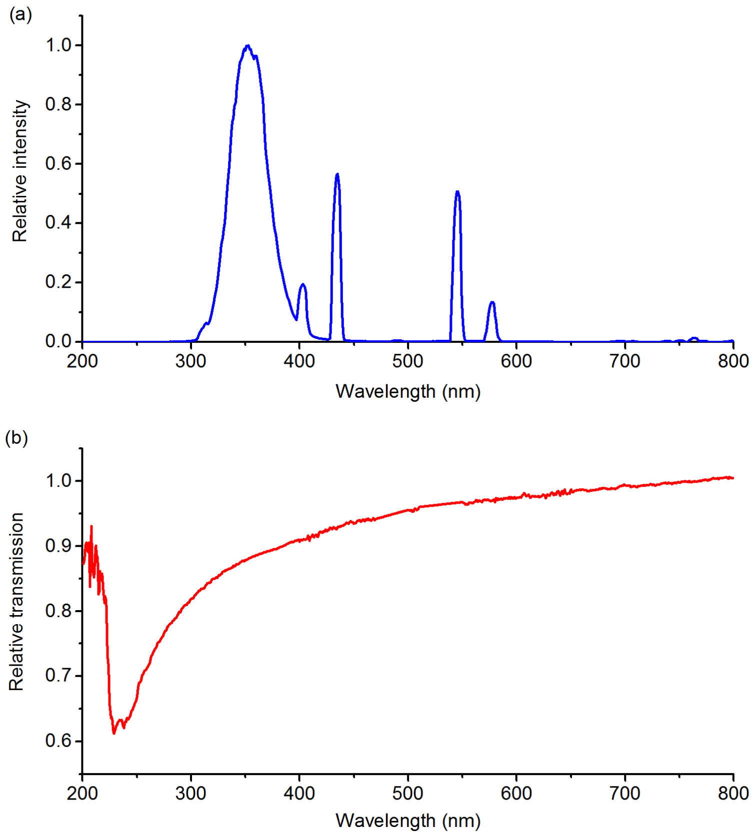

Figure S1: (a) Spectrum of tanning lamps installed in CASC facility. (b) Relative transmission of FEP film used for chamber walls, demonstrating good transmission at wavelengths above 300 nm.

Photolysis frequency of NO_2

A common approach to assess light intensity in atmospheric simulation chambers is to quantify the photolysis frequency of NO_2, J_{NO2}. Irradiation of NO_2 results in a photo-stationary state between NO, NO_2 and O_3. J_{NO2} can be calculated from these measured steady-state concentrations and the known bimolecular rate constant (k_{NO+O3} = 2 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, (Atkinson et al., 2004)) according to Equation S1:

$$J_{NO2} = \frac{k_{NO+O3}[NO][O_3]}{[NO_2]} \qquad \textbf{(S1)}$$

J_{NO2} was determined to be 0.49 ± 0.09 min^{-1}. Values of J_{NO2} from various chambers are compiled in Table S1.

Table S1: Comparison of NO_2 photolysis rates for different indoor chambers using artificial light sources.

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Chamber	J_{NO2} (min^{-1})	Light source	Reference
CASC	0.49	Tanning lamp	This work
Caltech	1.5	Black lamp	Cocker et al. (2001)
PSI	0.12	Xenon arc lamp	Paulsen et al. (2005)
GIG-CAS	0.49	Black lamp	Wang et al. (2014)

~~**Table S1: Comparison of NO_2 photolysis rates for different indoor chambers using artificial light sources.**~~

Chamber mixing

The mixing performance of the "air sprinkler" system was assessed by introducing α-pinene into chamber via the reactant port and monitoring its concentration over time at the sampling port via PTR-MS.

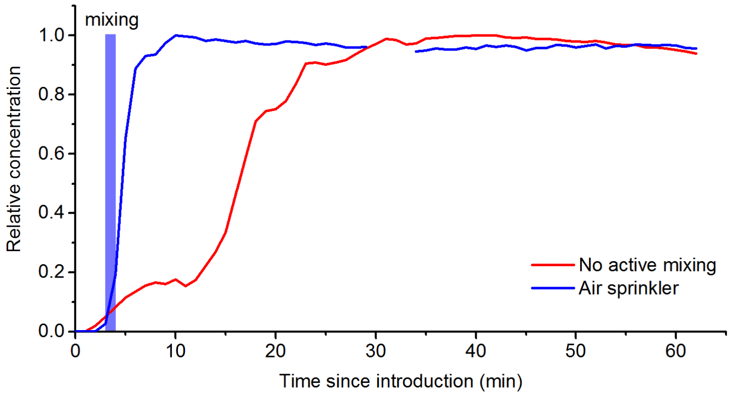

Figure S2: Relative concentration of α-pinene measured at the sampling chamber port after evaporation into the reactant chamber port. The use of 3 × 10s "bursts" of the air sprinkler mixes the chamber in a few minutes (blue curve) rather than 30-40 minutes by diffusion alone (red curve). The short gap in the blue data set at 30 minutes corresponds to an interruption to PTR-MS sampling.

Particle wall losses

The lifetime of particles in a simulation chamber is affected by wall losses which are dependent on the size distribution of the aerosol as well as chamber-specific properties such as volume and wall material. Wall losses were determined for the CASC facility by monitoring the evolving size distribution of ammonium sulfate (AS) aerosol over ten experiments between 0 and 70 % RH. Particles were generated from a 0.01 M aqueous AS solution ~~optionally~~ dried prior to introduction. A Kr-85 neutraliser (TSI 3077) was used to ensure an equilibrium aerosol charge distribution in some experiments, but the wall loss rates were not found to be substantially different without the neutraliser. No significant dependence on chamber RH was found for the range tested (0-70 %).

Deposition to the walls was treated as a first order process (Cocker et al., 2001). The total aerosol number and mass concentrations as a function of time can be described by Equations S2 and S3 respectively:

$$\frac{dN(D_p,t)}{dt} = -\beta_N N(D_p,t) \qquad \textbf{(S2)}$$

$$\frac{dM(D_p,t)}{dt} = -\beta_M M(D_p,t) \qquad \textbf{(S3)}$$

Where β_N and β_M are the characteristic number and mass weighted first order wall loss coefficients. 10 aerosol experiments were used to calculate $\beta_N = 0.201 \pm 0.025$ h^{-1} and $\beta_M = 0.166 \pm 0.020$ h^{-1}, respectively. This corresponds to aerosol lifetimes of 5-6 hours, comparable to other chambers as illustrated in Table S2.

