Investigation into the atmospheric degradation of α-phellandrene

A computational, experimental and modelling study

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Abstract

Biogenic sources dominate the global emission budget of volatile organic compounds into the atmosphere, with monoterpenes (C$_{10}$H$_{16}$) accounting for a significant fraction of nonmethane hydrocarbons emitted. Given their large emission rates and high chemical reactivity, monoterpenes play an important role in the chemistry of the troposphere, whilst the propensity of degradation products to form secondary organic aerosol (SOA) impacts both health and climate. Despite a considerable amount of research having been conducted into their tropospheric degradation, relatively little is known about one of the most reactive monoterpenes, $\alpha$-phellandrene. Primarily emitted by Eucalypts, the world’s most widely planted hardwood tree, previous research has shown $\alpha$-phellandrene to be highly reactive with all major atmospheric oxidants. This thesis builds upon simple rate study experiments by examining the tropospheric degradation chemistry of $\alpha$-phellandrene in detail for the first time.

Characterisation was achieved using a combination of computational chemistry, experimental and modelling techniques. High-level G4(MP2) quantum chemical calculations were used to elucidate the potential energy surface of ozone addition to both double bonds in $\alpha$-phellandrene. Results indicate that addition to the least-substituted double bond is preferred, whilst presenting two novel Criegee intermediate (CI) reaction channels, that are proposed to be important alongside conventional decomposition routes. Experimental work was performed using the smog chamber facility at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, which was fitted with a suite of analytical instruments for monitoring gas- and particulate phases. In particular, ozonolysis, NO$_2$-initiated, and photooxidation experiments were conducted, numbering 24 in total, with prominent gas-phase products detected and SOA both quantified and characterised. Further investigation of aerosol filter samples at the University of York, UK, identified important SOA constituents, indicating that stabilised CIs are important precursors for the high aerosol yields observed. Findings from the computational and experimental studies were used to assist the construction of an explicit $\alpha$-phellandrene chemical mechanism, developed consistent with the Master Chemical Mechanism (MCM) protocols and integrated with an explicit representation of gas-particle partitioning. The scheme, containing 2150 newly-developed reactions and 723 new radical and closed-shell species, represents a complete parameterisation of $\alpha$-phellandrene’s tropospheric degradation, with mechanism evaluation and refinement utilising the photooxidation dataset.

The multifaceted approach of this thesis thus provides a comprehensive description of the tropospheric decomposition of $\alpha$-phellandrene, with the mechanism constructed providing an initial representation on which future, more extensive computational and experimental work can build.
I’d like to start off by thanking my principal supervisor, Sam Saunders, firstly for introducing me to the field of atmospheric chemistry, before having the confidence in me to let me do my own thing, whilst you did yours. The highlights of my PhD were definitely the times I spent abroad; the trip to Europe at the end of my second year to participate in ERCA and visit the University of York, and my multiple visits to China. I am extremely grateful for these opportunities you gave me Sam.

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Declaration

I declare that this dissertation is the result of my own independent work and investigation, which has substantially been accomplished during my PhD enrolment. This work has neither been submitted or accepted for another degree or diploma at the University of Western Australia, or elsewhere, and no part of this work will be used in a submission in my name for any other degree or diploma without prior approval of The University of Western Australia. This thesis does not contain any material previously published or written by another person, except where due reference has been made in the text. This work is not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any persons.

F. A. Mackenzie-Rae
Peer-Reviewed Journal Articles

This thesis contains published material. Bibliographic detail of these works, and where they appear in the thesis, are outlined below. For each, the relative contribution of the PhD-candidate is provided as a percentage. A detailed description of the nature of the candidate’s contribution is provided within the thesis, as a preface to each publication.

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<td>AIOMFAC</td>
<td>Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficient</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, Toluene, Ethylbenzene and Xylene</td>
</tr>
<tr>
<td>BVOC</td>
<td>Biogenic Volatile Organic Compound</td>
</tr>
<tr>
<td>CRDS</td>
<td>Cavity Ring-Down Spectroscopy</td>
</tr>
<tr>
<td>CBS</td>
<td>Complete Basis Set</td>
</tr>
<tr>
<td>CC</td>
<td>Correlation Consistent basis set</td>
</tr>
<tr>
<td>CI</td>
<td>Criegee Intermediate (also briefly used for Configuration Interaction in Section 1.4, with distinction is clear from context)</td>
</tr>
<tr>
<td>CIMS</td>
<td>Chemical Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
</tr>
<tr>
<td>cps</td>
<td>Counts Per Second</td>
</tr>
<tr>
<td>DALY</td>
<td>Disability-Adjusted Life Years</td>
</tr>
<tr>
<td>DBE</td>
<td>Double Bond Equivalency index</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyser</td>
</tr>
<tr>
<td>DNPH</td>
<td>2,4-Dinitrophenylhydrazine</td>
</tr>
<tr>
<td>DOAS</td>
<td>Differential Optical Absorption Spectroscopy</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Impact</td>
</tr>
<tr>
<td>ELVOC</td>
<td>Extremely Low Volatility Organic Compound</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionisation</td>
</tr>
<tr>
<td>EVAPORATION</td>
<td>Estimation of VApour Pressure of ORganics, Accounting for Temperature, Intramolecular, and Non-additivity effects</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated Ethylene Propylene</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionisation Detector</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>FIGAERO</td>
<td>Filter Inlet for Gases and AERosols</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared</td>
</tr>
<tr>
<td>GC-MSD</td>
<td>Gas Chromatography - Mass Selective Detector</td>
</tr>
<tr>
<td>GIG-CAS</td>
<td>Guangzhou Institute of Geochemistry, Chinese Academy of Sciences</td>
</tr>
<tr>
<td>HCD</td>
<td>Higher energy Collisional Dissociation</td>
</tr>
<tr>
<td>HEPA</td>
<td>High Efficiency Particulate Air</td>
</tr>
<tr>
<td>HO\textsubscript{x}</td>
<td>OH and HO\textsubscript{2}</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>HR</td>
<td>High Resolution</td>
</tr>
<tr>
<td>HR-TOF-AMS</td>
<td>High Resolution Time of Flight Aerosol Mass Spectrometer; referred to as AMS throughout this thesis</td>
</tr>
<tr>
<td>I.D.</td>
<td>Inner Diameter</td>
</tr>
<tr>
<td>IE</td>
<td>Ionisation Efficiency</td>
</tr>
<tr>
<td>InChI</td>
<td>International Chemical Identifier</td>
</tr>
<tr>
<td>IPP</td>
<td>Ions Per Particle</td>
</tr>
<tr>
<td>ISC</td>
<td>Inter-System Crossing</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>IVOC</td>
<td>Intermediate Volatility Organic Compound</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
</tr>
<tr>
<td>LIF</td>
<td>Laser Induced Fluorescence</td>
</tr>
<tr>
<td>LVOC</td>
<td>Low Volatility Organic Compound</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>Low Volatility Oxygenated Organic Aerosol</td>
</tr>
<tr>
<td>MCM</td>
<td>Master Chemical Mechanism</td>
</tr>
<tr>
<td>MCP</td>
<td>Multichannel Plate</td>
</tr>
<tr>
<td>MP</td>
<td>Møller-Plesset perturbation theory</td>
</tr>
<tr>
<td>MPP</td>
<td>Molecules Per Particle</td>
</tr>
<tr>
<td>MSD</td>
<td>Mass Selective Detector</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NMHC</td>
<td>Non-Methane Hydrocarbons</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>NO and NO\textsubscript{2}</td>
</tr>
<tr>
<td>OA</td>
<td>Organic Aerosol</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary Differential Equation</td>
</tr>
<tr>
<td>PANs</td>
<td>Peroxyacyl Nitrates</td>
</tr>
<tr>
<td>PBL</td>
<td>Planetary Boundary Layer</td>
</tr>
<tr>
<td>PES</td>
<td>Potential Energy Surface</td>
</tr>
<tr>
<td>PFA</td>
<td>Perfluoroalkoxy Alkane</td>
</tr>
<tr>
<td>PILS</td>
<td>Particle Into Liquid Sampler</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PM$_{0.1}$</td>
<td>Particulate Matter with an aerodynamic diameter &lt; 0.1µm</td>
</tr>
<tr>
<td>PM$_{1}$</td>
<td>Particulate Matter with an aerodynamic diameter &lt; 1.0µm</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Particulate Matter with an aerodynamic diameter &lt; 2.5µm</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Particulate Matter with an aerodynamic diameter &lt; 10µm</td>
</tr>
<tr>
<td>POCP</td>
<td>Photochemical Ozone Creation Potential</td>
</tr>
<tr>
<td>POZ</td>
<td>Primary Ozonide</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion (by volume)</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (by volume)</td>
</tr>
<tr>
<td>ppt</td>
<td>parts per trillion (by volume)</td>
</tr>
<tr>
<td>PSLs</td>
<td>Polystyrene Latex Spheres</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PTOF</td>
<td>Particle Time Of Flight</td>
</tr>
<tr>
<td>PTR-MS</td>
<td>Proton Transfer Reaction Mass Spectrometer</td>
</tr>
<tr>
<td>PTR-TOF-MS</td>
<td>Proton Transfer Reaction Time of Flight Mass Spectrometer; referred to as PTR-TOF throughout this thesis</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity (also briefly used to denote saturated hydrocarbons in Section 1.3.1, with distinction clear from context)</td>
</tr>
<tr>
<td>RIE</td>
<td>Relative Ionisation Efficiency</td>
</tr>
<tr>
<td>ROPA</td>
<td>Rate Of Production Analysis</td>
</tr>
<tr>
<td>RT</td>
<td>Retention Time</td>
</tr>
<tr>
<td>SAR</td>
<td>Structure Activity Relationship</td>
</tr>
<tr>
<td>SC</td>
<td>Scaling Constant</td>
</tr>
<tr>
<td>SCF</td>
<td>Self Consistent Field</td>
</tr>
<tr>
<td>SCI</td>
<td>Stabilised Criegee Intermediate</td>
</tr>
<tr>
<td>SF</td>
<td>Scaling Factor</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SIM</td>
<td>Selected Ion Monitoring</td>
</tr>
<tr>
<td>slpm</td>
<td>standard litre per minute</td>
</tr>
<tr>
<td>SMILES</td>
<td>Simplified Molecular Input Line Entry System</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>SOZ</td>
<td>Secondary Ozonide</td>
</tr>
<tr>
<td>STO</td>
<td>Slater Type Orbital</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi Volatile Organic Compound</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>Semi Volatile Oxygenated Organic Aerosol</td>
</tr>
<tr>
<td>TDLAS</td>
<td>Tunable Diode Laser Absorption Spectroscopy</td>
</tr>
<tr>
<td>TS</td>
<td>Transition State</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>UMR</td>
<td>Unit Mass Resolution</td>
</tr>
<tr>
<td>UNIFAC</td>
<td>UNIversal Functional Activity Coefficient</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VBS</td>
<td>Volatility Basis Set</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
<tr>
<td>WRF</td>
<td>Weather Research and Forecasting</td>
</tr>
</tbody>
</table>
## List of Physical Constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Gas Constant</td>
<td>R</td>
<td>$8.3145 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Avogadro’s Number</td>
<td>$N_A$</td>
<td>$6.022 \times 10^{23} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Boltzmann Constant</td>
<td>$k_b$</td>
<td>$1.3806 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Planck’s Constant</td>
<td>$h$</td>
<td>$6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 The Earth’s Atmosphere

The Earth’s atmosphere is a layer of gas that surrounds the planet, held in place by the force of gravity. The most abundant constituents in the atmosphere are N$_2$ (78%), O$_2$ (21%) and Ar (1%), whose abundances are controlled over geological time scales through interactions with the lithosphere$^1$, hydrosphere$^2$ and biological systems (Seinfeld and Pandis, 1998). Water vapour has a highly variable concentration reaching as high as 3%, that is controlled by evaporation and precipitation. The remaining gaseous constituents are known as trace gases, and comprise less than 1% of the atmosphere. Nevertheless, trace gases play a crucial role in the Earth’s radiative balance and in controlling the chemical properties of the atmosphere (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). Examples of trace gases include CO$_2$, CH$_4$, O$_3$, NO, NO$_2$ and volatile organic compounds (VOCs).

The temperature and pressure of the Earth’s atmosphere varies considerably with height, with the thermal gradient used to distinguish different regions of the atmosphere. From the surface upwards these are the troposphere, stratosphere, mesosphere, thermosphere and exosphere, with all but the exosphere shown in Figure 1.1. The troposphere extends from the Earth’s surface up to the tropopause, which is around 10 to 17 km in altitude depending on latitude and time of year, and is characterised by a negative temperature gradient (Wayne, 2000). This is due to absorption of radiation at the Earth’s surface which heats the surrounding air. The hotter air then rises, resulting in strong vertical mixing; a characteristic trait of the troposphere. The lowest layer of the troposphere, whose behaviour is directly influenced by the presence of the Earth’s surface$^3$, is called the planetary boundary

---

$^1$Outermost shell of the Earth, consisting of the crust and a portion of the upper mantle.

$^2$Combined mass of water found on, under and above the Earth.

$^3$Surface forcings include frictional drag, terrain-induced flow modification, heat transfer, evaporation, evapotranspiration and pollutant emission.
CHAPTER 1. INTRODUCTION

Figure 1.1: Layers of the Earth’s atmosphere, distinguished by the gradient of air temperature (yellow line) with height. Image adapted from Encyclopedia Britannica (2015).

The depth of the PBL is typically around 1000 m, however can fluctuate between 100 and 3000 m with diurnal oscillations. The boundary layer is of considerable interest, because it is the part of the atmosphere with which humans directly interact.

Turbulent mixing in the PBL is dominated by radiative forcings, resulting in a strong temporal dependency (Seinfeld and Pandis, 1998). During the day, the PBL is in a convective state, with buoyancy driven by an upward heat flux, resulting in the rapid vertical mixing of emitted or entrained materials (Seinfeld and Pandis, 1998). After sunset the Earth’s surface, along with the air immediately above it, rapidly cools by emitting infrared radiation. Under calm conditions, radiative cooling can result in the air adjacent to the surface being cooler, and more dense, than the air above; forming an inversion. Above this is a residual layer, which neither mixes with the above free-troposphere or nocturnal PBL, and contains all species that were well-mixed in the PBL during the day. No longer in physical contact with the Earth, deposition rates of species in the residual layer are greatly reduced. At sunrise, heating of the Earth’s surface causes dissipation of the nocturnal PBL by mixing with the above residual layer. Depicted in Figure 1.2, such meteorological changes
1.2. Air Pollution

Air pollution may be defined as a situation whereby anthropogenically emitted substances attain sufficiently high concentrations above their normal ambient levels to produce measurable effects on humans, animals, vegetation or materials (Seinfeld and Pandis, 1998). This definition can include any substance, although the general implication is that the effects are undesirable. Smog is a term used to describe a
complex mixture of pollutants that is formed over large urban centres. The word is a portmanteau of *smoke* and *fog*, coined from the sulphurous air pollution which plagued large industrial cities such as London during the 19th and early 20th centuries (Finlayson-Pitts and Pitts, 2000). This black smog was prominent during winters, when coal burning was highest, and occurred during nocturnal inversions when smoke emissions from combustion mixed with fog to form a thick, black smog containing elevated levels of sulphurous compounds (e.g. SO$_2$ and sulphates) and particles. Black smog episodes are still observed today in developing nations such as China (Zhang et al., 2014a; Jiang et al., 2015).

In the late 1940’s a second type of air pollution phenomenon, associated with strongly oxidising species on warm, sunny days, began to impact the city of Los Angeles (Middleton et al., 1950; Haagen-Smit, 1952). It was soon realised to be the result of increased emissions from motor vehicle combustion engines, which introduced unprecedented levels of hydrocarbons and oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) into the city. Under bright conditions, the ensuing chemistry (discussed in Section 1.3) rapidly forms secondary pollutants, including gas-phase oxidants (e.g. ozone and nitrates) and atmospheric aerosols (Haagen-Smit, 1952; Haagen-Smit and Fox, 1954). Despite containing neither smoke or fog, this type of air pollution is known as photochemical smog, a homage to the earlier observed form of air pollution. The combined mixture is physiologically identifiable as a brown haze; with the colouring resulting from high NO$_2$ concentrations and reduced visibility an artefact of high aerosol loadings. Once unique to Los Angeles, photochemical smog is now encountered all over the world in major metropolises where there is heavy motor vehicle traffic (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000).