Table S2: Comparison of number-weighted and mass-weighted particle wall loss rates for different Teflon chambers.

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Chamber	Volume (m^3)	β_N (h^{-1})	β_M (h^{-1})	Reference
CASC	5.4	0.201	0.166	This work
Caltech	28	0.09-0.18	-	(Cocker et al., 2001)
PSI	27	0.209	0.139	(Paulsen et al., 2005)
EUPHORE	200	0.18		(Martın-Reviejo and Wirtz, 2005)

SAPHIR	270	0.27	-	(Rollins et al., 2009)
CMU	12	0.40	-	(Donahue et al., 2012)
GIG-CAS	30	0.17	-	(Wang et al., 2014)

~~**Table S2: Comparison of number-weighted and mass-weighted particle wall loss rates for different Teflon chambers.**~~

The procedure for particle wall loss correction is similar to that described by Rollins et al., (2009) who assume that particle concentration changes between consecutive measurements (~ 2 minutes) can be decomposed into two separate terms: wall deposition and SOA production. By iteratively increasing the measured concentration at each time step to offset the losses calculated from Equation S3, a loss-free concentration is calculated.

The resulting loss-corrected time series (Figure 3) suggests that for limonene ozonolysis SOA production continues for 2-3 hours via multi-generational reactions in the chamber and reaches a maximum value of 375 µg m^{-3}. This corresponds to an aerosol yield (defined as the mass of SOA formed per mass of reacted VOC) of 32 %. Aerosol yields are dependent on a number of parameters including aerosol mass loading and oxidation conditions, as well as chamber-specific factors. Our yields are consistent with previous studies at similar mass loadings, which occupy a broad range from ~30-90 % (Chen and Hopke, 2010; Leungsakul et al., 2005; Youssefi and Waring, 2014; Zhang et al., 2006).

Heterogeneous oxidation mechanism in PG-AM

The proposed mechanism which forms $C_9H_{14}O_5$ from $C_{10}H_{16}O_4$. This reaction is represented in PG-AM with a yield of 0.4 based on exo-C=C ozonolysis for β-pinene (Jenkin, 2004). The alternative branch which forms a C_9 Criegee intermediate and formaldehyde, is not included due to the uncertainties surrounding particle-phase Criegee intermediate chemistry.

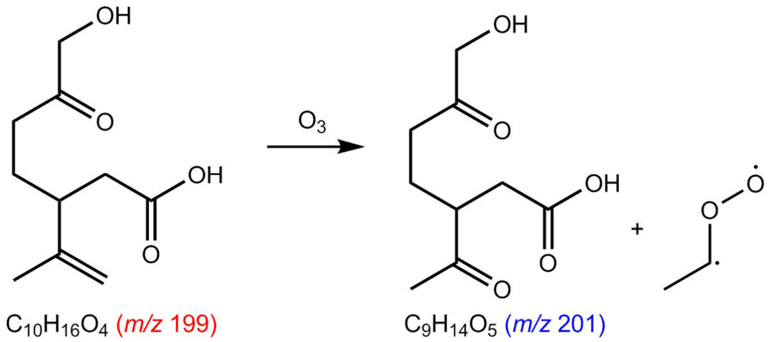

Figure S3: Proposed reaction of unsaturated $C_{10}H_{16}O_4$ (treated as 7-OH limononic acid in the model) with ozone to form the carbonyl product $C_9H_{14}O_5$. Model results from PG-AM are compared with time series for *m/z* 199 and 201 respectively (Figure 5(b)).

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Author response – Reviewer #1

Reviewer comments

This is an interesting paper highlighting the capabilities of a new simulation chamber in Cambridge. A variety of online measurement techniques were used to characterise the gas and particles formed during limonene ozonolysis. Of particular interest are the online reactive oxygen species measurements, showing potential difference in the times scale for ROS formation. I do have a number of concerns that need to be clarified before publication in ACP.

We thank the reviewer for these constructive comments and address them point-by-point below.

General comments

Experimental

Firstly there is too little experimental detail given in this paper. The authors direct the reader to other papers for basic details on the mass spectrometers. For instance the flow rate and mass analyser (and indeed the mass resolution) used for EESI is not given. Since this is a unique instrument, the reader should be given much more extensive details of the instrumentation and its capabilities without needing to read another paper alongside this one. There are lots of cases where the reader is directed to a paper that has been submitted and so I cannot judge the links inferred.

We have described the unique capabilities and operating conditions of the EESI-MS instrument in substantially more detail and subdivided the Chamber Instrumentation section to improve clarity. The submitted paper (Gallimore et al., 2017) is now published and cited in relevant parts of this manuscript.

The new section 2.2.1 (p8 line 10–p9 line 19) now reads:

"2.2.1 Extractive Electrospray Ionisation Mass Spectrometry

Extractive Electrospray Ionisation Mass Spectrometery (EESI-MS) is an online particle analysis technique and the design and optimisation of our EESI source is described in Gallimore and Kalberer (2013). It contains a commercial electrospray probe (Thermo Scientific HESI-II) with a custom-built aerosol injector and manifold. The primary electrospray was operated at a voltage of –3.0 kV and a N_2 sheath flow rate of 0.8 L min^{-1}. A water–methanol 1:1 mixture (Optima LC-MS grade solvents; Fisher Scientific) containing 0.05% formic acid (90%, Breckland Scientific) was infused into the ESI probe at 10 µL min^{-1}. Chamber air was delivered into the source at 1 L min^{-1}. Collision and extraction of the SOA particles by primary electrospray droplets occurs in an off-axis configuration with respect to the MS inlet, to minimise source contamination and memory effects through particle deposition. The EESI source was coupled to an ion-trap mass spectrometer (Thermo Scientific LTQ Velos). Spectra were acquired in the negative ionisation mode over the range *m/z* 50-500, with a mass resolution ~ 2000 (full width at half maximum, FWHM) at *m/z* 400.

Gallimore and Kalberer (2013) demonstrated that the relative EESI-MS ion intensity correlated with the mass concentration of tartaric acid particles delivered into the source, suggesting that the entire particle bulk is extracted for analysis. More recently, Gallimore et al., (2017) showed that the kinetics of particle-phase reactions could be monitored; loss rates derived from EESI-MS measurements compared well with other studies, and spectra were compared to Liquid Chromatography (LC) MS to confirm that the EESI-MS assignments were present in the aerosol rather than formed as artefacts in the ion source."

The following sub-headings have been added, and the OPROSI section expanded:

P9, line 26: "2.2.2. Proton Transfer Reaction Mass Spectrometry"

P10, line 9: "2.2.3 Online Particle-bound Reactive Oxygen Species Instrument"

P10, lines 13–25: "The continuous sample inflow (5 L min^{-1}) passes through a $PM_{2.5}$ cyclone (URG-2000-30E-5-2.5-S) and charcoal denuder prior to entering into a particle-into-liquid sampler (PILS). Particles are collected into a 1 mL min^{-1} spray containing horseradish peroxidase (HRP) (TypeVI, 1 unit mL^{-1} in 10% phosphate buffer solution (PBS), Sigma Aldrich) which reacts with ROS present in the particles. This is combined with a 1mL min^{-1} aqueous 2'7'-dichlorofluorescein (DCFH) solution (10µM, 10% PBS, Sigma Aldrich), which is oxidised to a fluorescent product (DCF) by the ROS-HRP solution. After a 10 minute reaction time at 40 °C the concentration of DCF is quantified via fluorescence spectroscopy. The fluorescence response is calibrated with H_2O_2 and quantitative ROS concentrations are reported as "[H_2O_2] equivalents". The assay also responds to organic peroxides. It is likely sensitive to HO_x radicals and ions such as superoxide but we are unable to obtain suitable standards to test this directly."

More general discussion of EESI-MS (previously p7 lines 4-9) has been moved from the Methods section to the Introduction (p4 line 14–p5 line 1): "EESI retains the key advantage of "soft" electrospray ionisation MS techniques, namely that quasi-molecular ions are produced from aerosol analytes with minimal fragmentation. Individual molecular species can be identified and relative intensity changes monitored over time as a measure of concentration changes with particles (Gallimore et al., 2017)."

Again, since this is the first chamber paper I need more details. The chamber is apparently collapsible but I couldn't work out if this was what was happening or was a dilution flow being used? What was the final volume of the chamber and does that impact wall losses? There are lots of details of the lamps and then the NOx chemistry, but then I assume these are not actually used in the one experiment that is shown? There seems to be a disconnect- is this a chamber characterisation paper (which is limited) or a SOA characterisation paper? Most of the chamber characterisation is in the SI.

We have added clarification regarding chamber sampling, which does not use a dilution flow (p7 lines 25–28): "Typically a maximum of 1.5 m^3 air was removed during a batch experiment, and guide rails on the chamber frame allow the bag to inflate and deflate at ambient pressure. Up to ~60 % of the chamber volume could be sampled using this system if required."

We have added an addition sentence to section 2.4 (p12 lines 23–24): "The potential impact of changes in chamber volume during sampling (maximum ~30 %) on wall loss rates was not considered."

We performed a thorough set of characterisation measurements, including on the light sources and resulting NO_x photo-stationary state, before embarking on SOA experiments. We felt it was important to benchmark the chamber so that future studies are informed by these measurements and the reader can compare CASC to other chambers. The SOA discussion which follows, although performed with the lights off, illustrates the instrumental and scientific capabilities of the chamber and uses characterisation measurements such as particle wall loss rates.

We have added the following clarification (p14 lines 18-19): "Ozonolysis was performed under dark conditions without the addition of NO_x."

Diffusion versus ozone uptake

Firstly more details are needed about the model. Is partitioning based solely on equilibrium partitioning and if so how were the vapour pressures of the products determined? How was the reaction rate coefficient of ozone with the products determined? I would have thought a C10 species with only 4 oxygens would be a semi-volatile species and so its profile could be impacted by its gas phase reactivity as well, with subsequent re-volatilisation. However, I cannot tell from the data presented how the model deals with this.

We have added additional details to this section which more fully describe partitioning and diffusion in the model. For the simulations presented in the discussion manuscript, we assumed the $C_{10}H_{16}O_4$ product was non-volatile. In response to the reviewer's question we calculated a partitioning coefficient and included a gas-phase loss for this species. Based on later comments about potential products of this reaction we have included such a product ($C_9H_{14}O_5$) in the model which can be compared to *m/z* 201.

The revised and extended section reads (p12 line 26–p14 line 2): "Illustrative model simulations were performed using the Pretty Good Aerosol Model (PG-AM). PG-AM is described in detail in Griffiths et al., (2009) and Gallimore et al., (2017). The model treats the following processes in a kinetic framework: chemical reaction in both the gas and particle phases, gas-particle exchange via uptake and evaporation, and diffusion within the particle. Fluxes between the gas and particle phases depend on the aerosol surface area as well as each species' accommodation coefficient (α, dimensionless) and partitioning coefficient (K, M atm^{-1}). Diffusion is parameterised according to Griffiths et al., (2009); the particle is treated as a series of nested shells, with the rate of transport of each species between shells determined by its diffusion coefficient (D, cm^2 s^{-1}). The differential equations governing reaction and diffusion are integrated forwards in time using Mathematica (v11, Wolfram).

In this study, reaction of unsaturated $C_{10}H_{16}O_4$ with ozone was simulated for a single particle of characteristic radius $r_{eff} = 3V_t/S_t = 84$ nm based on the measured total particle volume (V_t) and surface area (S_t). $C_{10}H_{16}O_4$ was assumed to be 7-hydroxy limononic acid for vapour pressure calculations and formation of a corresponding carbonyl oxidation product, $C_9H_{14}O_5$, was represented in the model mechanism (Figure S3). The vapour pressures of $C_{10}H_{16}O_4$ and $C_9H_{14}O_5$ were estimated at ~2.8×10^{-5} Pa and ~2.2×10^{-6} Pa using the online model EVAPORATION (Compernolle et al., 2011) which performed well in our tests for a species with known vapour pressure, pinic acid. The resulting partitioning coefficients calculated from these vapour pressures, $K \sim 2 \times 10^{10}$ M atm^{-1} and $\sim 2 \times 10^{11}$ M atm^{-1} means that both species are almost entirely condensed (< 99 %) under the experimental conditions.