### 1.2.1 Health Effects

Epidemiological studies have consistently demonstrated that exposure to poor air quality causes a wide spectrum of adverse health effects, ranging from acute respiratory symptoms to premature death (Dockery et al., 1993; Pope et al., 2002; Pope and Dockery, 2006; World Health Organization, 2013). Although associations with cardiopulmonary diseases and premature mortality have been reported for common air pollutants, such as NO$_2$, SO$_2$, CO and air toxics such as formaldehyde and BTEX (benzene, toluene, ethylbenzene and xylene), epidemiological evidence indicates that O$_3$ and suspended particulate matter (PM) are the leading risk factors for global disease burden (Lim et al., 2012; Forouzanfar et al., 2015). Exposure to elevated concentrations of ground-level ozone$^4$ has a detrimental impact on the pulmonary $^{4}$Ozone exists naturally throughout the atmosphere, with an average tropospheric concentration of $\sim$30 ppb (Vingarzan, 2004).
1.2. AIR POLLUTION

Figure 1.3: Photochemical smog over Los Angeles, with a visible inversion layer trapping the pollution. Photo taken during a visit to the Hollywood Hills, at 11:30am on 6th December, 2014.

and respiratory systems, especially on lung function, with long-term exposure significantly reducing lung performance and increasing the risk of death from respiratory causes (Bell et al., 2004; Jerrett et al., 2009). PM can have both solid and liquid components, and be derived from natural (e.g. sea spray, bushfires, crustal dust, flora and fauna) and anthropogenic (e.g. combustion engines, power stations, mining and farming) sources, or be formed in the atmosphere through secondary processes (Seinfeld and Pandis, 1998; Hallquist et al., 2009). Whilst undoubtedly the composition of PM has some influence over its capacity to affect human health (Kelly and Fussell, 2012; Rohr and Wyzga, 2012), the most important factor in deciding PM burden is size. Smaller particles are able to penetrate deeper into the respiratory tract, thereby aggravating a wider spectrum of physiological responses. Coarse PM, defined as particles having an aerodynamic diameter of less than 10 µm (PM$_{10}$), deposit in the primary bronchi; fine particles having diameters less that 2.5 µm (PM$_{2.5}$) penetrate the terminal bronchioles and alveoli, whilst; ultrafine particles having diameters less than 0.1 µm (PM$_{0.1}$) can enter the bloodstream and therefore impact extra-pulmonary organs (Oberdörster et al., 2005; Nemmar et al., 2013). Exposure to elevated concentrations of fine PM poses the greatest risk to human health, with short- and long-term exposure associated with increased cardiovascular, respiratory and allergenic morbidity, ultimately resulting in mortality in susceptible people (Lim et al., 2012; Forouzanfar et al., 2015; Lelieveld et al., 2015).

Air quality is a measure of air pollution, quantified as concentrations of gaseous
pollutants or size and number of particulate matter per unit volume of air (Monks et al., 2009). Air quality standards have been adopted by many countries around the world, to protect public health and welfare against the adverse health effects of air pollution. In fact, member countries of the World Health Organisation (WHO), numbering nearly 200, have adopted a constitution that sets guidelines on air pollutants. WHO air quality guidelines are generally created, updated or revised according to scientific information that demonstrates a plausible association between exposure to pollutants and health-related illnesses. However, different national policies and economic development have resulted in many countries setting air quality standards that are more relaxed, or more stringent, than the WHO standards.

Despite widespread adoption of standards, a recent model by Brauer et al. (2016) estimates that 87% of the world’s population is exposed to air quality levels which exceed the WHO PM$_{2.5}$ guidelines. Their work is consistent with the Global Burden of Disease 2013 study, which estimated that 5.5 million people die each year from causes directly attributable to air pollution, making it the fourth leading risk factor for deaths worldwide (Forouzanfar et al., 2015). 94% of these deaths are due to noncommunicable diseases, notably cardiovascular diseases, stroke, chronic obstructive pulmonary disease and lung cancer. Deaths caused by ambient air pollution are increasing, attributable to 3.1 million premature deaths in 2013. The spatial distribution of air pollution-related deaths globally is shown in Figure 1.4, with people living in low- and middle-income countries disproportionally experiencing the burden. Air pollution was additionally estimated to cause a loss of 141 million...
disability-adjusted life years\(^5\) (DALYs) globally in 2013 (Forouzanfar et al., 2015), with serious economic consequence (The World Bank, 2016b).

1.2.2 Climate Impacts

In addition to the discussed impacts on public health, air pollution has implications for a number of contemporary issues at urban, regional and global levels (Monks et al., 2009). For example ozone, being a strong oxidant, damages vegetation including crops, and materials containing olefin bonds such as natural and synthetic rubber. Perhaps most pressing however is the ability of air pollution to exhibit both strong direct and indirect climate-forcing effects. Chemically active climate compounds can either be emitted (e.g. CH\(_4\) and PM) or formed through secondary processes in the atmosphere (e.g. O\(_3\), sulphates and secondary aerosols). Pollutants such as CO, NO\(_x\), SO\(_2\) and volatile organics, which themselves have a negligible greenhouse effect, exert an important indirect effect on the climate by altering the abundance of radiatively active gases such as O\(_3\) and CH\(_4\). Importantly, VOCs can act as precursors to secondary organic aerosols (SOA), with the process representing a major uncertainty in climate-forcing models (Kanakidou et al., 2005; Fuzzi et al., 2006; Carslaw et al., 2010). This is because aerosols are cloud condensation and ice nuclei, and therefore play an important role in the atmospheric hydrological cycle and radiation budget. When combined with their own ability to scatter and absorb solar and terrestrial radiation, aerosols not only exert a substantial impact on the Earth’s albedo and greenhouse effect, but also influence large-scale meteorological and biosphere processes (Pöschl, 2005; IPCC, 2013). Indeed, the overall effect of aerosols is one of negative radiative forcing (i.e. a cooling effect). The wide array of impacts air pollution has on society therefore makes the study of the fundamental processes driving its formation of scientific and political interest.

1.3 Chemistry of the Atmosphere

The atmosphere represents a complex chemical environment; where large quantities of both anthropogenic and biogenic chemical compounds are emitted, transported and removed whilst exposed to highly variable physical and chemical conditions. Over the past 30 to 40 years a vast number of both laboratory and field studies, concerned with the physical and chemical processes occurring in the atmosphere, have been conducted, with accumulated knowledge summarised in a number of reviews, evaluations and books (Atkinson, 1990; Atkinson and Arey, 2003; Atkinson

\(^5\)DALY is a measure of overall disease burden, expressed as the number of years lost due to ill-health, disability or premature death.
et al., 2004, 2006; Calvert et al., 2000, 2008; Hallquist et al., 2009; Jenkin et al., 1997; Johnson and Marston, 2008; Kroll and Seinfeld, 2008; Monks et al., 2009; Seinfeld and Pandis, 1998). A simplified overview of the key elementary processes controlling VOC degradation in the troposphere, especially those concerned with photochemical smog formation, will now be summarised to provide important background information for research presented later in this thesis. Nevertheless, one should be mindful that the reactions discussed are only a small subset of the entire realm of atmospheric chemistry, with all chemical processes inextricably linked.

### 1.3.1 General Photochemistry

Chemical reactions in the troposphere are initiated by photolysis, which is the major source of energy into the tropospheric system. Photolysis of stable species, including complex carboxyls, hydroperoxides and organic nitrates, leads to the formation of radicals which initiate free-radical reactions. Together, photolysis and free-radical reactions constitute the major reactive pathways of atmospheric chemistry (Seinfeld and Pandis, 1998; Monks et al., 2009).

The rate of photolysis \((J, s^{-1})\) is the product of actinic flux \((F, \text{photon cm}^{-2} \text{s}^{-1})\), absorption cross-section \((\sigma, \text{cm}^2 \text{molecule}^{-1})\) and quantum yield \((\Phi, \text{molecule}^{-1})\).
1.3. CHEMISTRY OF THE ATMOSPHERE

 photon$^{-1}$), where absorption cross-sections and quantum yields are functions of wavelength ($\lambda$) (Finlayson-Pitts and Pitts, 2000):

$$J = \int_{\lambda_1}^{\lambda_2} F_\lambda \sigma(\lambda) \Phi(\lambda) d\lambda$$  \hspace{1cm} (1.1)

Actinic flux is calculated by integrating the spectral radiance over all directions and is dependent on latitude, longitude, time of day and the absorption capacity of the atmosphere at the specific location (IUPAC, 1997). Absorption cross-section is a measure of the specified molecules’ ability to absorb radiation at the given wavelength. Lastly, quantum yield is the fraction of absorbed radiation that initiates the desired chemical change. Absorption cross-sections and quantum yields have been recorded for a large number of atmospherically important reactions, over wavelengths pertinent to solar radiation and temperatures and pressures characteristic of different regions of the atmosphere (Keller-Rudek et al., 2013).

Tropospheric ozone is formed through photolysis of nitrogen dioxide gas, which undergoes photodissociation at wavelengths of less than 424 nm to yield atomic oxygen and nitric oxide (Seinfeld and Pandis, 1998). The atomic oxygen subsequently reacts with molecular oxygen, in the presence of a third body, which absorbs excess vibrational energy (M, usually O$_2$ or N$_2$), to produce ozone.

$$\text{NO}_2 \xrightarrow{hv} \text{NO} + \text{O}(^3\text{P})$$  \hspace{1cm} (1.2)

$$\text{O}(^3\text{P}) + \text{O}_2 \xrightarrow{M} \text{O}_3$$  \hspace{1cm} (1.3)

Note that in keeping with convention in the field, common inorganic radicals will not be explicitly labelled either in chemical formula or text (e.g. NO$_2$ and NO are strictly radical species). The nitric oxide produced in Equation 1.2 reacts with oxidants, most notably ozone in the troposphere to reform nitrogen dioxide.

$$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$$  \hspace{1cm} (1.4)

The dynamic relationship between ozone and NO$_x$ consumption and production presented in Equations 1.2 – 1.4 keeps ozone concentrations in the troposphere relatively low (Seinfeld and Pandis, 1998). Ozone is also responsible for production of the hydroxyl radical (OH), which is one of the major species controlling the oxidative capacity of the troposphere. Photolysis of ozone forms an excited atomic oxygen atom, which can react with water to yield the hydroxyl radical.

$$\text{O}_3 \xrightarrow{hv} \text{O}_2 + \text{O}(^1\text{D})$$  \hspace{1cm} (1.5)

$$\text{O}(^1\text{D}) + \text{H}_2\text{O} \longrightarrow 2\text{OH}$$  \hspace{1cm} (1.6)
Reaction with the hydroxyl radical is the major removal process for most VOCs in the troposphere. The hydroxyl radical predominately reacts with saturated hydrocarbons (RH) via a hydrogen abstraction (Equation 1.7), while participating in an addition reaction with unsaturated hydrocarbons (Equation 1.8) (Kwok and Atkinson, 1995). Addition reactions are generally faster than abstraction reactions, with both mechanisms resulting in an organic radical being produced.

\[
\text{OH} + \text{RH} \longrightarrow \text{R} \cdot + \text{H}_2\text{O} \tag{1.7}
\]
\[
\text{OH} + \text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 \longrightarrow \text{R}_1\text{R}_2\hat{\text{C}} - \text{C}(\text{OH})\text{R}_3\text{R}_4 \tag{1.8}
\]

The alkyl radicals will typically rapidly react with molecular oxygen forming a peroxy radical.

\[
\text{R} \cdot + \text{O}_2 \xrightarrow{\text{M}} \text{ROO} \cdot \tag{1.9}
\]

The peroxy radical can participate in a number of reactions, including reactions with nitric oxide, nitrogen dioxide, nitrate radicals, hydropersyloxyl radicals (HO\textsubscript{2}) and with itself and other peroxy radicals (R'O\textsubscript{2}·).

\[
\text{ROO} \cdot + \text{NO} \longrightarrow \text{RO} \cdot + \text{NO}_2 \tag{1.10}
\]
\[
\text{ROO} \cdot + \text{NO} \longrightarrow \text{RONO}_2 \tag{1.11}
\]
\[
\text{ROO} \cdot + \text{NO}_2 \xrightarrow{\text{M}} \text{ROONO}_2 \tag{1.12}
\]
\[
\text{ROO} \cdot + \text{NO}_3 \longrightarrow \text{RO} \cdot + \text{NO}_2 + \text{O}_2 \tag{1.13}
\]
\[
\text{ROO} \cdot + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2 \tag{1.14}
\]
\[
\text{ROO} \cdot + \text{R'O} \cdot \longrightarrow \text{RO} \cdot + \text{R'O} \cdot + \text{O}_2 \tag{1.15}
\]
\[
\text{ROO} \cdot + \text{R'O} \cdot \longrightarrow \text{R'}\text{H}_2\text{O} + \text{R'OH} + \text{O}_2 \tag{1.16}
\]
\[
\text{ROO} \cdot + \text{R'O} \cdot \longrightarrow \text{R'}\text{H}_2\text{O} + \text{ROH} + \text{O}_2 \tag{1.17}
\]

Under high NO\textsubscript{x} conditions, such as in polluted environments, Reactions 1.10 – 1.13 are the major consumption channels. Of these, radical propagation in which RO\textsubscript{2} is efficiently converted into RO by reaction with NO (Equation 1.10) dominates, although the competing alkyl nitrate radical termination channel (Equation 1.11) generally becomes more important as the size of the organic group increases (Atkinson et al., 2006). The peroxyperoxinitrates formed in Equation 1.12 rapidly decompose in the troposphere to reform the starting products, with the channel only of importance for acylperoxy radicals, which form relatively stable peroxyacyl nitrate type compounds (PANs). PANs are secondary pollutants noted for causing...
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respiratory and eye irritation, however they are also important nitrogen sinks in the troposphere; dissociating slowly to reproduce RO₂ and NO₂, often away from the urban or industrial point of origin, making them important in long-range transport of NOₓ (Seinfeld and Pandis, 1998).

Under low-NOₓ conditions, the reactions of RO₂ with HO₂ and other peroxy radicals becomes competitive. For the majority of peroxy radicals, reaction with HO₂ is dominated by a hydroperoxide (ROOH) forming termination reaction. Self- and cross-reactions with other RO₂ radicals are partially propagating, generating oxy-radicals, and partially terminating, generating alcohols and carbonyl products. As a result there is a progressive change in the product distribution away from nitrate containing compounds and towards more hydroperoxide, carbonyl, hydroxycarbonyl and alcohol containing species as the ambient NOₓ concentration decreases.

Behaviour of the oxy-radical formed in Equations 1.10, 1.13 and 1.15 is dominated by three modes of action; reaction with O₂ to form a carbonyl and hydroperoxy radical, thermal decomposition through cleavage of a C–C bond adjacent to the alkoxy carbon to form a carbonyl and alkyl radical and isomerisation through a hydrogen shift.

\[
\begin{align*}
    R_1CHOR_2 + O_2 & \longrightarrow R_1C(O)R_2 + HO_2 \quad (1.18) \\
    R_1R_2C\dot{O}R_3 & \xrightarrow{\text{decomp.}} R_1C(O)R_2 + R_3 \cdot \quad (1.19) \\
    R_1CHOR_2 & \xrightarrow{\text{isom.}} \text{hydroxy alkyl radical} \quad (1.20)
\end{align*}
\]

Reactions rates are strongly dependent on the molecular structure of the alkoxy radical (Atkinson, 2007). The rate of dissociation is dependent on the level of substitution of the alkyl radical formed, and is also highly favoured when the adjacent carbon has either ketone or alcohol functionality. Isomerisation requires that a suitable hydrogen be available for abstraction, typically located four carbons away from the radical center for a 1,5-hydrogen shift. Similarly, the rate of isomerisation increases with both the level of substitution of the carbon from which the hydrogen is abstracted, and by the presence of an OH group either on, or neighbouring, to that carbon. Thus reaction of alkoxy radicals with O₂ becomes less influential as the size of the radical increases.