The accommodation coefficient for organic species was fixed at $\alpha_{org} = 0.1$. Ozone partitioning ($K_{O3} = 0.1$ M atm^{-1}) (Morris et al., 2002) and accommodation ($\alpha_{O3} = 10^{-3}$) (Gallimore et al., 2017) were fixed based on the literature for oleic acid particles. The particle phase bimolecular rate constant for ozonolysis (k_p^{II}) and the ozone and organic diffusion coefficients (D_{O3} and D_{org}) were varied as described in the results. A fixed gas-phase rate constant for exo double bond ozonolysis, $k_g^{II} = 7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} (Zhang et al., 2006) was also included. However, gas-phase loss was not competitive with particle phase oxidation due to this relatively small rate constant and the low vapour pressure of $C_{10}H_{16}O_4$. The carbonyl product $C_9H_{14}O_5$ was formed with a yield of 0.4, based on the branching of exo-C=C ozonolysis products for β-pinene (Jenkin, 2004). We did not attempt to account for the fate of the other reaction branch featuring a C_{10} Criegee intermediate due to the wide range of possible Criegee intermediate products in the condensed phase including peroxides, carbonyls and secondary ozonides (Lee et al., 2012; Maksymiuk et al., 2009)."

The "submitted" paper (Gallimore et al., 2017), which includes a full model description and characterisation also is now published and referred to here.

Clearly m/z 199 shows a different profile than the other species shown. However, this is not the only ion shown with a double bond. m/z 185 is most likely limonic acid (C9H13O4). This also has an intact double bond but clearly does not show the same effect. Have you looked for any other species with an intact double bond? Can you predict what the product of m/z 199 might be and look for the trend in that? I realise it may be complicated by isobaric species.

We agree that *m/z* 185 and other ions may be unsaturated, and add the following discussion (p20 line 28–p21 line 2): "We note here that other potentially unsaturated ions such as *m/z* 185 do not exhibit a decrease at longer times. Limonic acid is one likely assignment but Walser et al., (2008) have proposed saturated alternatives. It may be that the stable *m/z* 185 signal at longer times is a combination of loss of limonic acid and compensating production of other isobaric species, but we are unfortunately unable to investigate this further here."

We show a number of time series with a similar time dependence over a wide *m/z* range in Figure 7 which may plausibly be unsaturated. We do not wish to speculate on their specific structures without supporting evidence but add the following sentence

(Line p27 lines 3–5): "An alternative explanation is that, like *m/z* 199, at least a partial contribution to the signals may be unsaturated and therefore oxidised over time."

Following the reviewer's suggestion, we have investigated possible products of *m/z* 199 ozonolysis and find the most likely particle-phase product to have *m/z* 201. We have added discussion (p20 lines 11–15): "Assuming $C_{10}H_{16}O_4$ to be 7-hydroxy-limononic acid, a major ozonolysis product would be a carbonyl with formula $C_9H_{14}O_5$ (*m/z* 201, Figure S3). The *m/z* 201 time series in **Error! Reference source not found.**(b) increases slowly during the period after 50 minutes when *m/z* 199 is depleted, consistent with this hypothesis. We explore this proposed reaction further using the PG-AM model below."

This proposed reaction is illustrated in the supporting information (Figure S3).

Additional discussion is provided in the PG-AM section (p21 lines 21–23): "Formation of the predicted carbonyl product of $C_{10}H_{16}O_4$ ozonolysis, $C_9H_{14}O_5$, was also simulated and the resulting reactant and product time series were compared to *m/z* 199 and 201 respectively in **Error! Reference source not found.**(b)."

This continues (p22 lines 1–4): "There is good correspondence between the model and measurements for both $C_{10}H_{16}O_4$ (*m/z* 199) and $C_9H_{14}O_5$ (*m/z* 201). This is consistent with the hypothesis that 7-hydroxy limononic acid and its carbonyl oxidation product make the dominant contribution to the measured *m/z* 199 and 201 signals."

A product time series has been added to an updated Figure 5(b), and the caption has been updated accordingly (p19 lines 5–6): "The dotted lines are a PG-AM simulations for the heterogeneous reaction of $C_{10}H_{16}O_4$ with ozone to form $C_9H_{14}O_5$, assuming semisolid SOA."

Given this additional discussion we have subdivided the molecular composition section (3.1) into PTR-MS and EESI-MS measurements from CASC (3.1.1, p15 line 7) and PG-AM modelling (3.1.2).

ROS quantification

I have a concern here about the method used to correct the data. Was the ROS and/or the SOA mass corrected for particle loss? On reading its seems like you use the ROS measured in the chamber and divide this by the loss corrected particle mass (I have assumed this is what you have done). If this is the case, I disagree with his approach. The ROS you have measured is based on what is actually in the chamber when you measure. The amount of SOA mass is much lower than the corrected number. Thus you are normalising to particle mass that is not present. If you used the actual measured particle mass the trend would look very different, increasing at longer reaction times. This needs to be clarified and the approach justified.

Apologies for the confusion. Both the particle mass (SMPS) and particle-bound ROS signal (OPROSI) were loss corrected using the same procedure. Before correction, both raw signals decrease at longer times due to wall losses. We have added the following clarification (p23 lines 4–5): "The raw ROS concentration data were wall loss corrected using the same procedure as for the particle mass, and the corrected data are presented in **Error! Reference source not found.**.”

Specific points

In general the text is well written and easy to follow.

Page 1: not sure you need “new” in the title

Since this is the first characterisation and demonstration of CASC, we would like to keep “new” in the title.

Page 3, line 3: Give estimate of limonene emission

The sentence now reads (p3 lines 3–4): “Limonene is one of the most abundant BVOCs in the troposphere, with an estimated biogenic emission rate of 11 Tg yr^{-1} (Guenther et al., 2012).”

Page 3: There is very little given here about previous studies of limonene. I would expect some more background.

We have included some extra background on the chemistry of limonene SOA. The revised background reads (p3 line 13–p4 line 3): “Limonene contains two reactive C=C double bonds which results in multiple generations of oxidation products (Bateman et al., 2009; Kundu et al., 2012; Walser et al., 2008) containing a range of functional groups including carboxylic acids, carbonyls, peroxides and alcohols. Previous studies have mainly focused on the reaction of limonene with ozone (Kundu et al., 2012; Zhang et al., 2006), with relatively few OH-aging experiments reported, particularly with respect to chemical characterisation (Zhao et al., 2015). Ozone is a major sink for limonene under a range of atmospheric conditions (Atkinson and Arey, 2003) and will dominate in indoor scenarios which may be most relevant for the health effects of limonene SOA (Waring, 2016). The endo C=C of limonene is more susceptible to ozonolysis by a factor of 10-50 (Zhang et al., 2006) and some of the first-generation ring opening products are condensable (**Error! Reference source not found.**). Subsequent oxidation of the remaining double bond may therefore occur in either the gas or condensed phases depending on the properties of the initial products and the aerosol loading.

The ability of limonene to form multifunctional products via successive oxidation steps results in high aerosol yields relative to other terpenes (Hoffmann et al., 1997; Zhang et al., 2006). Aside from ozonolysis, other condensed-phase reactions further modify the composition of limonene SOA. Kundu et al., (2012) report the reactive uptake of carbonyls to form oligomeric products, while the formation of light-absorbing “brown carbon” via uptake and reaction of ammonia and amines appears to be particularly efficient for limonene SOA compared to other precursors (Bones et al., 2010; Updyke et al., 2012).”

Page 4, line 1: Change to “was studied”

This has been changed (p4 line 9).

Page 4, line 3: FEP given before explained

We have changed "FEP" to "Teflon" (p4 line 11).

Page 5, Fig 2: Collapsible spelt wrong. Im assuming there is no dilution here. What is the mechanism that allows the chamber to collapse?

The spelling has been corrected (Figure 2). The modified experimental section discussed above now describes the guide rails which allow the bag to inflate and deflate without dilution (p7 lines 25–28).

Page 6, line 5: How clean is the zero air? Any peaks in PTR-MS above detection limit?

We have modified the following sentence (p7 lines 2–4): "The chamber is filled with air from a zero air generator (KA-MT2, Parker Hannifin, UK) which uses a molecular sieve, an activated charcoal bed and filters to remove water, VOCs and particulates respectively." See response to the comment below for contaminant quantification via PTR-MS.

Page 6, line 9: Im surprised you don't see any OVOC from the water. How often is it changed?

The water is changed every week at minimum, as now detailed (p7 line 7): "…which is replaced at least each week."

On revisiting the detailed PTR-MS data we could observe OVOC introduction – apologies for this earlier error. We have amended the discussion accordingly (p7 lines 8–10): "We monitored changes in particle and VOC concentrations during water introduction and found particle formation to be negligible, but observed up to ~10 ppb acetone and lesser quantities (< 2 ppb) of C_1-C_2 aldehydes and acids."

Page 7: As described above there is far too little experimental detail included here, especially for the ROS and EESI-MS. How many OVOC standards have you investigated to ensure there is no in-source dimers formed or in-source fragmentation? Ive looked at the Gallimore and Kalberer paper, but there is very limited information on using the signal as a pseudo-quantification. Do you think the changing mix of organics will lead to any matrix effects?

As discussed in the general section, we have created sub-sections and included substantially more experimental detail for EESI-MS (p8 line 11–p9 line 19) and OPROSI (p10 lines 10–28).

The EESI-MS section cites the now-published Gallimore et al., (2017) and emphasises that our EESI-MS spectra compare well with LC-MS (suggesting ions correspond to aerosol analytes rather than in-source artefacts) and can be used for kinetic experiments (suggesting that relative quantification is not significantly influenced by evolving SOA composition).

Page 8, lines 3-4: Need spaces between units

We have introduced spaces (p10 lines 1–2).

Page 8, line 11: change to "can be associated"

This has been changed (p10 line 10).

Page 8, line 21: I assume this should be "Stainless steel'. Was a filter used in the PTR-MS sample line?

We have corrected this to "Stainless steel" (p11 line 2). The PTR-MS sample line was not filtered.

Page 10, line 1: a-pinene is a rather volatile species to use to account for wall losses. Please justify its use here.

We have deleted reference to α-pinene wall losses in this section.

Page 10, line 16: This section lacks details rather than relying on a different paper.

As discussed in the general comments above we have revised and extended this section extensively (p12 line 26–p14 line 2).

Page 11: I was rather surprised after the characterisation section that only 1 experiment was included. How representative are the results here of other ozone – limonene experiments? Why not show a OH reaction as well?

The experiment shown following the characterisation section was intended to be illustrative of the capabilities of the chamber during SOA experiments, particularly the unique EESI-MS and OPROSI instruments. We compare to other studies of limonene SOA formation and find good agreement, for example in terms of oxidation products identified, but also make new contributions, for example in terms of the time dependence and yield of ROS from SOA.

We presented an ozonolysis experiment for two reasons: Firstly, ozone is a major sink for limonene under all conditions, especially indoors. Secondly, previous studies focus on ozonolysis, with few OH studies reported, and comparison of results from our new chamber with previous studies was an important aspect of this paper. We emphasised these points in the introduction discussed above (p3 lines 17–22) and add an additional sentence here (p14 lines 5–9): "We focus on ozonolysis in order to compare the results from CASC with a range of previous studies which measure SOA chemical composition (Bateman et al., 2009; Kundu et al., 2012; Maksymiuk et al., 2009; Walser et al., 2008). In addition, from a human health perspective, exposure to limonene SOA is most likely to occur indoors, where ozone is the dominant sink of limonene."

Page 11, line 14: give ± 1σ on diameter

This now reads (p14 lines 22–23): "…a single mode with diameter ~160 nm and standard deviation σ=0.21."