The alkyl and hydroxy alkyl radicals generated in Equations 1.19 and 1.20 respectively propagate through another cycle of the aforementioned radical reactions. Indeed chains of free radical reactions typify atmospheric oxidation, with recursion further oxidising the VOC with each iteration yielding a suite of highly functionalised and often multifunctional species. Compared to radical species, closed-shell products formed through radical-termination channels have respectively long tropospheric lifetimes, and so are termed first-generation products. Stable closed-shell
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Figure 1.6: Simplified mechanism for the atmospheric oxidation of a generic VOC. Alkene ozonolysis is omitted for clarity, and is shown in Figure 1.8. Image adapted from Kroll and Seinfeld (2008).

first- and higher-generation products degrade similarly to the primary VOC. Due to the increased basicity of hydrogen atoms neighbouring highly electronegative atoms, such as oxygen and nitrogen, the hydroxyl radical preferentially attacks functional groups (Atkinson, 1987; Kwok and Atkinson, 1995). Decomposition occurs until either the fragments are removed from the atmosphere (e.g. deposition), partition into a solid or liquid phase (refer to Section 1.3.4), or yield CO or CO$_2$. A summary of the major atmospheric decomposition reactions for a VOC is provided in Figure 1.6.

In addition to reacting with peroxy radicals, the hydroperoxyl radical formed in Equation 1.18 favourably reacts with nitric oxide to reform nitrogen dioxide and the hydroxyl radical.

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}
\]  

(1.21)

In doing so the hydroxyl radical is re-formed, simultaneously being both the initiator and final product of VOC degradation. The hydroxyl radical therefore plays a catalytic role in VOC photochemical oxidation in the troposphere. A schematic overview of the discussed photochemical cycle is shown in Figure 1.7. It is evident that Reactions 1.10 and 1.21 perturb the natural NO$_x$–ozone equilibrium set up by Equations 1.2 – 1.4. This perturbation can only occur upon the introduction of a
third party to the system, such as a VOC, which enables the cycling of NO into NO$_2$ without the consumption of O$_3$. The net result is enhanced ozone production, explaining the photochemical smog observations.

1.3.2 The Nitrate Radical

At night, tropospheric processes driven by photochemistry (e.g. free radical HO$_x$ = OH + HO$_2$ production) ceases, with the highly reactive nitrate radical becoming the most important oxidising species in the troposphere (Wayne et al., 1991; Seinfeld and Pandis, 1998). The nitrate radical is predominantly formed from reaction of nitrogen dioxide with ozone.

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  

(1.22)

Alternatively, the nitrate radical may be formed through dissociation of dinitrogen pentoxide.

\[ \text{N}_2\text{O}_5 \xrightarrow{M} \text{NO}_3 + \text{NO}_2 \]  

(1.23)

However, since N$_2$O$_5$ is formed through the reverse reaction, a temperature dependent equilibrium between the three species is quickly established (Mentel et al., 1996). N$_2$O$_5$ therefore acts as a temporary reservoir for NO$_3$, often transporting it to
warmer conditions where thermal decomposition of $\text{N}_2\text{O}_5$ occurs more rapidly. Nevertheless, $\text{N}_2\text{O}_5$ is itself an important product, since it can react heterogeneously with $\text{H}_2\text{O}$ to yield $\text{HNO}_3$, thereby contributing to atmospheric acidification and aerosol formation (Wayne et al., 1991; Kalberer et al., 2004; Monks et al., 2009).

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (1.24)$$

During the day the nitrate radical is rapidly photolysed.

$$\text{NO}_3 \xrightarrow{hv} \text{NO}_2 + \text{O}^{(3\text{P})} \quad (1.25)$$

$$\text{NO}_3 \xrightarrow{hv} \text{NO} + \text{O}_2 \quad (1.26)$$

The nitrate radical also rapidly reacts with NO.

$$\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2 \quad (1.27)$$

Equations 1.25 – 1.27 result in the nitrate radical having an extremely short lifetime in the troposphere during the day. However at night, its concentration is allowed to build up sufficiently such that it becomes the main remover of hydrocarbons that would otherwise be available for daytime ozone production. $\text{NO}_3$ acts similarly to the OH radical, rapidly adding across $\pi$-bonds of unsaturated VOCs to form a $\beta$-nitrooxy alkyl radical, or by abstracting a hydrogen from saturated VOCs (Atkinson, 1991).

$$\text{NO}_3 + \text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 \rightarrow \text{R}_1\text{R}_2\dot{\text{C}} - \text{C}($$\text{ONO}_2)\text{R}_3\text{R}_4 \quad (1.28)$$

$$\text{NO}_3 + \text{RH} \rightarrow \text{HNO}_3 + \text{R} \cdot \quad (1.29)$$

However, under either NO$_x$-free or irradiated chamber studies considered in this thesis, the nitrate radical and nocturnal chemistry are, in general, not anticipated to play a major role and so are not discussed further.

### 1.3.3 Ozonolysis Mechanism

Ozone is one of the most important atmospheric oxidising species, along with the OH and NO$_3$ radicals. Whilst OH radicals are present at high concentrations during the day and very low concentrations at night, and conversely NO$_3$ is a maximum at night and negligible during the day, O$_3$ is present all the time. For alkenes, reaction with ozone is therefore a major tropospheric consumption pathway, and starts one of the most complex and highly studied reaction sequences in atmospheric chemistry (Calvert et al., 2000; Johnson and Marston, 2008; Vereecken et al., 2015). Indeed the importance of ozonolysis for unsaturated compounds, along with high mecha-
Figure 1.8: Generic ozonolysis mechanism showing \([3 + 2]\) cycloaddition of ozone to the olefin bond, forming two sets of Criegee intermediate and carbonyl products. Both resonance canonicals of the Criegee intermediates are shown.

Ozonolysis is generally agreed to occur through a concerted \([3 + 2]\) cycloaddition of ozone to the olefin bond, forming a 1,2,3-trioxolane intermediate species known as a primary ozonide (POZ) (Johnson and Marston, 2008; Vereecken et al., 2015). The POZ, whose generic structure is shown in Figure 1.8, retains a \(\sigma\)-bond between the two carbons which are now bridged by three oxygen atoms. Addition of ozone is highly exothermic, with the excess energy retained in the POZ structure. Rapid decomposition results in homolytic cleavage of the C–C and one of the O–O bonds, which forms, in the case of asymmetrically substituted alkenes, a pair of products containing a carbonyl and a carbonyl oxide reactive intermediate (Criegee intermediate, CI). Both products retain a significant portion of the nascent energy. Whilst insufficient for the carbonyl compound, sufficient vibrational and rotational excitation exists in the CI to permit further unimolecular decomposition (Vereecken and Francisco, 2012).

Excited CIs predominantly decompose through one of two unimolecular channels, as shown in Figure 1.9. Firstly, excited CIs can cyclise, forming a dioxirane, which in turn decomposes by breaking an O–O bond to form either a carboxylic acid, ester or lactone, depending on neighbouring substituents. This reaction sequence is known as the ester or ‘hot’ acid channel (Johnson and Marston, 2008). For small alkenes, overall reaction exothermicity can be sufficient for the acid or ester to eliminate \(\text{CO}_2\), generating shorter alkane chains or radical fragments. Larger esters and acids however will be collisionally stabilised, preventing decomposition (Vereecken and Francisco, 2012). Alternatively, when available, excited CIs can isomerise via a 1,4-hydrogen shift, forming an excited vinylhydroperoxide, which subsequently decomposes into a vinoxy radical and \(\text{OH}\) (Niki et al., 1987; Calvert et al., 2000).
Figure 1.9: Atmospheric fate of Criegee intermediates. Relative importance of each channel depends on the functional groups $R_1$ and $R_2$. Products decompose as shown in Figure 1.6.

Known as the hydroperoxide channel, the pathway represents an important source of non-photolytic OH radicals in the troposphere (Finlayson-Pitts and Pitts, 2000). For endocyclic hydrocarbons, rupturing of the POZ does not segment the molecule as a whole. Tethered CIs are therefore able to participate in a third unimolecular reaction process, whereby the carbonyl oxide and carbonyl functionalities re-cyclise to form a 1,2,4-trioxolane cyclic adduct (Secondary Ozonide, SOZ). Nascent fragments generated from exocyclic hydrocarbons rapidly separate in the gas-phase, making prompt recombination chemistry highly unlikely (Finlayson-Pitts and Pitts, 2000).

The relative prevalence of the ester or ‘hot’ acid and hydroperoxide channels is strongly linked to the conformation of the CI. As shown in Figure 1.8, CIs can either be represented as biradicals or zwitterions, with the true electronic structure best represented as something in-between (Johnson and Marston, 2008). Zwitterionic influence results in the C–O bond having some $\pi$-character, with high barriers of rotation existing between geometric CI isomers. It is traditional to refer to the conformer with the terminal oxygen pointing towards an alkyl group as being in $\text{syn}$ orientation, and the conformer having the oxygen orientated towards a hydrogen substituent as the $\text{anti}$-CI (Vereecken and Francisco, 2012). In general, $\text{syn}$-CIs participate in the hydroperoxide channel, whilst $\text{anti}$-CIs, which have no access to the traditional hydroperoxide channel, decompose through the ester or ‘hot’ acid channel (Johnson and Marston, 2008; Vereecken and Francisco, 2012).

Decomposition of CIs through unimolecular rearrangement reactions occurs in competition with thermalisation by collisions with the bath gas. If collisional quench-
ing stabilises the CI sufficiently, then the lifetime of unimolecular processes may become longer than the time required for bimolecular encounters, resulting in reactions of stabilised CIs with atmospherically important trace species (e.g. H$_2$O, SO$_2$, NO, NO$_2$, CO, aldehydes, ketones, acids and alcohols) becoming potentially important (Johnson and Marston, 2008). The most atmospherically important bimolecular reactions are thought to be reaction with H$_2$O, which is potentially a significant source of organic acids and H$_2$O$_2$ in the atmosphere, or reaction with NO$_x$ in polluted environments to form a carbonyl compound. The reaction of CIs with acids is often exploited in laboratory experiments wanting to scavenge stabilised CIs (Bonn et al., 2002; Winterhalter et al., 2009). Saturated stable products formed through either the uni- or bi-molecular processes then react with OH or NO$_3$ radicals through mechanisms previously discussed.

1.3.4 Secondary Organic Aerosol

The described gas-phase oxidation of VOCs by photolysis, reaction with OH radicals, NO$_3$ radicals and O$_3$, results in the addition of one or more polar oxygenated functional groups. Increased functionality generally makes the products less volatile and more water soluble (Pankow and Asher, 2008; Hallquist et al., 2009). If the reduction in VOC polarity is sufficient, then gas to particle partitioning can occur. Nevertheless functionalisation occurs in tandem with fragmentation, which yields lower molecular weight products that tend to be more volatile. The relative importance of the isomerisation and decomposition channels is therefore an important connector between molecular structure and change in volatility of a compound upon oxidation (Ziemann and Atkinson, 2012).

Partitioning Theory

Absorptive partitioning of semivolatile compounds is mathematically described by the theory of Pankow (1994), which was extended to SOA formation by Odum et al. (1996). The fundamental concept is that SOA comprises a complex mixture of semivolatile organic compounds that are continuously partitioning between the gaseous and particulate phases. Partitioning of each species is described by an equilibrium partitioning coefficient $K_p$ (m$^3$ g$^{-1}$):

$$K_p = \frac{P}{GM} = \frac{RT f_{om}}{MW_{om} \gamma p_L}$$

(1.30)

where $P$ (g m$^{-3}$) is the mass concentration of semivolatile species in the particle phase, $G$ (g m$^{-3}$) is the mass concentration of semivolatile species in the gaseous phase and $M$ (g m$^{-3}$) is the mass concentration of the total particulate matter into
which partitioning can occur. The partitioning coefficient is thus inversely proportional to the saturation vapour pressure \((C^*)\) of the pure semivolatile compound (Donahue et al., 2006). The right-hand side expression is the commonly encountered form of the equilibrium partitioning coefficient which was first proposed by Pankow (1994), where \(R\) is the ideal gas constant \((8.314 \text{ J K}^{-1} \text{ mol}^{-1})\), \(T\) is the temperature \((\text{K})\), \(MW_{om}\) is the mean molecular weight of the condensed organic material \((\text{g mol}^{-1})\), \(f_{om}\) is the weight fraction of the particle phase that is absorbing organic material, \(\gamma\) is the activity coefficient of the given species in the condensed organic phase and \(p_o^i\) is its liquid vapour pressure \((\text{Pa})\). Equation 1.30 shows that whilst partitioning is highly dependent on species vapour pressures, all semivolatile species can contribute to the particle phase to some extent as long as there is an absorbing mass present. Partitioning therefore occurs irrespective of whether a species vapour pressure is below its saturation vapour pressure. The fraction of a semivolatile compound in the particle phase \((F)\) is given by:

\[
F = \frac{P}{P + G} = \frac{MK_p}{1 + MK_p}
\]  

(1.31)

Consequently, as the amount of absorbing material increases, compounds of higher volatility (lower \(K_p\)) will increasingly partition into the particle phase (Seinfeld and Pankow, 2003).

Odum et al. (1996) defined the total aerosol yield \((Y)\) as the mass of aerosol formed per mass of hydrocarbon reacted, and showed that it could be expressed in terms of partitioning of a collection of semivolatile species:

\[
Y = \frac{\Delta M}{\Delta HC} = M \sum_i \alpha_i K_{p,i} \frac{1}{1 + MK_{p,i}}
\]  

(1.32)

where \(\alpha_i\) is the stoichiometric factor and \(K_{p,i}\) the temperature-dependent equilibrium partitioning constant of product \(i\). In principle, aerosol yield can be calculated by summing contributions from all semivolatile compounds formed in a given reaction, however this degree of detail is generally impossible owing to the large number of reaction products formed and the difficulty in measuring semivolatile compounds. In practice, two (notionally fictitious) surrogate products have traditionally been used to express aerosol formation from a given precursor, with higher order fits found to be superfluous (Odum et al., 1996; Kroll and Seinfeld, 2008). It is evident from Equation 1.32 that aerosol yield from a given precursor is not a straightforward stoichiometric quantity, but rather varies with total organic particulate loading. This dependency has been verified experimentally for a large number of VOCs, forming characteristic yield curves which are fitted using the ‘two-product model’ \((i = 2)\) (Hoffmann et al., 1997; Griffin et al., 1999; Song et al., 2005; Ng et al., 2007b).
SOA production from experimentally studied VOCs can then be easily incorporated into atmospheric chemistry models using optimised parameters (e.g. Chung and Seinfeld, 2002; Tsigeridis and Kanakidou, 2003; Henze and Seinfeld, 2006; Santiago et al., 2012; Jathar et al., 2016).

The two-product model has its limitations in transcribing experimental results to ambient conditions (Donahue et al., 2006), being unable to accurately represent the wide range of organic aerosol loadings in the atmosphere or the ongoing oxidation of semivolatile organics in the gas and particle phases (Hallquist et al., 2009). To address this, Donahue and co-workers have proposed the use of a ‘volatility basis set’ (Donahue et al., 2006, 2011, 2012b), in which the volatility distribution is represented by volatility bins of prescribed vapour pressures separated by an order of magnitude. Partitioning over a broader range of organic aerosol loadings is more accurately represented using the volatility basis set, with the mass balance of more volatile co-products additionally maintained.

SOA Growth and Ageing

The organic particle phase remains highly chemically active during its lifetime, participating in both homogeneous and heterogeneous processes such that SOA composition and physical properties remain dynamic. Ageing of SOA has three primary facets (Rudich et al., 2007; Kroll and Seinfeld, 2008); condensed-phase organics can be oxidised via heterogeneous uptake of oxidants such as OH, O₃, NO₂ and NO₃; further oxidation of gas-phase precursors can yield more low-vapour pressure products that condense and contribute to the SOA; and condensed-phase organic monomers can participate in accretion reactions forming oligomeric compounds. As a large fraction of atmospheric organics contributing to SOA are semivolatile, changes to the composition of either the condensed or gaseous phases can have repercussions on the equilibrium, forcing mass transfer of organics in either direction.