Page 12, line 6: You use the term "characteristic" but I don't know what this applies to? It sounds like a description of more than one experiment but that is not presented here.

We have rephrased this sentence to read (p9 lines 9–10): “Limonene was lost from the chamber over a period of 30 minutes, due to reaction with ozone (**Error! Reference source not found.**).”

Page 12, line 6: insert “the PTR”

We have corrected this (p15 line 11).

Page 12, line 14: Which of these structures is most likely based on mechanisms.

All the possible structures require multiple secondary reactions and we are not in a position to assess which if any are most likely. We have added the following discussion (p15 line 19–p16 line 2): “Plausible structures require secondary OH-mediated fragmentation of the limonene backbone and could include known atmospheric consituents such as propanoic acid (Chebbi and Carlier, 1996), hydroxyacetone (Zhou et al., 2009) or methyl acetate (Christensen et al., 2000).”

Page 12, Fig 4: The purple and blue lines are very similar. Can an ozone profile be included for comparison.

Adding an ozone profile to Fig 4 would result in a very crowded plot. We have therefore added the profile to Fig 3 (p4 line 1) and updated the caption accordingly (p4 lines 2–5): “Figure 3: Time series showing evolution of SOA mass (primary y-axis) and ozone concentration (secondary y-axis) in the chamber. The measured SOA concentration (red curve) was corrected to account for particle deposition to the chamber walls (black curve).”

We have also added discussion of the ozone profile in the context of particle-phase ozonolysis (p20 lines 3–5): “In addition to SOA composition changes, oxidation at longer times is also indicated by a continuing decrease in ozone after limonene has been consumed (**Error! Reference source not found.**).”

Page 12, line 8: Limonaldehyde appears to form slightly later that the limonaketone. How do these compare to the ROS short profile?

The reviewer is correct; limononaldehyde peaks at 14 minutes, limonaketone at 11. We have noted the limononaldehyde time in the text (p16 line 17).

The shape of these species resembles $\text{ROS}_{\text{short}}$, which peaks later at 23 minutes (added, p26 line 3). Although possibly tracers for short-lived ROS, the OPROSI should not respond to gas-phase VOCs due to the charcoal denuder on the instrument’s inlet.

Page 13, line 12: Can these species be seen in previous studies using PTR-MS. I don't know but Im surprised you don't see them at all.

These peaks were present in the PTR-MS study of Ishizuka et al., (2010). We added a note to this effect (p17 lines 1–2): “The same peaks were observed in limonene ozonolysis experiments performed by Ishisuka et al., (2010).”

Page 13, line 26: Do you think that dimers are present based on the masses observed? I would think even if both double bonds are oxidised you would still see species up to C18, say from reaction of the stabilised Criegee intermediate with other products.

We agree that dimers could form even following the oxidation of both C=C, and we see evidence of oligomerisation reactions which are now mentioned (p17 lines 14–17): "*m/z* 245 ($C_{11}H_{18}O_6$), one of the most abundant products from Kundu et al., (2012) is observed here and is along with other C_{11}-C_{15} products is indicative of oligomerisation, specifically via the reactive uptake of gas-phase carbonyls to the particle phase."

We have added a sentence discussing possible stabilised CI oligomers (p17 lines 20–22): "Reactions of stabilised Criegee intermediates with initial products could plausibly produce other high molecular weight species. However, these are not observed here and it is likely that…"

Page 14, line 12: can you estimate the elemental composition of these ions?

We now discuss *m/z* 201 ($C_9H_{14}O_5$) as a likely oxidation product of *m/z* 199 (p20 lines 11–15, response to general comment above) and have added an estimated composition for *m/z* 215 ($C_{10}H_{16}O_5$, p18 line 6).

Page 15, line 19: I got a bit confused as to how small carbonyls were related? Do you mean heterogeneous or in-particle chemistry of two smaller OVOC is forming a C10 compound rather than the first stages of limonene oxidation?

That is correct. We have added the following clarification (p19 line 20–p20 line 1): "Secondary formation routes may include reaction of small carbonyls with initial $C_{<10}$ oxidation products in the particle phase, as discussed for *m/z* 245 above…"

Page 19, line 2: I don't like the use of the word decomposed – suggests some chemistry. Perhaps use "split".

We have used "split" as suggested (p6 line 7).

Page 20, fig 7: Can you predict possible elemental formulae for the small ions? How efficient is gas phase removal of OVOC products in the ROS injection system?

For the major products discussed above our assignments are based on previous literature reports. Since the small ions discussed here (m/z 107 and 153) have not been previously proposed as products we are reluctant to speculate. P26 line 29–p27 line 1 now reads: "All of these ions could contain enough oxygen atoms to possess ROS-active functional groups, although we do not obtain definitive molecular formulae with low resolution EESI-MS and a lack of previous assignment in the literature."

We emphasise that major products are assigned based on previous literature (p17 line 11): "We base potential assignments on previous literature."

We employ a charcoal denuder to remove VOCs from the gas phase before ROS analysis. The denuder removes ozone to below detection limit levels and while we have not tested organic standards, such denuders are routinely used in aerosol sampling to remove VOCs (Grover et al., 2005; Salvador and Chou, 2014).

Page 23, line 9: I don't understand what is meant by "collected in an offline manner". Needs some more details.

We have clarified this point (p29 lines 10–12): "We note that the oleic acid aerosol samples were collected onto filters, stored at room temperature for different lengths of time and extracted into solution for offline analysis, which decoupled ROS$_{\text{short}}$ production and loss."

SI

Table legends need to be above the tables.

The table legends have been moved.

Page 3, Table S1: can you add what kind of lamps are in the other chambers for comaprsion.

The light sources for each chamber have been added (p3, Table S1).

Page 5, line 7: Were the particles dried or not for the wall loss experiments?

We have deleted "optionally" (p5, line 7) and added the following sentence (p5 lines 9–10): "No significant dependence on chamber RH was found for the range tested (0-70 %)."

Page 6, line 13: How does this yield compare to previous studies?