Particle-phase accretion reactions have received considerable attention in the literature, since the vapour pressure of an organic species decreases by about an order of magnitude for every two carbons added (Pankow and Asher, 2008; Kroll and Seinfeld, 2008). As a result, more aerosol mass is formed than what would be inferred from vapour pressures of monomeric gas-phase products alone. Oligomerisation pathways that have been proposed based on experimental evidence include alcohol and carbonyl reactions to form hemiacetals and acetals, hydroperoxide and carbonyl reactions to form peroxycetals and peroxyacetals, alcohol and carboxylic acid reactions to form esters, carboxylic acid–carboxylic acid reactions to form acid anhydrides, aldehyde-aldehyde reactions to form aldols and reaction of CIs with alcohol, water, acids or other oxygenates (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Ziemann and Atkinson, 2012, and references therein). These reaction processes
are summarised in Figure 1.10. Many of the reactions shown in Figure 1.10 are catalysed by acidic conditions (Hallquist et al., 2009), explaining observations of increased SOA yields in the presence of acidic seed particles (e.g. Jang et al., 2002; Czoschke et al., 2003; Inouma et al., 2004; Gao et al., 2004; Offenberg et al., 2009; Lambe et al., 2015). However, oligomer formation does not necessarily require strong acidity to occur rapidly, with oligomeric species having been measured in SOA where no inorganic seeds are present (Kalberer et al., 2004; Surratt et al., 2006; Heaton et al., 2007; Camredon et al., 2010; Hall and Johnston, 2012).

In the absence of seed particles, SOA must initially be formed through nucleation processes. Recently it has been shown that in the most pristine of environments highly condensable biogenic vapours may homogeneously nucleate through an ion-induced process (Kirkby et al., 2016). However in most scenarios, sulphuric acid vapour is almost always involved in atmospheric new-particle formation (Sihto et al., 2006; Kuang et al., 2008; Sipilä et al., 2010; Kulmala et al., 2013). Nevertheless, extremely low-volatility organic vapours remain essential for stabilising (along with amines and ammonia) and then driving the growth of newly formed sulphuric acid-
based clusters from a few nanometers, up to sizes where they can influence feedbacks involving the biosphere, clouds and climate (Wang et al., 2010; Kulmala et al., 2013; Schobesberger et al., 2013; Donahue et al., 2013). Indeed this mechanism provides the dominant source of particles by number in the PBL (Spracklen et al., 2008; Merikanto et al., 2009; Pierce et al., 2012).

The formation of extremely low-volatility organic compounds (ELVOCs), required for fresh particle growth, has recently been proposed to occur in the gas-phase through an autoxidation process, whereby a fraction of RO$_2$ radicals achieve a high oxygen content through rapid and successive intramolecular hydrogen abstractions followed by molecular oxygen additions (Crounse et al., 2013; Ehn et al., 2014; Kurtén et al., 2015). In particular, high yields of ELVOCs have been observed experimentally from the ozonolysis of endocyclic biogenics (Jokinen et al., 2015), with potentially important and widespread implications to new particle formation and subsequent growth over forested regions (Ehn et al., 2014; Öström et al., 2017).

### 1.3.5 Monoterpenes

Biogenic volatile organic compounds (BVOCs) are emitted into the troposphere through processes associated with life, such as the growth and maintenance of flora and fauna (e.g. metabolic waste products, hormones used for signalling or defence) as well as from the decay of organic matter by microbes (Goldstein and Galbally, 2007). Consequently, emission rates are generally dependent on temperature and light intensity, and so vary with time of day, season and geographical location (Fuentes et al., 2000). BVOCs dominate the global emission budget of organic vapours into the atmosphere (Guenther et al., 1995, 2012), with SOA production from BVOCs accounting for a significant fraction of non-refractory aerosol mass globally (Tsigaridis and Kanakidou, 2003; Andreea and Rosenfeld, 2008).

BVOCs include simple alkanes and alkenes, alcohols, aldehydes, ketones, organic acids, ethers, esters and terpenoids (Guenther, 2002). Emitted by vegetation, the simplest terpenoid, isoprene (C$_5$H$_8$), has the largest single contribution to the global BVOC emission budget (Guenther et al., 1995, 2012). However monoterpenes (C$_{10}$H$_{16}$), consisting of two isoprene units, have received considerable interest owing to their large emission rates, estimated by different groups to be between 30 – 127 Tg C year$^{-1}$ globally (Guenther et al., 1995, 2012; Lathière et al., 2006; Schurgers et al., 2009; Sindelarova et al., 2014), high tropospheric reactivity (Calvert et al., 2000; Atkinson and Arey, 2003), and propensity of oxidation products to form SOA (Griffin et al., 1999; Lee et al., 2006a,b; Zhao et al., 2015a). Global modelling studies having estimated up to 15 Tg year$^{-1}$ of organic SOA to be derived from monoterpane emissions (Goto et al., 2008; Pye et al., 2010), representing an impor-
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Figure 1.11: Structures of commonly emitted monoterpenes.

A significant fraction of the global SOA budget. Monoterpenes therefore exert a controlling influence over the oxidative chemistry of the troposphere near their emission source, with widespread effects.

Globally monoterpane emissions are dominated by α-pinene, β-pinene, Δ3-carene, trans-β-ocimene, limonene, camphene, myrcene and sabinene, whose structures are shown in Figure 1.11, although emission composition is species dependent, with other monoterpenes being regionally important (Geron et al., 2000; Guenther et al., 2012). Assessing the impact of a particular monoterpene on atmospheric chemistry requires a knowledge of its atmospheric lifetime, which is controlled by the rate of its reaction with common atmospheric oxidants, O3, OH and NO3; the mechanism of its oxidation, that is the radical chemistry that follows initial attack by the oxidant and the nature of the stable products formed; and propensity of products to form or contribute to SOA nucleation and growth. Rate coefficients for reaction of most monoterpenes with OH, NO3 and O3 (Atkinson and Arey, 2003) along with SOA yields from either photooxidation or ozonolysis studies (Hoffmann et al., 1997; Griffin et al., 1999; Lee et al., 2006a,b; Saathoff et al., 2009; Zhao et al., 2015a) have been experimentally measured. However, outside of the most commonly emitted monoterpenes, the mechanisms involved in oxidation and the nature of the products formed are not nearly so well-established.

1.4 Computational Chemistry

Computational chemistry has emerged as a valuable tool in elucidating the chemical processes active in the atmosphere, complimenting pre-existing experimental and modelling techniques. With an exponential growth in computing power, advanced theoretical methodologies are now applicable to solve increasingly complex problems.
Applications include detailing temperature and pressure dependencies of kinetic parameters, thereby expanding conditions accessed by experiments; unravelling intricate and often novel mechanistic details of complex multi-step reaction processes, which increases the accuracy of chemical mechanism construction; and determining chemical and physical properties of a large number of atmospheric species, many of which precede experimental measurements. Computational chemistry has quickly become an indispensable tool in the field of atmospheric chemistry (Vereecken and Francisco, 2012; Vereecken et al., 2015).

As this is not principally a computational chemistry thesis, focus will be on applicability as opposed to the intricate details of theoretical methodologies. However, a brief diversion into underlying theory and methodology is nonetheless provided, to acquaint the unfamiliar reader on the foundations of quantum mechanics and computational chemistry, and introduce basic terminology in preparation for Chapter 2. More extensive literature can be found by referring to any number of the highly recommended quantum chemistry textbooks (e.g. Jensen, 2007; Szabo and Ostlund, 1982; Parr and Yang, 1994; Atkins and Friedman, 2010).

1.4.1 Theoretical Background

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. – P. A. M. Dirac, 1929

Schrödinger Equation

The Schrödinger equation is the fundamental equation of non-relativistic quantum mechanics, and describes the temporal evolution of the state of a physical system. For a collection of particles, such as a molecule containing \( N \) nuclei and \( n \) electrons, the Schrödinger equation can be written as:

\[
\hat{H}\Psi(R, r, t) = \frac{i\hbar}{2\pi} \frac{\partial\Psi(R, r, t)}{\partial t} \tag{1.33}
\]

where \( \Psi \) is the wavefunction as a function of the 3\( N \) nuclear coordinates, \( R = (R_i) = (X_i, Y_i, Z_i) \), 3\( n \) electronic coordinates, \( r = (r_i) = (r_{i1}, r_{i2}, r_{i3}) \) and time \( (t) \), \( \hbar \) is Planck’s constant and \( i \) is the imaginary unit. \( \hat{H} \) is the many body Hamiltonian operator, which is made up of kinetic (\( T \)) and potential (\( V \)) energy terms:

\[
\hat{H} = T + V \tag{1.34}
\]

\(^6\text{Refer to Section 1.6.1 for a definition of a chemical mechanism.}\)
CHAPTER 1. INTRODUCTION

The kinetic energy is a summation of the Laplace operator\(^7\), \(\nabla^2\), over all particles in the molecule.

\[
T = \frac{\hbar^2}{8\pi^2} \sum_i \frac{1}{m_i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)
\]  
(1.35)

The potential energy component is the Coulomb repulsion between each pair of charged entities:

\[
V = \frac{1}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{e_i e_j}{\Delta r_{ij}}
\]  
(1.36)

where \(\Delta r_{ij}\) is the distance between the two particles and \(e_i\) and \(e_j\) are the charges on particles \(i\) and \(j\) respectively. For an electron the charge is \(-e\), whilst for a nucleus the charge is \(Ze\), where \(Z\) is the atomic number for that atom. Therefore,

\[
V = \frac{1}{4\pi\epsilon_0} \left( -\sum_i \sum_I \left( \frac{Z_i e^2}{\Delta r_{iI}} \right) + \sum_i \sum_{j<i} \left( \frac{e^2}{\Delta r_{ij}} \right) + \sum_I \sum_{J<I} \left( \frac{Z_I Z_J e^2}{\Delta R_{IJ}} \right) \right)
\]  
(1.37)

where the first term corresponds to electron-nuclear attraction, the second to electron-electron repulsion and the third to nuclear-nuclear repulsion.

The potential field in which particles exists, and by extension the Hamiltonian, do not change with respect to time in molecular systems. This enables the time-independent Schrödinger equation to be used:

\[
H\psi(R, r) = E\psi(R, r)
\]  
(1.38)

Note that this is an eigenvalue equation, where the Hamiltonian operator solves for the total energy of the system, \(E\). Therefore the energy, and many other properties of the system, can be obtained by solving the Schrödinger equation for \(\psi(R, r)\) using appropriate boundary conditions. Many solutions are available to Equation 1.38 corresponding to different stationary states, with the solution of lowest energy representing the ground state.

**Born-Oppenheimer Approximation**

A closed form solution of the Schrödinger equation is only possible for the simplest systems containing no more than two interacting particles (e.g. a Hydrogen atom). This is due to correlation of all particles with one another, which rapidly

\(^7\)The Laplace operator is given by the sum of second partial derivatives of the function with respect to each independent variable. For Cartesian coordinates this equates to, 
\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]
increases the variables in the many-body wavefunction. As a result, several approximations are used to simplify the solution of the Schrödinger equation. The Born-Oppenheimer approximation is used almost universally, and separates nuclear and electronic motions by assuming nuclei are stationary with respect to electrons. The approximation is valid because the mass of a typical nucleus is thousands of times greater than that of an electron. As a result, nuclear motion is considerably slower, with electrons reacting essentially instantaneously to changes in nuclear position. The Born-Oppenheimer approximation thus reduces to describing electronic wavefunctions as occurring in a field of fixed nuclei. Nuclear and electronic motions are thus decoupled, allowing the two parts of the problem to be solved independently.

Molecular Orbitals

The simplest method of constructing $\Psi$ is by taking the Hartree product of molecular orbitals:

$$\Psi(r) = \sum_i \phi_i(r_i) \quad (1.39)$$

where $\phi$ is a molecular orbital. However as electrons are fermions, a physical requirement of $\Psi$ is that it is antisymmetric to satisfy the Pauli exclusion principle, which Equation 1.39 is not. This is because interchanging two $r_i$’s, which is equivalent to swapping the orbitals of two electrons, does not result in a sign change.

One factor which needs to be accounted for is electron spin, which can either be spin up (+1/2) or down (–1/2). For closed shell calculations, orbitals are doubly occupied holding two electrons of opposite spin. This is parameterised by the two spin functions, $\alpha$ and $\beta$, as follows:

$$\alpha(\uparrow) = 1 \quad \alpha(\downarrow) = 0 \quad (1.40)$$
$$\beta(\uparrow) = 0 \quad \beta(\downarrow) = 1 \quad (1.41)$$

Multiplying a molecular orbital function by $\alpha$ or $\beta$ forms what is known as a spin orbital, and includes electron spin as part of the overall electronic wavefunction. For a system with $n$ electrons, a closed shell wavefunction can now be constructed by defining $n/2$ molecular orbitals, and then assigning electrons to these orbitals in pairs of opposite spin:

$$\psi(r) = \frac{1}{\sqrt{n!}} \left| \begin{array}{cccccc}
\phi_1(r_1)\alpha(1) & \phi_1(r_1)\beta(1) & \phi_2(r_1)\alpha(1) & \phi_2(r_1)\beta(1) & \cdots & \phi_{n/2}(r_2)\alpha(2) & \phi_{n/2}(r_2)\beta(2) \\
\phi_1(r_2)\alpha(2) & \phi_1(r_2)\beta(2) & \phi_2(r_2)\alpha(2) & \phi_2(r_2)\beta(2) & \cdots & \phi_{n/2}(r_2)\alpha(2) & \phi_{n/2}(r_2)\beta(2) \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\phi_1(r_n)\alpha(n) & \phi_1(r_n)\beta(n) & \phi_2(r_n)\alpha(n) & \phi_2(r_n)\beta(n) & \cdots & \phi_{n/2}(r_n)\alpha(n) & \phi_{n/2}(r_n)\beta(n) \\
\end{array} \right| \quad (1.42)$$
This is known as a Slater determinant, where each row is formed by representing all possible assignments of electron $i$ to all orbital-spin combinations. The initial factor is required for normalisation. As swapping two electrons corresponds to interchanging two rows of the determinant, which inevitably changes its sign, the system now satisfies the anti-symmetry requirement.

Basis Sets

A basis set is a mathematical description of the orbitals within a system. Any set of appropriately defined functions may be used to express molecular orbitals, however basis functions are usually centred on atomic nuclei and so bear resemblance to atomic orbitals. It is therefore common that molecular orbitals be built up from a linear combination of atomic orbitals (LCAO):

$$\phi_i = \sum_{\mu=1}^{N} C_{\mu i} \chi_{\mu}$$

(1.43)

where $\chi_i$ are normalised atomic orbitals and $C_{\mu i}$ the molecular orbital expansion coefficients. Most electronic structure programs use Gaussian-type atomic functions as basis functions, which have the general form:

$$g(\alpha, r) = c x^n y^m z^l e^{-\alpha r^2}$$

(1.44)

where $\alpha$ is a constant determining the radial extent of the function and $r$ is composed of $x$, $y$ and $z$. Initially Slater-type orbitals (STOs) were used, as these exponentially decay with distance from the nuclei. However, it was found that approximating STOs as linear combination of Gaussian orbitals was computationally superior. Nowadays hundreds of basis sets are composed of linear combination of primitive Guassian-type orbitals, having the form:

$$\chi_{\mu} = \sum_{\nu} d_{\mu \nu} g_{\nu}$$

(1.45)

where $g_{\nu}$ are primitive Gaussian functions and $d_{\mu \nu}$ are fixed contraction coefficients within a given basis set, which are determined by least-square fitting to accurate atomic orbitals.

The minimum basis set contains the minimum number of basis functions required to contain all electrons in a neutral atom, e.g. a single $s$ function for hydrogen and helium, or two $s$-functions ($1s$, $2s$) and one set of $p$-functions ($2p_x$, $2p_y$, $2p_z$) for first-row elements of the periodic table. However minimal basis sets typically give rough results. Larger basis sets impose fewer restrictions on the location of electrons in space, and so more accurately approximate atomic orbitals. A simple
way of doing this is to double all basis functions, producing a double zeta type basis. More economical however is to only concern oneself with the valence electrons, which is where most chemical properties are determined, with split valence basis sets having two (or more) sizes of basis function for each valence orbital. For example, Pople’s split valence basis sets are denoted n-ijG or n-ijkG, where n is the number of primitives for the inner shells, and i, j and k the number of primitives used for contractions of the first, second and third STO of the now double zeta or triple zeta split valence shells (Binkley et al., 1980; Gordon et al., 1982; Frisch et al., 1984).