We have added the following comparison (p6 lines 13–16): "Aerosol yields are dependent on a number of parameters including aerosol mass loading and oxidation conditions, as well as chamber-specific factors. Our yields are consistent with previous studies at similar mass loadings, which occupy a broad range from ~30-90 % (Chen and Hopke, 2010; Leungsakul et al., 2005; Youssefi and Waring, 2014; Zhang et al., 2006)."

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Author response – Reviewer #2:

General comments

This manuscript showed interesting results about the online composition changes of gas and particle phase products during the photolysis of limonene by using mass spectrometry. Meanwhile, they also measured the reactive oxygen species (ROS) formation by limonene SOA in water by using a fluorescent assay. Based on these experiments and mathematic modelling, the authors claimed that diffusion-limited and bulk reaction-limited scenarios might have resulted in the low loss of some low volatile compounds like 7-hydroxy limononic acid ($C_{10}H_{16}O_4$). Furthermore, the authors also claimed that stable ROS dominate the total ROS formed by limonene SOA in water especially in a long timescale during the oxidation of limonene in the Cambridge Atmospheric Simulation Chamber (CASC). Overall the results are interesting and the manuscript was written well. If my following concerns can be addressed, I would like to recommend this manuscript to be published in Atmos. Chem. Phys.

We thank the reviewer for these comments and respond point-by-point below.

Specific points:

1. The title of "Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)" shows that the ROS in this article was generated during the limonene oxidation in CASC. However, the ROS data in Fig. 6 and 7 were relevant to the limonene SOA dissolved water solutions by using Online Particle-bound Reactive Oxygen Species Instrument (OPROSI). Even though some kind of ROS (organic peroxides etc.) could be generated during the limonene SOA formation process, the title is not accurate to describe the source of the ROS in this article.

The reviewer points out that the detected ROS may be a combination of ROS formed in the aerosol, and additional ROS formed in aqueous solution following particle collection. While recent studies have indicated that OH radicals form when SOA is dissolved in water (Badali et al., 2015; Tong et al., 2016) the proposed mechanisms involve light or transition metals, neither of which are present in the OPROSI collection system.

Organic peroxides and other related functional groups have long been shown to be a major component of monoterpene SOA (Camredon et al., 2007; Docherty et al., 2005) and in Wragg et al., (2016) we demonstrated that the assay used in our study is sensitive to organic peroxide standards. We therefore prefer to keep the title as is, and address some of the specific points about different types of ROS in response to comment 2.

2. In line 16-18 of page 2: "Similarly, organic reactive oxygen species (ROS), including organic peroxides and oxygen centred radicals, are thought to be associated with the observed negative health effects of airborne particles (Verma et al., 2009)." The authors introduced the definition of ROS for the first time in this article. However, they did not clarify the difference of the term ROS used in this article from that in literatures (e.g. Klaus Apel and

Heribert Hirt., Annu. Rev. Plant Biol. REACTIVE OXYGEN SPECIES: Metabolism, Oxidative Stress, and Signal Transduction. 55, 373-399, 2004; Josep M. Anglada et al., Interconnection of Reactive Oxygen Species Chemistry across the Interfaces of Atmospheric, Environmental, and Biological Processes. Acc. Chem. Res. 48, 575-583, 2015.), especially the authors should clarify the ROS species their method (OPROSI) could characterize.

We have modified the introduction to clarify this definition of ROS (p2 lines 16–22): "Similarly, species including hydrogen peroxide and oxygen-centred radicals and ions can cause biological stress and damage (Anglada et al., 2015; Apel and Hirt, 2004). Related organic compounds including peroxides have been shown to be major SOA components (Camredon et al., 2007; Docherty et al., 2005). Together, these reactive oxygen species (ROS) are thought to be associated with the observed negative health effects of airborne particles (Verma et al., 2009)."

An OPROSI experimental subsection (2.2.3) has been added which describes the species characterised by OPROSI (p10 lines 21–25): "The fluorescence response is calibrated with H_2O_2 and quantitative ROS concentrations are reported as "[H_2O_2] equivalents". The assay also responds to organic peroxide standards. It is likely sensitive to HO_x radicals and ions such as superoxide but we are unable to obtain suitable standards to test this directly."

3. In Fig. 6 at page 18, the author showed a plateau of ROS formation in limonene SOA water solutions (0.42 nmol [H2O2] μg -1). Afterwards, the authors used the equations 1 and 2 (page 19) to categorize the total ROS to short and long modes. During this analysis, the assumption of "[ROSlong] scales with the total particle mass in proportion to the final mass weighted ROS concentration (as do most individual aerosol components in Figure 5(b))….." has been used. However, the plateau in Fig. 6 may be induced by a homeostasis of long and short lifetime ROS. So the used equivalence of [ROSlong]=0.42×MASSSOA can overestimate the yield of ROSlong. In the same timescale, the yield of limonene SOA is also relatively stable (Fig.3), so it is reasonable to see the plateau of EESI mass spectrum intensity in Fig. 5(b). If the authors would like to connect the plateau of Fig. 5(b) with the plateau Fig. 6, they need a response sensitivity test to confirm the ROS value indicated by the OPROSI system are real relevant to the ions showed in Fig. 5.

By definition in Equation 2, the final ROS_{long} yield will be 0.42 nmol [H_2O_2] μg^{-1}. We have added discussion of possible overestimated ROS_{long} yields at the start of the experiment (p24 line 31–p25 line 2): "If some ROS_{short} were converted to ROS_{long} during the early part of the experiment, Equation 2 could underestimate the ROS_{short} contribution to [ROS_{total}] and correspondingly overestimate [ROS_{long}] early in the experiment."

Regarding connecting the "plateaus" in Fig 5(b) and Fig 6, we are not proposing a direct link between the specific ions in Fig 5(b) and ROS, but using this as an illustration that the general aerosol composition (and gas phase composition and particle mass) is not changing significantly in the ROS plateau region.