Split valence basis sets allow orbitals to change size, but not shape, which is an important feature for the accurate description of bonding. Polarised basis sets remove this limitation, by adding orbitals with higher angular momentum than what is required for describing the ground state of an atom. For example, by adding in d orbitals to second row atoms, denoted by n-ijkG(d) or n-ijkG* in Pople’s basis sets, or additionally adding p functions to hydrogen atoms, denoted n-ijkG(d,p) or n-ijkG**.

A further improvement on basis functions is the addition of s- and p-type functions with small exponents, such that they occupy a large region in space. These diffuse functions allow for an improved description of electrons far from the nucleus. Inclusion of diffuse functions are usually denoted with a ‘+’. For example n-ijk+G basis set includes one diffuse s- and p-type functions for heavy atoms, whilst n-ijk++G additionally includes s-type diffuse functions for hydrogen atoms.

Also widely employed are the correlation consistent basis sets developed by Dunning and co-workers (Dunning, 1989; Kendall et al., 1992). These basis sets are designed towards recovering the correlation energy of valence electrons, and so have become the current mainstay for correlated calculations. The basis set is denoted as cc-pVNZ; where ‘cc’ denotes that it is a correlation consistent basis, VNZ indicates that it is a split valence basis with cardinal number N = D, T, Q, . . . for

\[
\left( \frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2} \quad \left( \frac{128\alpha^5}{\pi^3} \right)^{1/4} ye^{-\alpha r^2} \quad \left( \frac{2048\alpha^7}{\pi^3} \right)^{1/4} xy e^{-\alpha r^2}
\]
double-, triple-, quadruple-zeta respectively and ‘p’ denotes that polarised functions are included on all atoms. The inclusion of diffuse functions leads to the augmented correlation-consistent basis sets, aug-cc-pVNZ.

The Variational Principle

The variational principle states that; the expectation value for the energy of any antisymmetric normalised wavefunction will always be greater than or equal to the energy for the exact ground state wavefunction. Alternatively, the energy of the exact ground state wavefunction serves as a lower bound to the energies calculated from all other normalised antisymmetric wavefunctions. Thus the problem now reduces to finding the set of coefficients \( C_i \) in Equation 1.43 that minimises the energy of the wavefunction.

1.4.2 Quantum Chemical Methodologies

There are two main quantum-chemical strategies for solving the Schrödinger equation and hence determining the wavefunction and energy. Firstly, the problem can be made simpler by utilising spectroscopic data and physical properties in conjunction with strategic approximations. Methods which utilise such procedures are known as empirical or semi-empirical methods, and are often important for treating large systems. Secondly, quantum-chemical methods may be derived entirely from theoretical principles. Such methods are termed \textit{ab initio}. Whilst \textit{ab initio} methods are in no way exact, they are solved within a known error margin.

\textit{Ab Initio}

The simplest type of \textit{ab initio} electronic structure calculation is the Hartree-Fock method, which assumes that the wavefunction can be approximated by a single Slater determinant. Roothaan (1951) and Hall (1951) showed independently that solving for the molecular orbital expansion coefficients was equivalent to solving (using linear combination to express in matrix form):

\[
FC = SC\epsilon
\]

where \( F \) is the Fock matrix, which represents the average effects of the field of all the electrons on each orbital, \( S \) is a matrix of overlap integrals, indicating the overlap between orbitals, \( \epsilon \) is a diagonal matrix of orbital energies, with each element \( \epsilon_i \) being the one-electron orbital energy of molecular orbital \( \chi_i \) and \( C \) is a matrix formed from the orbital coefficients, \( C_{\alpha i} \). Included in construction of the Fock matrix is what is known as the density matrix \( P \), defined as:
The molecular orbital coefficients are summed over the occupied orbitals, with the factor of two derived from the fact that each orbital holds two electrons. Therefore both \( F \) and \( C \) depend on molecular orbital expansion coefficients, making Equation 1.46 a non-linear system which must be solved iteratively. For this reason, the Hartree-Fock method is also known as the self-consistent field (SCF) method. The general strategy used by the SCF method is to:

1. Choose a basis set.
2. Calculate all required integrals in the Fock and \( S \) matrices.
3. Form an initial guess for the molecular orbital coefficients and construct the density matrix.
4. Form the Fock matrix.
5. Solve for \( C \) and then construct a new density matrix.
6. Test for convergence, i.e., determine whether the new density matrix is the same as the previous density matrix within a specified criterion. If the procedure has not converged, return to step (4) with the new density matrix.

At convergence the energy is at a minimum, and the orbitals generate a field which produces the same orbitals. With the resulting solution, expectation values for other quantities of interest, such as dipole moments and population analysis, can be calculated.

Under Hartree-Fock treatment, each electron sees all of the other electrons as an average distribution. There is no instantaneous electron-electron interaction included, leading to inaccuracies in calculated energies. Correlation arising from pairs of electrons is known as exchange correlation. It is therefore common for methods to start with a Hartree-Fock calculation, before improving results by accounting for exchange energy, with these methods known as post-SCF or post-Hartree Fock methods. Commonly used approaches to account for electron correlation include: configuration interaction (CI; Sherrill and Schaefer, 1999), which mixes virtual orbitals with occupied orbitals in the Hartree-Fock determinant, including single excitations (CIS), double excitations (CID), single and doubles (CISD) and so on; couple cluster (CC; Čiček and Paldus, 1980) which constructs multi-electron wavefunctions through the action of an exponential operator on the Hartree-Fock determinant, which can account for single (S), double (D), triple (T) and higher order excitations, e.g. CCSDT; and Møller-Plesset Perturbation Theory (MP; Møller

\[
P_{\lambda\sigma} = 2 \sum_{i=1}^{\text{occupied}} c_{\lambda i}^* c_{\sigma i} \tag{1.47}
\]
and Plesset, 1934) which adds higher excitations to Hartree-Fock theory as non-iterative corrections, usually to the second (MP2), third (MP3) or fourth (MP4) order. Post-Hartree-Fock methods typically improve on initial Hartree-Fock calculations, although they do come at the expense of added computational cost, as shown in Figure 1.13.

Density Functional Theory

Density functional theory (DFT) methods are somewhat considered to be \textit{ab initio} methods for determining molecular electronic structure, despite many of the most common functionals using parameters derived from empirical data. The central focus of DFT is the electron density, $\rho$, rather than the wavefunction (Parr and Yang, 1994). The energy is calculated as a function of electron density, $E(\rho)$, which itself is calculated as a function of position, $\rho(\mathbf{r})$. Energy being a function of a function is the source of the name ‘functional’ in DFT. The electron probability density is calculated directly from occupied orbitals:

$$\rho(\mathbf{r}) = \sum_m |\phi_i(\mathbf{r})|^2$$

(1.48)

which themselves are calculated from the Kohn-Sham equations (Kohn and Sham, 1965). The approximate functionals employed by current DFT methods partition electronic energy into several terms:

$$\{ E_T + E_V + E_J + E_{XC} \} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

(1.49)
where $\epsilon_i$ is the orbital energy of the corresponding Kohn-Sham orbital, $\phi_i$, $E_T$ is the kinetic energy term, $E_V$ is the potential energy term describing nuclear-electron attraction and nuclei-nuclei repulsion, $E_J$ is the electron-electron repulsion term and $E_{XC}$ is the exchange-correlation term and includes the remaining part of the electron-electron interactions. All terms except for the nuclear-nuclear repulsion are functions of $\rho$.

The challenge with DFT is the construction of $E_{XC}$, which Hohenberg and Kohn (1964) demonstrated is a functional of $\rho$. Typically, $E_{XC}$ is separated into two parts, termed exchange functionals, $E_X$ and correlation functionals, $E_C$:

$$E_{XC}(\rho) = E_X(\rho) + E_C(\rho)$$ (1.50)

In principle these functionals can be obtained from a priori arguments, although derivation is complex. Instead the most widely-used functionals incorporate empirical parameters. For example, one of the most popular functionals, B3LYP, formed by pairing the gradient-corrected exchange functional of Becke (1993) with the gradient-corrected correlation functional of Lee, Yang and Parr (Lee et al., 1988), has 8 parameters fitted to a benchmark set of data including experimental enthalpies of formation and reaction energies.

The Kohn-Sham equations are solved iteratively and self-consistently (Parr and Yang, 1994). First, the electron density is guessed. It is common to use a superposition of atomic electron densities to do this. Next, the Kohn-Sham equations are solved to obtain an initial set of orbitals. This set of orbitals is then used to obtain a better approximation of the electron density, with the process repeating until the density and exchange-correlation are constant within some tolerance limit. The resemblance to SCF calculations is notable, with DFT calculations scaling just as favourably. Because of this, DFT has become a highly popular method, especially for molecular structure calculations of larger systems, and for most purposes has all but replaced the use of HF and MP2 in geometry optimisations and frequency calculations.

**Composite Methods**

Quantum chemistry composite methods are approaches designed for obtaining high accuracy results for total energies, for less computational effort, by combining output from several calculations. This is achieved by combining results from higher levels of theory, calculated with smaller basis sets, with lower levels of theory calculated with larger basis sets. One of the more popular composite methods is the Gaussian-\(n\) method (G-\(n\), where \(n = 1, 2, 3, 4\)), developed by Pople and coworkers (Pople et al., 1989; Curtiss et al., 1991, 2007a). For example, the G4 method uses the following
steps to calculate energy:

1. Molecular geometry is obtained by a B3LYP optimisation using the 6-31G(2df,p) basis set.

2. The Hartree-Fock energy at the basis set limit is calculated by an exponential extrapolation from results obtained using slightly reduced versions of the aug-cc-pVQZ and aug-cc-pV5Z basis sets.

3. A series of single point energy calculations are carried out and compared with a calculation done at the MP4/6-31G(d) level of theory. The highest level of theory is a CCSD(T) calculation with the 6-31G(d) basis set, whilst the effect diffuse and polarisation functions are assessed by using MP4 calculations with the 6-31G(2df,p) and 6-31+G(d) basis sets.

4. A correction for larger basis set effects is carried out at the MP2 level of theory, with the largest basis set used being G3LargeXP – which is a slightly extended version of the 6-311G(2df,2p) basis set.

5. Correction terms from steps (2), (3) and (4) are combined in an additive manner along with a spin-orbit correction and an empirical higher level correction to account for deficiencies in the energy calculations, to yield the total energy.

Hence the combined energy is an estimate of the total energy as if it was calculated at the CCSD(T)/G3LargeXP level of theory. There are many variants to this general procedure that employ subtle changes in methods at various stages, e.g. G4(MP2) and G4(MP3) which use second- and third-order perturbation theories in place of MP4 (Curtiss et al., 2007b). Another common composite method is the complete basis set (CBS) method, developed by Petersson and co-workers (Petersson et al., 1988; Ochterski et al., 1996), which is similar to the Gaussian formalism, but contains an extrapolation to the complete basis set limit rather than using additive corrections. The reliability of composite methods is routinely examined against extensive test set libraries, containing hundreds of molecules representing a large variety of molecular systems. These test sets show that methods such as G4(MP2) and CBS-Q can both provide relative energies to within 3.5 kJ mol\(^{-1}\).

1.4.3 Computational Chemistry Software Packages

Major software packages that perform high-level electronic structure calculations include Gaussian (Frisch et al., 2009), GAMESS (Schmidt et al., 1993), Molpro (Werner et al., 2015), Dalton (Aidalas et al., 2014) and Q-Chem (Kong et al., 2000). Software packages all contain a large number of methods and basis sets; far more
than what has been discussed. Consequently there are many possible combinations of basis sets and methods that one can choose to provide a solution to a molecular system, with the ultimate aim of being as close to experiment as possible. Nevertheless, the final choice is often based on a compromise between accuracy and computational cost, which is driven by the size of the system being investigated. It is common practice to first optimise the system of interest at lower levels of theory and basis sets, prior to commencing the final and more expensive calculation.

1.4.4 Potential Energy Surface and Application

Quantum chemical methods are used to predict critical points in atmospheric reaction processes, which are then used to construct what is known as a Potential Energy Surface (PES). On the PES, these critical points are all stationary, that is with first-derivatives with respect to each geometric parameter being equal to zero. Second-derivatives are then used to identify the mechanistic nature of critical points. When the second-derivatives are larger than zero, that is all eigenvalues of the Hessian matrix\(^8\) are positive, the critical point corresponds to a local minimum, being either a reactant, intermediate or product. Any movement away from this minimum, that is displacement of any of the nuclei, gives a conformation of higher energy. The global minimum corresponds to the most stable conformation on the PES. Transition states are saddle points, with a negative second-derivative in the direction of the PES reaction coordinate. Transition states therefore have a Hessian which contains a negative eigenvalue. Once diagonalised, the Hessian additionally provides normal frequency modes, which are proportional to the square root of the diagonal elements. Therefore a saddle point will be a stationary point with an imaginary frequency. First-order saddle points, containing only one imaginary frequency, are of particular interest in chemical kinetics because they lie on the most favourable path connecting reactants with products on the PES.

The aim of atmospheric quantum chemistry studies is to characterise PESs (Vereecken and Francisco, 2012; Vereecken et al., 2015). Once described, the PES provides all reaction pathways and associated energetics for underlying chemical steps and processes controlling complex chemical transformations. Used in conjunction with experimental measurements and theory at the macroscopic level, quantum chemistry thus provides unprecedented detail between structure and behaviour for atmospheric chemical systems.

\(^8\)The Hessian (H) is a symmetric matrix with second derivatives as elements.


1.5 Smog Chambers

In ambient studies, it is difficult to identify and assess the impact of underlying chemical processes due to the complex and dynamic nature of the troposphere. Consequently closed systems have been developed that mimic the ambient, whilst allowing isolation of specific compounds and control over the oxidising environment, free from the complexities of continual emissions, meteorology and mixing effects including advection and dispersion (Finlayson-Pitts and Pitts, 2000). One such experimental system used to investigate the chemical and physical processes related to air pollution are smog chambers.

Smog chambers consist of large confined volumes in which predefined air mixtures containing traces gases react in a controlled environment under simulated or natural light (IUPAC, 1997). Physical and chemical properties are monitored either online or offline by a suite of specialised analytical instruments connected to the reactor. Originally smog chambers were used to understand and develop gas-phase atmospheric oxidation mechanisms (Leone et al., 1985; Carter and Lurmann, 1991; Bloss et al., 2005), however smog chambers have since become important tools in investigating SOA formation and the physicochemical properties of aerosols (Griffin et al., 1999; Hallquist et al., 2009; Donahue et al., 2012a). Smog chamber facilities have been engineered around the world, with a selection given in Table 1.1.

There is considerable variability in the design of smog chambers. Reactor walls are essential to performance, needing to be both inert with excellent transparency to solar radiation (Hynes et al., 2005). Satisfying this criteria, fluoropolymers, such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP), are commonly employed. However these Teflon walls are not impervious to heterogeneous processes, including losses, with chamber size often exploited to reduce the impact of wall effects by minimising the surface area to volume ratio (Finlayson-Pitts and Pitts, 2000). For this reason, large outdoor smog chambers are common (Becker, 1996; Lee et al., 2004; Rohrer et al., 2005). However, outdoor chambers are susceptible to minor fluctuations in irradiation (e.g. changing cloud cover), and have diurnal, daily and seasonal variations in temperature and actinic flux. These uncontrolled variables make systematic studies investigating the effects of temperature and humidity difficult, and increase uncertainties in experimental conditions for model evaluation. Addressing these concerns, indoor smog chambers have been developed that house reactors inside temperature controlled rooms, containing an artificial light source that mimics the solar spectrum (Cocker et al., 2001b; Carter et al., 2005; Hynes et al., 2005; Paulsen et al., 2005). Black lamps (low-pressure mercury vapour lamps) have found considerable chamber use, providing good light
Table 1.1: Selection of major smog chamber facilities around the world.