4. In line 6-10: "We propose that ROSlong are a group of relatively stable long-lived products (such as organic peroxides) which constitute the stable ROS at the end of the experiment, and ROSshort are reactive species (possibly radicals or otherwise short-lived compounds such as reactive peroxides) species which are produced directly from ozonolysis or other early-generation reactions." The authors should discuss more about the component of ROSlong and ROSshort. In addition, numerous studies indicated that limonene SOA and other precursor-generated SOA particles could show high oxidative potential and generate ROS, like: Chen, X., and Hopke, P. K.: A chamber study of secondary organic aerosol formation by limonene ozonolysis, Indoor air, 20, 320-328, 2010.; Wang, Y., Kim, H., and Paulson, S. E.: Hydrogen peroxide generation from α-and β-pinene and toluene secondary organic aerosols, Atmospheric environment, 45, 3149-3156, 2011.; McWhinney, R. D., Zhou, S., and Abbatt, J. P. D.: Naphthalene SOA: redox activity and naphthoquinone gas–particle partitioning, Atmos. Chem. Phys., 13, 9731-9744, 10.5194/acp-13-9731-2013, 2013.; Badali, K. M., Zhou, S., Aljawhary, D., Antiñolo, M., Chen, W. J., Lok, A., Mungall, E., Wong, J. P. S., Zhao, R., and Abbatt, J. P. D.: Formation of hydroxyl radicals from photolysis of secondary organic aerosol material, Atmos. Chem. Phys., 15, 7831-7840, 2015.; Tong, H., Arangio, A., Lakey, P., Berkemeier, T., Liu, F., Kampf, C., Pöschl, U., and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition in water, Atmos. Chem. Phys., 16, 1761-1771, 2016. Tuet, W. Y., Chen, Y., Xu, L., Fok, S., Gao, D., Weber, R. J., and Ng, N. L.: Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, Atmospheric Chemistry and Physics, 17, 839-853, 2017.

We have added the following additional detail for $\mathrm{ROS}_{\mathrm{long}}$ (p24 lines 11–14): "We propose that $\mathrm{ROS}_{\mathrm{long}}$ are a group of relatively stable long-lived products (such as hydrogen peroxide and organic peroxides) which constitute the stable ROS at the end of the experiment and which have been shown to be major products of monoterpene ozonolysis (Docherty et al., 2005; Wang et al., 2011)."

We are not in a position to speculate more on the identity of $\mathrm{ROS}_{\mathrm{short}}$ than we already do (p24 line 15): "…radicals or otherwise short-lived compounds such as reactive peroxides…") because unlike the long lived components where surrogate standards are available, we are unsure of the relative reactivity of the OPROSI assay towards different short-lived species.

We have cited some of the suggested references throughout the manuscript and we discuss Chen and Hopke (2010) in more detail below.

5. In 2010, Chen and Hopke have measured the ROS formation by limonene SOA (Chen, X., and Hopke, P. K., Indoor air, 20, 320-328, 2010.) using a similar fluorescent assay system. Their study showed a maximum ~0.2 nmol [H2O2] µg -1 . However, current study showed a yield of 0.4 nmol [H2O2] µg -1 , which is 2 times higher. More recently, they also found that when limonene SOA mass concentration ranged from 30.3 to 157.3 µg m-3 , the ROS concentration could range from 6.1 to 29.4 nmol m-3 of H2O2 (Chen, et al., Aerosol and Air Quality Research, 17, 59-68, 2017.), this value is also much lower than the value of ~150 nmol m-3 in Fig. 6. How to explain this?

Thank you for bringing these relevant studies to our attention. We discuss and explain differences between the studies (p27 line 10–p28 line 5): "Chen and Hopke (2010), Chen et al., (2011) and Chen et al., (2017) studied ROS formation from the ozonolysis of limonene using a similar chemical assay with an offline sampling and sonication extraction method. Like the current study, both short-lived and long-lived ROS are reported. However, ROS_{long} yields for Chen and Hopke (2010) and Chen et al., (2017) (0.15-0.19 nmol [H_2O_2] μg^{-1}) were lower than those determined here (0.42 nmol [H_2O_2] μg^{-1}). A number of experimental differences may be important. The three other studies employed dry conditions, compared to 40% RH here. The presence of water may influence the gas-phase fate of initial products and promote ROS formation (for instance, hydroperoxides from reaction of stabilised Criegee intermediates with water (Docherty et al., 2005)) as well as potentially modifying Henry's law partitioning of species such as hydrogen peroxide, and facilitating oligomerisation and hydrolysis reactions in the condensed phase (Gallimore et al., 2011). The higher mass loading here (375 $\mu g\ m^{-3}$) compared to these previous studies (30-160 $\mu g\ m^{-3}$) may be an important parameter through its influence on gas-particle partitioning and subsequent particle-phase reaction.

Chen et al., (2011) reported a correlation between [O_3]/[VOC] and [ROS_{long}] for a range of VOCs, and found higher ROS yields when ozone was in excess, presumably as a result of increased formation of oxygenated products such as peroxides. This is consistent with the higher [ROS_{long}] reported here ($[O_3]_{max}$/$[\text{limonene}]_0$ = 2.4) compared to Chen et al., (2017) ($[O_3]_0$/$[\text{limonene}]_0$ = 0.45). Furthermore, we proposed above that oxidation of the second (exo) double bond is partly occurring in the particle phase; this direct ROS formation in the particle may result in higher measured yields than gas phase only routes. These findings contrast with Chen and Hopke (2010) who do not see a systematic trend in [ROS_{long}] with varying [O_3]/[limonene]."

We subdivided the ROS discussion into CASC measurements (3.2.1, p23 line 2) and comparison with other studies (3.2.2, p27 line 10) to improve readability of this extended ROS section.

6. In 2014, Epstein et al. indicated that photolysis can influence the abundance of peroxide in biogenic SOA (Environ. Sci. Technol., 48, 11251-11258, 2014.). The authors are encouraged to discuss the potential impact of the photolysis on their ROS values.

Photolysis is clearly an important fate for peroxides and ROS-relevant species, as indicated by Epstein et al., (2014) and other references from point 4. However, the ROS data in Figure 6/7 were obtained under dark conditions. This is now clarified (p14 lines 18–19): "Ozonolysis was performed under dark conditions without the addition of NO_x."

7. Some typos should be corrected: page 5: line 3 "1/4" and 1/2"", line 17 and 18:"160W", "75W". Page 9: line 15: "4mm".

We have now added spaces between the number and unit in each case (p5 line 29, p6 lines 14–15, p 11 line 25).

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