<table>
<thead>
<tr>
<th>Chamber and Location</th>
<th>Type</th>
<th>Volume (m³)</th>
<th>Wall Material</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>University of North Carolina (UNC), USA</td>
<td>Outdoor</td>
<td>135 (dual)</td>
<td>FEP</td>
<td>Lee et al. (2004)</td>
</tr>
<tr>
<td>Simulation of Atmospheric PHoto-chemistry...</td>
<td>Outdoor</td>
<td>270</td>
<td>FEP</td>
<td>Rohrer et al. (2005)</td>
</tr>
<tr>
<td>European PHotoREactor (EU-PHORE), Fundación...</td>
<td>Outdoor</td>
<td>200 (dual)</td>
<td>FEP</td>
<td>Becker (1996)</td>
</tr>
<tr>
<td>California Institute of Technology (CALTECH), USA</td>
<td>Indoor</td>
<td>28 (dual)</td>
<td>FEP</td>
<td>Cocker et al. (2001b)</td>
</tr>
<tr>
<td>College of Engineering Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, USA</td>
<td>Indoor</td>
<td>90 (dual)</td>
<td>FEP</td>
<td>Carter et al. (2005)</td>
</tr>
<tr>
<td>Georgia Tech Environmental Chamber (GTEC), Georgia Institute of Technology, USA</td>
<td>Indoor</td>
<td>12 (dual)</td>
<td>FEP</td>
<td>Boyd et al. (2015)</td>
</tr>
<tr>
<td>Paul Scherrer Institute Simulation Chamber for Atmospheric Chemistry (PSI-SCAC), Paul Scherrer Institute, Switzerland</td>
<td>Indoor</td>
<td>27</td>
<td>FEP</td>
<td>Paulsen et al. (2005)</td>
</tr>
<tr>
<td>LEipziger AerosolKammer (LEAK), Leibniz Institute for Tropospheric Research, Germany</td>
<td>Indoor</td>
<td>19</td>
<td>FEP</td>
<td>Inuma et al. (2007)</td>
</tr>
<tr>
<td>Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia</td>
<td>Indoor</td>
<td>18</td>
<td>FEP</td>
<td>Hynes et al. (2005)</td>
</tr>
<tr>
<td>Centre for Research into Atmospheric Chemistry (CRAC), University College Cork, Ireland</td>
<td>Indoor</td>
<td>4</td>
<td>FEP</td>
<td>Thüner et al. (2004)</td>
</tr>
<tr>
<td>Carnegie Mellon University (CMU), USA</td>
<td>Indoor</td>
<td>10</td>
<td>PTFE/FEP</td>
<td>Presto et al. (2005a)</td>
</tr>
<tr>
<td>Harvard Environmental Chamber (HEC), Harvard University, USA</td>
<td>Indoor</td>
<td>5</td>
<td>PFA</td>
<td>King et al. (2009)</td>
</tr>
<tr>
<td>Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), University of Leeds, UK</td>
<td>Indoor</td>
<td>2.25</td>
<td>Metal</td>
<td>Glowacki et al. (2007)</td>
</tr>
<tr>
<td>Forschungszentrum Jülich, Germany</td>
<td>Dark</td>
<td>256</td>
<td>FEP</td>
<td>Mentel et al. (1996)</td>
</tr>
<tr>
<td>Aerosol Interaction and Dynamics in the Atmosphere (AIDA), Forschungszentrum Karlsruhe, Germany</td>
<td>Dark</td>
<td>84</td>
<td>Metal</td>
<td>Bunz et al. (1996)</td>
</tr>
</tbody>
</table>

Intensity in the 340 to 400 nm range, in which significant tropospheric photochemistry occurs. However output from black lamps on either side of this is poor, resulting in a spectrum significantly different from that of the sun (Carter et al., 1995). A more realistic solar spectrum is provided by xenon or argon lamps, which are com-
monly found in smog chambers alongside cheaper and more efficient black lamps (Carter et al., 2005; Paulsen et al., 2005).

Smog chambers are not without their uncertainties, with background effects depending on reactor walls, light source and background air matrix all affecting the reliability of experimental data. Chemical processes unique to smog chambers are termed auxiliary mechanisms, and have been the focus of numerous studies (Carter and Lurmann, 1991; Carter et al., 2005; Bloss et al., 2005; Zádor et al., 2006; Matsunaga and Ziemann, 2010; Zhang et al., 2014b), which have determined the following processes as important for consideration when interpreting data collected from smog chamber simulations:

1. The introduction of free radicals from heterogeneous wall processes.

2. Light dependent adsorption/desorption of NO$_x$ species (NO$_x$, HNO$_3$, HONO, etc) to/from chamber walls.

3. Loss of ozone, organic vapours and particles to the chamber walls.

4. The off-gassing of reactive species, including particulate precursors, from the chamber walls.

5. Dilution of chamber trace constituents as bulk gas is added to the reactor to compensate for losses due to chamber leaks and removal by instruments.

6. Non-representative or ill-defined lighting conditions in indoor or outdoor chambers respectively.

1.6 Modelling and Mechanisms

Computational modelling both tests and increases our understanding of the chemical and physical processes occurring in the troposphere. By constraining atmospheric chemistry models with measured or estimated data, significant detail can be extracted such that models can be used to interpret observations, test our current understanding and make future predictions, the last being useful in policy development. Nevertheless, logistical and conceptual limitations require models to compromise on representing the large-scale complexity of real-life atmospheric physical and chemical processes, although, with advances in software tools and computational resources and power, this boundary is constantly being pushed (Grell et al., 2005; Archer-Nicholls et al., 2014; Ling et al., 2014).
1.6. MODELLING AND MECHANISMS

1.6.1 Chemical Mechanisms

Atmospheric chemical models include the physical and chemical components of the environment to be investigated. The physical component can be described with relative simplicity: temperature, mixing ratios, surface/volume ratios, transport, diurnal fluctuations, etc. The chemical component however, represented by chemical mechanisms, is more complex. Chemical mechanisms consist of chemical species, the reactions they take part in, corresponding rate coefficients and photochemical data which are used to define photolysis frequencies (Stockwell et al., 2012). Chemical mechanisms are translated into differential equations which are then solved by a numerical solver, thereby simulating the fate of modelled species. Coupled with experimental studies, whether in the laboratory or field, and guided by insights from computational chemistry, chemical mechanisms are invaluable in allowing the intricacies of atmospheric processes to be studied in detail.

Only a very small number of the reactions occurring in the troposphere have been studied experimentally (Monks et al., 2009). The kinetics and products for the majority of elementary reactions involved in the degradation of the simplest hydrocarbons and oxygenates (e.g. methane, ethane, methanol, acetaldehyde, acetone) to CO$_2$ and H$_2$O have been investigated (Atkinson et al., 2006). Meanwhile, some important aspects of the degradation of larger and more complex VOCs (e.g. terpenes and aromatics) have been studied experimentally (Atkinson and Arey, 2003; Calvert et al., 2000, 2002, 2008). This information guides the construction of their chemical mechanisms, which is supplemented by the inclusion of reactions and associated parameters inferred from the more detailed understanding of the chemical fate of smaller compounds (Jenkin et al., 2003, 2012, 2015; Pinho et al., 2007). However, for the majority of VOCs, little or no experimental information exists, with chemical mechanisms constructed almost exclusively by inference. Therefore, when constructing a chemical mechanism, fundamental assumptions need to be made on how to represent the kinetics and products of unstudied chemical reactions. Chemical mechanisms also incorporate strategic simplifications to limit overall size, which could otherwise include millions of reactions (Aumont et al., 2005; Szopa et al., 2005). The application of different approaches to simplify chemical mechanisms, and different assumptions to represent areas of uncertainty, has resulted in numerous chemical mechanisms being developed. Surrogate and aggregate chemical mechanisms group classes of species (Gery et al., 1989; Carter, 2010; Goliff et al., 2013), whilst near-explicit chemical mechanisms represent reaction mechanisms for all compounds explicitly (Jenkin et al., 1997; Saunders et al., 2003; Aumont et al., 2005).
The Master Chemical Mechanism

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism that describes the detailed gas-phase chemical processes involved in the tropospheric photochemical degradation of methane and 142 other primary VOCs (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003). The current version, MCMv3.3.1, contains 17224 elementary reactions involving 5833 primary, secondary and radical species, including the complete degradation mechanism of isoprene and four terpenes; α-pinene, β-pinene, limonene and β-caryophyllene.

The MCM considers the complete degradation of gas-phase VOCs to CO₂ and H₂O as an iterative process, as shown in Figure 1.14. VOCs are initially consumed by reactions with O₃, OH and NO₃ radicals, or through photolysis. The first-generation radicals generated (RO₂, RO and Criegee biradicals) undergo further reactions to form a wide range of functionalised secondary products, including alcohols, carboxylic acids, hydroperoxides, nitrates etc. The system then feeds back upon itself, with the secondary species reacting through the primary initiation pathways until completely broken down into CO or CO₂.

The MCM utilises laboratory, theoretical and modelling data to describe the kinetics and mechanisms of reactions of VOCs and their degradation products (Jenkin et al., 1997, 2012, 2015). For unstudied reactions, where kinetic and mechanistic data are not available, the MCM utilises results from similar chemical species, ei-

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**Figure 1.14:** Schematic of MCM protocol outlining the major reactions, intermediate classes and product classes considered during the gas-phase degradation of a VOC. Image adapted from Saunders et al. (2003).
1.6. MODELLING AND MECHANISMS

ther by analogy or through use of structure activity relationships (SARs). SARs are developed using large databases of compounds, and work on the principle that the reactivity of a given bond can be defined by analogy to structurally similar (often simpler) species, with neighbouring functional groups accounted for through multiplicative corrections. Each bond in a given compound is treated individually, before being summed to yield the total reactivity of that compound. In the MCM, SARs have predominantly been used to calculate unknown OH radical rate coefficients through methods devised by Kwok and Atkinson (1995), Porter et al. (1997) and Peeters et al. (2007), with additional recent adoption of the oxy-radical SAR developed by Vereecken and Peeters (2009).

The MCM also employs strategic simplification measures designed to reduce the number of reactions and therefore computational costs. Mechanism contraction is predominantly achieved in three ways:

1. Reaction routes of low probability are excluded. For example, during OH initiation to relatively small molecules (≤ C₆), minor channels representing less than 10% of the reaction are disregarded, with the importance of the remaining channels scaled proportionally to maintain the overall rate coefficient.

2. Peroxy radicals are pooled to represent the many permutation reactions of each peroxy radical. This is achieved by defining a parameter, ‘RO2’, which is the sum of the concentrations of all peroxy radicals, excluding HO₂. The collective rate of all the permutation reactions of a particular peroxy radical (Reactions 1.15 – 1.17) is then represented by a single parameterised reaction.

3. The degradation reaction of products is simplified, whilst those formed through minor reaction pathways (e.g. organic nitrates, peroxynitrates, hydroperoxides, percarbonic acids, carboxylic acids and alcohols) are significantly simplified.

The implementation of simplification methods makes the MCM a near-explicit chemical mechanism. Further details regarding MCM simplification and parameterisation techniques can be found in protocol papers by Jenkin et al. (1997) and Saunders et al. (2003). The MCM can be accessed and downloaded in its entirety from its website, http://mcm.leeds.ac.uk.

1.6.2 Gas-Particle Partitioning

Gas-phase chemical mechanisms represent the oxidation of VOCs, which results in the formation of lower volatility products through functionalisation. Given the widespread importance of SOA in terms of health and climate, it is necessary to include gas-particle partitioning in atmospheric models.
Simple two-product gas-aerosol partitioning models, with empirically constrained values of $\alpha_i$ and $K_{p,i}$, have been widely incorporated into atmospheric chemical transport and general circulation models to represent SOA formation from specific VOCs (Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Henze and Seinfeld, 2006; Jiang et al., 2012; Santiago et al., 2012; Jathar et al., 2016). The laboratory-derived parameters can be extrapolated to different temperatures, using an assumed (or measured) effective value of the latent heat of vaporisation of the SOA (Hallquist et al., 2009). Whilst this model is simple enough to be implemented into global scale SOA modelling, in practice many more than two products are involved in SOA formation from a single VOC, with the simple two-product approach unable to account for the complexity and dynamics of SOA systems. For this reason use of the volatility basis set is becoming more attractive (Robinson et al., 2007; Pye et al., 2010).

The approach to modelling SOA formation that, at least in principle, is most chemically rigorous is to represent gas-to-particle partitioning for each compound formed in a chemical mechanism through explicit calculation of $K_p$. The challenge with this approach is that it requires an accurate gas-phase chemical mechanism, knowledge of vapour pressures for each semivolatile species, calculation of molecular properties such as activity coefficients of the absorbing organic/water mixture, and necessitates the inclusion of particle phase reactions (Hallquist et al., 2009). Indeed, for many, if not most of the identified SOA compounds this critical information is missing. Semi-empirical methods have been developed to estimate VOC vapour pressures (Myrdal and Yalkowsky, 1997; Capouet and Müller, 2006; Pankow and Asher, 2008; Nannoolal et al., 2008; Moller et al., 2008; Compernolle et al., 2011), often necessitating prior estimations of boiling points (Joback and Reid, 1987; Stein and Brown, 1994; Nannoolal et al., 2004), with current methodologies having been subject to comprehensive reviews by Barley and McFiggans (2010), Compernolle et al. (2010) and O’Meara et al. (2014). Likewise, a number of modelling tools for predicting activity coefficients in non-ideal mixed organic-inorganic systems relevant to atmospheric aerosols have been developed, including the semi-empirical group contribution methods UNIFAC (Fredenslund et al., 1975; Hansen et al., 1991) and its extensions (Yan et al., 1999; Topping et al., 2005; Erdakos et al., 2006a,b; Chang and Pankow, 2006), and AIOMFAC (Zuend et al., 2008, 2011). Utilising estimative techniques, gas-particle partitioning has successfully been coupled to pre-existing chemical mechanisms (Chen et al., 2006; Tulet et al., 2006; Simpson et al., 2007; Camredon et al., 2007; Jenkin et al., 2012), with implementation of condensed-phase reactions also assessed (Jenkin, 2004; Capouet et al., 2008; Camredon et al., 2010; Li et al., 2015; Khan et al., 2017).
1.7 Thesis Motivation and Overview

The tropospheric degradation chemistry of a few select monoterpenes has received considerable attention (Calvert et al., 2000; Atkinson and Arey, 2003), owing to their influencing role over the oxidative capacity of the troposphere and ability to produce SOA. This effort has been maintained in recent years through theoretical (Zhang and Zhang, 2005; Vereecken et al., 2007; Nguyen et al., 2009a; Zhao et al., 2010; Baptista et al., 2011; Oliveira and Bauerfeldt, 2015; Kurtén et al., 2015), experimental (Lee et al., 2006a,b; Saathoff et al., 2009; Heaton et al., 2009; Bateman et al., 2009; Herrmann et al., 2010; Fry et al., 2011; Zhao et al., 2015a; Zhang et al., 2015; Lopez-Hilfiker et al., 2015) and mechanism development studies (Jenkin, 2004; Leungsakul et al., 2005b; Pinho et al., 2007; Camredon et al., 2010; Carslaw et al., 2012; Carslaw, 2013), leading to a progressive improvement in the understanding of their general degradation chemistry and resulting tropospheric implications.

So far, the most detailed literature is focussed on the monoterpenes \(\alpha\)-pinene, \(\beta\)-pinene and limonene. However, even for these species, the distribution of first-generation products, mechanisms leading to their formation, subsequent degradation chemistry and SOA forming properties are far from completely characterised. Where experimental data have been sparse, theoretical methods have been applied to elucidate some of the more complex aspects of degradation, especially for \(\alpha\)-pinene (Peeters et al., 2001; Fantechi et al., 2002; Zhang and Zhang, 2005; Vereecken et al., 2007; Kurtén et al., 2015), often leading to the development of novel reaction pathways. Nonetheless, comprehensive chamber datasets, focussed on the oxidation of \(\alpha\)-pinene, \(\beta\)-pinene and limonene (Jenkin, 2004; Pinho et al., 2007; Carslaw et al., 2012), have allowed for the detailed construction of their chemical mechanisms, ultimately leading to the inclusion of these monoterpenes in the MCM.

Understanding the degradation and impacts of other monoterpenes is encumbered by the enormous variety in their structures and reactivity. Kinetic data have been measured for a wide variety of monoterpenes (Calvert et al., 2000; Atkinson and Arey, 2003), and shows atmospheric lifetimes to range from a minute to a few hours. Similarly measured SOA yields are also highly variable. For example, monoterpenes with two double bonds appear to have higher aerosol yields than those with one double bond (Griffin et al., 1999; Ng et al., 2006), whilst monoterpenes containing one or more double bonds internal to a ring structure have been shown to have higher yields than those with exocyclic double bonds (Lee et al., 2006a,b). Meanwhile Ortega et al. (2012) showed that different monoterpenes may play different roles in aerosol nucleation and growth. The use of surrogate monoterpenes in global and regional modelling studies can therefore only lead to erroneous results.

The role and impact of less abundant monoterpenes is slowly gaining interest.
Numerous field studies have shown that the impact of monoterpenes is not quantitatively understood, with evidence suggesting that additional reactive species are present in forested regions that are currently unaccounted for (Di Carlo et al., 2004; Holzinger et al., 2005; Kim et al., 2011; Mogensen et al., 2011; Jardine et al., 2015). For example, measurements from a Eucalypt forest in Tumbarumba, Australia, has shown Eucalypts (Eucalyptus delegatensis and Eucalyptus dalrympleana) to be particularly strong sources of new aerosol particles (Suni et al., 2008; Lee et al., 2008). Whilst new particle formation was observed during the day, of particular interest and potential climatic importance are the frequent and intense nucleation events observed at night. In contrast to other forested environments, such as Hyytiälä in southern Finland (Junninen et al., 2008), nocturnal nucleation events observed at Tumbarumba are significantly more prominent. A plausible explanation is the differing native BVOC compositions. Hyytiälä is primarily composed of Scots pine, with α-pinene, β-pinene and carene being the most abundant monoterpenes. Eucalypt forests are known to be large emitters of monoterpenes (Emmerson et al., 2016), with one major difference being the abundance of eucalyptol (1,8-cineol) in Eucalypt forests. Nevertheless Ortega et al. (2009) ruled out eucalyptol participation in nocturnal nucleation events. In a follow-up study, Ortega et al. (2012) was able to reproduce characteristic nocturnal nucleation events via the ozonolysis of different monoterpenes in a smog chamber, concluding that it is the oxidation of monoterpenes emitted by Eucalypts that is responsible for the prominently observed nocturnal nucleation events. The identity of the species responsible and resulting mechanisms, however, remain uncertain.

Considering the current discrepancies in the variety of monoterpenes represented in the literature, the aim of this PhD thesis is to investigate and characterise the tropospheric degradation of a monoterpene for which little literature currently exists, α-phellandrene, which, among other species, is commonly found in Eucalypts. Characterisation will be achieved through a combination of theoretical and experimental work, with the ultimate aim of deriving its chemical mechanism consistent with the MCM protocols.

1.7.1 α-phellandrene

The structure of α-phellandrene (1-methyl-4-isopropyl-1,5-cyclohexadiene) is shown in Figure 1.15. It was named after Eucalyptus phellandra (now called Eucalyptus radiata), from which it can be isolated. It is a monocyclic monoterpene containing two endocyclic conjugated double bonds, one stereocenter, and a carbon skeleton similar to the monoterpenes β-phellandrene, limonene, terpinolene and α-, β and γ-terpinene. α-phellandrene exists as a colourless liquid at room temperature, with
an earthy aroma similar to eucalyptus and fennel, a density of 0.85 g mL$^{-1}$ and a boiling point of 171 – 174°C (Sigma-Aldrich, 2014).

Only field studies in the Amazon rainforest in Brazil (Kesselmeier et al., 2000, 2002) and Wakayama Forest in Japan (Ramasamy et al., 2016) have detected α-phellandrene in the ambient, albeit at low concentrations. In the laboratory, α-phellandrene has been identified in emissions from seedlings of the Tasmanian blue-gum (*Eucalyptus globulus*, 0.08 µg g$^{-1}$ h$^{-1}$), Tuart tree (*Eucalyptus gomphocephala*, 0.08 µg g$^{-1}$ h$^{-1}$), swamp mahogany (*Eucalyptus robusta*, 0.27 µg g$^{-1}$ h$^{-1}$), salt river gum (*Eucalyptus sargentii*, 0.10 µg g$^{-1}$ h$^{-1}$) and white gum (*Eucalyptus wandoa*, 0.23 µg g$^{-1}$ h$^{-1}$) (He et al., 2000), with Maleknia et al. (2009) identifying α-phellandrene in emissions from both fresh and senescent leaves from the rose gum (*Eucalyptus grandis*). Kim et al. (2011) reported α-phellandrene to comprise 4.5% of the BVOC emission from Beech (species not specified). Meanwhile in their biomass burning study, Ciccioli et al. (2001) detected α-phellandrene from flaming (6.4 ± 0.9 mg kg$^{-1}$) and smouldering (0.8 ± 0.2 mg kg$^{-1}$) emissions from the wood of stone pine (*Pinus pinea*).

Despite limited studies having identified α-phellandrene in the ambient, Table 1.2 lists all species in which α-phellandrene has been identified as a major constituent of plant extracts. The vapour pressure of a particular monoterpene depends on both its volatility and concentration in the foliage, with monoterpene emission rates scaling according to Henry’s Law, that is, linearly with concentration in the plant tissue (Fuentes et al., 2000). It is therefore expected that α-phellandrene be emitted, to varying degrees, by the plant species listed in Table 1.2 (Hutchinson and Blackman, 2002). Indeed, the absence of its detection has been noted in a field study by Saxton et al. (2007), in Benin, who remark that, despite being available for emission, species with short tropospheric lifetimes, such as α-phellandrene, ‘would be difficult to detect in the ambient air samples due to the light winds and the distance between the inlet and the vegetation sources’. Of importance then, especially from an Australian context, is the identification of α-phellandrene as a major constituent in
extracts from various eucalypt species, with the absence of field studies sampling eucalypt forests noted (Winters et al., 2009). It is therefore not unreasonable to assume that $\alpha$-phellandrene is a non-negligible contributor to the large monoterpene emissions reported from Eucalypt forests (Emmerson et al., 2016), or the prominent nucleation events observed (Lee et al., 2008; Suni et al., 2008). Furthermore, the adaptability, fast growth rates and prized wood properties of eucalypts has driven plantations in more than 100 countries across six continents (> 20 million ha, Figure 1.16), making eucalypts the most widely planted hardwood forest trees in the world (Myburg et al., 2014). Due to its pleasant odour, $\alpha$-phellandrene is also used as an additive to household cleaning products, detergents and air fresheners (Steinemann, 2015), with the European EPHECT project reporting $\alpha$-phellandrene at a concentration of 16.7 $\mu$g m$^{-3}$ in a study of a passive air freshener in a 1 m$^3$ room after 5 hours (Stranger, 2013). Similar maximum $\alpha$-phellandrene concentrations have been reported in Australian dwellings (Maisey et al., 2013).

Rate coefficients for the reaction of $\alpha$-phellandrene with major atmospheric oxidants have been measured (Table 1.3), which show it to be a highly reactive monoterpene (Atkinson and Arey, 2003). Indeed Geron et al. (2000) estimated that only 40% of $\alpha$-phellandrene emitted from foliage would escape a given forest canopy into the atmosphere above. It is therefore expected that $\alpha$-phellandrene largely impacts the local environment in which it is emitted. Reaction product and mechanistic studies are scarce. OH radicals are expected to primarily add across the double bonds, with Peeters et al. (1999) reporting a hydrogen-abstraction channel yield
1.7. THESIS MOTIVATION AND OVERVIEW

<table>
<thead>
<tr>
<th>Species</th>
<th>Common Name</th>
<th>%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Eucalyptus viminalis</em></td>
<td>White gum</td>
<td>0.1–40</td>
<td>Pavlova et al. (2015); Maghsoodlou et al. (2015)</td>
</tr>
<tr>
<td><em>Eucalyptus microtheca</em></td>
<td>Coolibah</td>
<td>16.5</td>
<td>Maghsoodlou et al. (2015)</td>
</tr>
<tr>
<td><em>Eucalyptus delegatensis</em></td>
<td>Alpine ash</td>
<td>0.2–27</td>
<td>Boland et al. (1982, 1991); Li et al. (1995)</td>
</tr>
<tr>
<td><em>Eucalyptus amygdalina</em></td>
<td>Black peppermint</td>
<td>16</td>
<td>Li et al. (1995)</td>
</tr>
<tr>
<td><em>Eucalyptus dives</em></td>
<td>Broad-leaved peppermint</td>
<td>20–80</td>
<td>Brophy and Southwell (2002)</td>
</tr>
<tr>
<td><em>Eucalyptus nitida</em></td>
<td>Smithton peppermint</td>
<td>11–16</td>
<td>Brophy and Southwell (2002)</td>
</tr>
<tr>
<td><em>Eucalyptus piperita</em></td>
<td>Sydney peppermint</td>
<td>18</td>
<td>Brophy and Southwell (2002)</td>
</tr>
<tr>
<td><em>Eucalyptus radiata</em></td>
<td>Narrow-leaved peppermint</td>
<td>8–26</td>
<td>Li et al. (1995); Brophy and Southwell (2002)</td>
</tr>
<tr>
<td><em>Eucalyptus subangusta</em></td>
<td>Warralakin Mallee</td>
<td>16</td>
<td>Bignell et al. (1997)</td>
</tr>
<tr>
<td><em>Eucalyptus rodwayi</em></td>
<td>Swamp peppermint gum</td>
<td>43</td>
<td>Boland et al. (1991)</td>
</tr>
<tr>
<td><em>Eucalyptus tenuiramis</em></td>
<td>Silver peppermint</td>
<td>11</td>
<td>Li et al. (1995)</td>
</tr>
<tr>
<td><em>Eucalyptus calicola</em></td>
<td>Hamelin Bay mallee</td>
<td>11</td>
<td>Bignell et al. (1997)</td>
</tr>
<tr>
<td><em>Eucalyptus vetarensis</em></td>
<td>–</td>
<td>5–29</td>
<td>Pryor et al. (1995)</td>
</tr>
<tr>
<td><em>Anacardium occidentale</em></td>
<td>Cashew tree</td>
<td>12</td>
<td>Saxton et al. (2007)</td>
</tr>
<tr>
<td><em>Schinus molle</em> L.</td>
<td>Pepper tree</td>
<td>17.3</td>
<td>Bernhard et al. (1983)</td>
</tr>
<tr>
<td><em>Lantana camara</em> L.</td>
<td>Wild-sage</td>
<td>16.4</td>
<td>da Silva et al. (1999)</td>
</tr>
<tr>
<td><em>Curcuma longa</em></td>
<td>Turmeric</td>
<td>8–53</td>
<td>Lim (2016)</td>
</tr>
<tr>
<td><em>Anethum graveolens</em></td>
<td>Dill</td>
<td>26–47</td>
<td>Huopalaiti and Linko (1983); El-Zaeddi et al. (2016)</td>
</tr>
<tr>
<td><em>Alpinia malaccensis</em></td>
<td>–</td>
<td>31.8</td>
<td>Bhuiyan et al. (2010)</td>
</tr>
<tr>
<td><em>Haplophyllum tuberculatum</em></td>
<td>–</td>
<td>10.9</td>
<td>Al-Burtamani et al. (2005)</td>
</tr>
</tbody>
</table>

Table 1.2: Plant species containing α-phellandrene (percentage composition > 10%) in their extracts.

<table>
<thead>
<tr>
<th></th>
<th>(k) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>at T (K)</th>
<th>Lifetime (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>(3.2 \times 10^{-10} \pm 20%)</td>
<td>294</td>
<td>27(^a)</td>
<td>Atkinson et al. (1986); Peeters et al. (1999)</td>
</tr>
<tr>
<td>(O_3)</td>
<td>(3.0 \times 10^{-15} \pm 35%)</td>
<td>298</td>
<td>8(^b)</td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>(NO_3)</td>
<td>(7.3 \times 10^{-11} \pm 40%)</td>
<td>298</td>
<td>0.9(^c)</td>
<td>Calvert et al. (2000)</td>
</tr>
<tr>
<td>(NO_2)</td>
<td>(1.30 \times 10^{-17} \pm 33%)</td>
<td>295</td>
<td>1800(^d)</td>
<td>Atkinson et al. (1984)</td>
</tr>
</tbody>
</table>

\(^a\)Assuming OH radical concentration of \(2.0 \times 10^6\) molecule cm\(^{-3}\), 12 hour daytime average.

\(^b\)Assuming \(O_3\) concentration of \(7 \times 10^{11}\) molecule cm\(^{-3}\), 24 hour average.

\(^c\)Assuming \(NO_3\) radical concentration of \(2.5 \times 10^8\) molecule cm\(^{-3}\), 12 hour night time average.

\(^d\)Assuming \(NO_2\) concentration of \(2 \times 10^{11}\) molecule cm\(^{-3}\), 24 hour average.

Table 1.3: Rate coefficients (\(k\)) and lifetimes for the reaction of α-phellandrene with major tropospheric oxidants.
of 27 $\pm$ 10 % through direct observation of H$_2$O as a reaction product. Reissell et al. (1999) observed acetone as a minor reaction product from the reaction of $\alpha$-phellandrene with both OH radicals (8 $\pm$ 4 %) and ozone (< 2%), but in either scenario could not ascribe a plausible reaction pathway leading to its formation. OH yields from the ozonolysis of $\alpha$-phellandrene have been measured, with Herrmann et al. (2010) reporting yields of 26 – 31% and 8 – 11% for the addition of ozone to the tri- and di-substituted double bonds in $\alpha$-phellandrene respectively. Lastly, the addition of NO$_3$ to the conjugated system in $\alpha$-phellandrene has been shown to form $p$-cymene, with a yield of $\sim$18% at atmospheric pressures (Berndt et al., 1996). The mechanism of formation however remains unknown. Organic nitrates were also observed as products of the reaction, although no structural information was obtained, with carbonyl and peroxynitrate products reported to be absent from the product distribution (Berndt et al., 1996). There exists no prior literature investigating $\alpha$-phellandrene’s aerosol forming potential, characteristics or composition.

1.7.2 Project Aims

This thesis is separated into three distinct, yet interrelated chapters: computational study, experimental study and modelling study, which combine to provide a detailed account of the tropospheric degradation of $\alpha$-phellandrene.

Computational Study

In keeping with growing use in the field, the first aim of this project is to evaluate the ozonolysis mechanism of $\alpha$-phellandrene using computational techniques. The ozonolysis mechanism is considered due to its importance in the tropospheric degradation of $\alpha$-phellandrene (Table 1.3) and the inherent variability in its mechanism for different monoterpenes. The goal of the study is to assess the importance of the various ozonolysis mechanistic pathways (e.g. hydroperoxide, ester or ‘hot acid’, SOZ formation channels) in the degradation of $\alpha$-phellandrene, and subsequently identify the major products that are formed. Results from the computational study will then assist in experimental analysis and mechanism construction. Discussion of the theoretical component of this project is given in Chapter 2.

Experimental Study

The large majority of monoterpene oxidation knowledge is derived from smog chamber experiments. Therefore the second aim of this project is to experimentally characterise the tropospheric degradation of $\alpha$-phellandrene, under different physical and chemical conditions, through use of an indoor smog chamber facility at the
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). The goal of the experiments conducted is the robust characterisation of the physical properties and chemical composition of the gas- and particle-phases formed from oxidation of \(\alpha\)-phellandrene through ozonolysis and photooxidation. In addition, the reaction with \(\text{NO}_2\) is also investigated as previous studies have shown that conjugated dienes can react sufficiently rapidly with \(\text{NO}_2\) to be of interest. The photooxidation experiments will additionally provide a dataset to assess chemical mechanism constructs. Experimental methodologies and results are discussed in Chapter 3.

**Modelling Study**

The third and final aim of this project is to construct a near-explicit chemical mechanism, describing the tropospheric degradation of \(\alpha\)-phellandrene consistent with the MCM protocols and integrated with explicit gas-particle partitioning coding. The constructed chemical mechanism will be optimised and assessed against the measured photooxidation chamber dataset, with the ultimate aim of up-scaling towards inclusion in atmospheric modelling studies. Mechanism construction, optimisation and analysis are discussed in Chapter 4.

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9Guangzhou is a city that regularly experiences poor air quality, as shown in Appendix A.
2.1 Computational investigation into the ozonolysis of α-phellandrene.

A theoretical description of the addition of ozone to an olefin bond is complex and requires careful selection of theoretical method, as the wavefunctions for ozone, the pre-reactive complex and TS all show significant multi-reference character\(^1\) (Vereecken and Francisco, 2012; Vereecken et al., 2015). However, with 13 non-hydrogen atoms, the level of theory that can feasibly be applied to an extensive characterisation of the α-phellandrene + O\(_3\) electronic PES is restricted. Considerable variability in methodology exists for studying the ozonolysis of monoterpenes in the literature, with Table 2.1 listing published studies and the highest level of theory used. Previous theoretical investigations on the ozonolysis of smaller alkenes have systematically evaluated different computational approaches to identify a reliable, yet economic method to describe the reaction, showing that choice of both quantum-chemical method and basis set are important for accurate energy calculations (Wheeler et al., 2008; Lan et al., 2011; Zhao et al., 2009). For smaller alkenes, DFT provides an acceptable description for geometries of ozonolysis products when compared to higher-levels of theory (Gutbrod et al., 1997; Wheeler et al., 2008; Anglada et al., 2011; Sharkas et al., 2012), resulting in widespread application for characterising larger systems (Table 2.1). Nevertheless, for studies requiring a higher level of accuracy, composite methods have proven popular (Kuwata et al., 2005; Vereecken et al., 2007; Kuwata et al., 2011; Peeters et al., 2009; Nguyen et al., 2009a). Wheeler et al. (2008) systematically evaluated the composite methods, CBS-QB3, CBS-APNO, G3, B3B3, G3(MP2)B3, G4, G4(MP3) and G4(MP2) with respect to the initial stages of the ethene + O\(_3\) and ethyne + O\(_3\) reactions, concluding that the G4 series predicts the best barrier heights when compared to the focal

\(^1\)Systems requiring multiple determinants for an accurate description.
<table>
<thead>
<tr>
<th>Species</th>
<th>Method(^a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta)-pinene</td>
<td>CBS-QB3</td>
<td>Nguyen et al. (2009a)</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>CCSD(T)/6-31G(d)</td>
<td>Lin et al. (2014)</td>
</tr>
<tr>
<td>(\alpha)-pinene</td>
<td>CCSD(T)-F12a/VDZ- F12</td>
<td>Kurtén et al. (2015)</td>
</tr>
<tr>
<td>(\alpha-, \beta)-pinene</td>
<td>CCSD(T)/6-31G(d)(^b)</td>
<td>Zhang and Zhang (2005)</td>
</tr>
<tr>
<td>limonene</td>
<td>CCSD(T)/6-31G(d)(^b)</td>
<td>Jiang et al. (2010)</td>
</tr>
<tr>
<td>limonene</td>
<td>BHandHLYP/cc-pvdz</td>
<td>Baptista et al. (2011)</td>
</tr>
<tr>
<td>camphene</td>
<td>B3LYP/6-311++G(2d,2p)</td>
<td>Oliveira and Bauerfeldt (2012)</td>
</tr>
<tr>
<td></td>
<td>mPW1K/6-311++G(2d,2p)</td>
<td></td>
</tr>
<tr>
<td>sabinene</td>
<td>B3LYP/6-311+G(3df,2p)</td>
<td>Zhao et al. (2010)</td>
</tr>
<tr>
<td>ocimene</td>
<td>MPWB1K/6-311+G(3df,2p)</td>
<td>Sun et al. (2011)</td>
</tr>
<tr>
<td>(\alpha-, \beta)-pinene, camphene, sabinene</td>
<td>B3LYP/6-31+G(2d,2p)</td>
<td>Oliveira and Bauerfeldt (2015)</td>
</tr>
</tbody>
</table>

\(^a\) Used for final single-point energy calculation.
\(^b\) With additional MP2 derived basis-set correction factor.

Table 2.1: Comparison of computational methods used in investigating the ozonolysis of various monoterpenes in the literature.

point approach of Allen and co-workers (Allen et al., 1993; East and Allen, 1993; Császár et al., 1998; Schuurman et al., 2004).

Based on these findings, G4(MP2) is selected for analysis of the ozone + \(\alpha\)-phellandrene PES, with initial geometry optimisation carried out using B3LYP/6-31+G(d), with the D3 version of Grimme’s dispersion (Grimme et al., 2010, 2011) with Becke-Johnson damping (Becke and Johnson, 2005; Johnson and Becke, 2005, 2006). All calculations were carried out using the Gaussian 09 quantum chemistry software package (Frisch et al., 2009), with assistance from computational resources of the high-performance computing cluster of the Faculty of Science at the University of Western Australia. The complete study was published in *Physical Chemistry Chemical Physics*, with the article now presented in its published form.
2.1.1 Article Presentation

Title Computational investigation into the gas-phase ozonolysis of the conjugated monoterpene α-phellandrene.

Authors Felix A. Mackenzie-Rae
Amir Karton
Sandra M. Saunders

Journal Physical Chemistry Chemical Physics 18, 27991–28002.

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Date of Publication 26th of September 2016

Candidate Contribution I have contributed at an overall level of about 90% to the published work. Contributions were made to all aspects of the study, including research design, performing necessary calculations, analysing output and manuscript preparation and submission.
Computational investigation into the gas-phase ozonolysis of the conjugated monoterpene α-phellandrene†

F. A. Mackenzie-Rae,* A. Karton and S. M. Saunders

Reaction with ozone is a major atmospheric sink for α-phellandrene, a monoterpene found in both indoor and outdoor environments, however experimental literature concerning the reaction is scarce. In this study, high-level G4(MP2) quantum chemical calculations are used to theoretically characterise the reaction of ozone with both double bonds in α-phellandrene for the first time. Results show that addition of ozone to the least substituted double bond in the conjugated system is preferred. Following addition, thermal and chemically activated unimolecular reactions, including the so-called hydroperoxide and ester or ‘hot’ acid channels, and internal cyclisation reactions, are characterised to major first generation products. Conjugation present in α-phellandrene allows two favourable Criegee intermediate reaction pathways to proceed that have not previously been considered in the literature; namely a 1,6-allyl resonance stabilised hydrogen shift and intramolecular dioxirane isomerisation to an epoxide. These channels are expected to play an important role alongside conventional routes in the ozonolysis of α-phellandrene. Computational characterisation of the potential energy surface thus provides insight into this previously unstudied system, and will aid future mechanism development and experimental interpretation involving α-phellandrene and structurally similar species, to which the results are expected to extend.

1. Introduction

Biogenic sources dominate the global emission budget of volatile organic compounds into the atmosphere, with monoterpenes accounting for a significant fraction of nonmethane hydrocarbons emitted.1–4 Considering source strength, estimated to be 30–127 Tg C year\(^{-1}\), along with high chemical reactivity,5,6 monoterpenes are thought to play an important role in the chemistry of the atmosphere; influencing its oxidative capacity,7–11 the tropospheric ozone budget and by producing secondary organic aerosol (SOA) which impacts both health and climate.7–11 Indeed the ozonolysis of monoterpenes is thought to be one of the major sources of SOA in the atmosphere.11

Despite extensive experimental work on the ozonolysis of monoterpenes,5,6,10,11–18 there is still considerable uncertainty in their reaction mechanisms. The Criegee mechanism, that is, concerted cycloaddition of ozone to the double bond of the alkene forming a 1,2,3-trioxolane intermediate species (primary ozonide, POZ), is widely accepted,5,19 however experimental detection of intermediate species is extremely difficult due to their short lifetimes. Attempts at coupling experimental results with proposed mechanisms are often hindered by uncertainty in the fates of reactive intermediates. In addition, competition between prompt unimolecular and bimolecular reactions may result in pressure- and time-dependent yields. Inevitably theoretical studies have been utilised to describe the intricacies involved in monoterpene ozonolysis.20–26

One monoterpene that has received some attention in the literature is α-phellandrene. Emitted by a variety of plants27–32 and found in the indoor setting as an additive to household cleaning products and air fresheners,33,34 α-phellandrene is an extremely reactive monoterpene with a large SOA forming potential,35 that can have an immediate impact on the environment to which it is emitted. The rate constant of α-phellandrene with ozone has been measured in a number of studies,36–38 with a rate constant of 3.0 \(\times 10^{-15}\) (±35%) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) favoured.3 Less information is available on the products of the reaction; with OH radical yields of 26–31% and 8–11% reported for the ozonolysis of the two double bonds39 and acetone having been measured as a minor product (<2%).40

Whilst experimental data is sparse, α-phellandrene is an interesting species for theoretical appraisal, containing a cyclic, conjugated moiety that has not previously been investigated in...
the literature. In this study the reaction mechanism of ozone with α-phellandrene is elucidated, including formation of POZs, subsequent cleavage to form Criegee intermediates (CIs), and unimolecular reactions of the CIs to first generation products. A generalised scheme is shown in Fig. 1. Density functional theory (DFT) and \textit{ab initio} methods are employed to obtain accurate geometries and energies of transition states (TSs), reactive intermediates, and products, thus producing a potential energy surface (PES) that identifies key reaction pathways. Results show unconventional routes, which have not previously been considered in the ozonolysis of alkenes, are important in the decomposition of the conjugated system. These findings potentially extend to other structurally similar compounds. Key species that are likely to be important first generation products in the ozonolysis of α-phellandrene are also described.

2. Computational methods

The high-level composite G4(MP2) theory was used in order to explore the Gibbs-free energy surface at 298 K for the reaction of ozone with α-phellandrene.\textsuperscript{41} The G4(MP2) composite protocol is an efficient composite procedure for approximating the CCSD(T) (coupled cluster energy with singles, doubles, and quasiperturbative triple excitations) energy in conjunction with a large triple-\(\zeta\)-quality basis set.\textsuperscript{42,43} This protocol is widely used for the calculation of thermochemical and kinetic properties (for a recent review of the G\textit{n} methods see Curtiss \textit{et al.}\textsuperscript{42}). G4(MP2) theory has been found to produce thermochemical gas-phase properties (such as reaction energies, bond dissociation energies, and enthalpies of formation) with a mean absolute deviation of 4.4 kJ mol\(^{-1}\) from the 454 experimental energies of the G3/05 test set.\textsuperscript{44,45} It has also been found that G4(MP2) shows a similarly good performance for reaction barrier heights.\textsuperscript{45-48} The geometries of all structures have been optimized at the B3LYP/6-31G(2df,p) level of theory as prescribed in the G4(MP2) procedure.\textsuperscript{41,49-51} Harmonic vibrational analyses have been performed to confirm each stationary point as either an equilibrium structure (\textit{i.e.}, all real frequencies) or a transition structure (\textit{i.e.}, with one imaginary frequency). Zero-point vibrational energy (ZPVE), thermal enthalpy (\(\Delta H_{298}\)), and entropy (\(S\)) corrections were obtained from these frequencies within the rigid rotor-harmonic oscillator approximation and are used for converting the G4(MP2) electronic energies into Gibbs free energies at 298 K (\(\Delta G_{298}\)). The connectivities of the local minima and saddle points were confirmed by performing intrinsic reaction coordinate (IRC) calculations.\textsuperscript{52,53} These calculations were carried out at the B3LYP/6-31+G(d) level of theory. All calculations were carried out using the Gaussian 09 program suite.\textsuperscript{54}

3. Results and discussion

3.1 Formation of the CIs

Initial approach of ozone to the two double bonds of α-phellandrene can occur, in principle, on either side of the ring structure to produce four distinct POZ species. Additionally, each POZ formed has two conformers, depending on the relative spatial orientation of the central oxygen atom in the newly formed five-membered ring. Consequently, eight distinct reaction channels exist for the addition of ozone to α-phellandrene. The energy of the TS and POZ for each of these pathways is given in Table 1; with the more favourable attack site found to be dependent on the face of α-phellandrene that ozone approaches.

Frontier molecular orbital theory predicts that addition of ozone to the more substituted double bond (C2–C3, \textbf{DB1}) is favoured over addition to the less substituted double bond (C6–C7, \textbf{DB2}).\textsuperscript{18} Meanwhile experimental evidence from the ozonolysis of isoprene\textsuperscript{55-58} and miscellaneous conjugated dienes\textsuperscript{59} shows addition to the less substituted double bonds is favoured,
suggesting that steric effects are more influential. The driving steric factor in \( \alpha \)-phellandrene is found to be the relative orientation of carbons \( C_4 \) and \( C_5 \), which buckles due to ring strain and forced onto opposing sides of the plane formed by the conjugated carbons. The relative orientation of \( C_4/C_5 \) is thought to predominantly impact approach of ozone to the double bond to which it is adjacent, that is, if ozone approaches from the face where \( C_4 \) is notionally ‘up’, then DB2 is favoured and vice versa, as shown in Fig. 2. The effect is non-negligible, with differences greater than 4.4 kJ mol\(^{-1}\) observed for analogous attacks from either face. We note that, according to the Arrhenius equation, an change of 5.7 kJ mol\(^{-1}\) in the barrier corresponds to a change of one order of magnitude in the reaction rate at 298 K. Overall, addition to DB2 has the lowest barriers, suggesting that addition to the least substituted double bond is favoured in \( \alpha \)-phellandrene, consistent with what has been observed experimentally in other diene systems.

Once the POZ ruptures, conformational isomerism resulting from differing attack faces disappears. For this reason, and to reduce computational costs, only four unique addition pathways are thought necessary for further analysis to capture the chemistry of \( \alpha \)-phellandrene’s ozonolysis; that being attack at either double bond with the central oxygen of the POZ both syn (b) and anti (a) to \( \alpha \)-phellandrene’s 6-membered carbon ring. Chirality effects were found to have no impact on results (S.1, ESI†).

The PES for ozone addition to \( \alpha \)-phellandrene is given in Fig. 3 and 4. The reaction proceeds via formation of a van der Waals complex (vdW1, vDW2, vDW3, vDW4), followed by concerted cycloaddition through TS1, TS2, TS3 and TS4 to yield POZ1a, POZ1b, POZ2a and POZ2b respectively. The van der Waals complexes and TSs both lie lower in electronic energy and enthalpy than the free reactants (S.2, ESI†), such that addition of ozone to \( \alpha \)-phellandrene is essentially a barrierless reaction. Formation of the van der Waals complex is accompanied by negligible structural perturbations compared to the reactants. Similarly, minor distortions of the reactants occur upon formation of the TS (bond changes less than 0.04 Å, ozone angle deviations less than 5°), with the majority of structural perturbations occurring after passing through the TS (e.g. S.3, ESI†). Most notably, the C–O distances shrink whilst the C–C distance elongates to become a single bond. The calculated

<table>
<thead>
<tr>
<th>Addition pathway</th>
<th>( \Delta G_{298}^{TS} )</th>
<th>( \Delta G_{298}^{POZ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DB1a</td>
<td>46.8</td>
<td>-171.3</td>
</tr>
<tr>
<td>DB1b</td>
<td>45.7</td>
<td>-171.1</td>
</tr>
<tr>
<td>DB2a</td>
<td>38.7</td>
<td>-167.9</td>
</tr>
<tr>
<td>DB2b</td>
<td>37.6</td>
<td>-166.0</td>
</tr>
<tr>
<td>DB1a(^a)</td>
<td>41.3</td>
<td>-175.0</td>
</tr>
<tr>
<td>DB1b(^a)</td>
<td>41.3</td>
<td>-175.6</td>
</tr>
<tr>
<td>DB2a(^a)</td>
<td>43.4</td>
<td>-167.9</td>
</tr>
<tr>
<td>DB2b(^a)</td>
<td>46.1</td>
<td>-166.0</td>
</tr>
</tbody>
</table>

\(^a\) Denotes attack from the face with the dashed red line in Fig. 2.

Table 1 Change in Gibbs free energy (\( \Delta G_{298} \), G4(MP2), in kJ mol\(^{-1}\)) with respect to free ozone and \( \alpha \)-phellandrene for the 8 distinct initiation pathways possible in the ozonolysis of \( \alpha \)-phellandrene

Fig. 2 Preferred O\(_3\) attack faces of \( \alpha \)-phellandrene for the two double bonds.

Fig. 3 Gibbs-free energy profile (\( \Delta G_{298} \), G4(MP2), in kJ mol\(^{-1}\)) outlining the initial steps of the PES for the ozonolysis of DB1 in \( \alpha \)-phellandrene. \( \Delta G \) is with respect to the free reactants.
C–C and C–O bond distances for all POZs investigated ranged from 1.558–1.563 Å and 1.420–1.454 Å respectively, with an O–O bond angle between 101.9–102.6°. These geometries are in good agreement with previous literature results for the ozonolysis of other alkenes, suggesting parent hydrocarbon structure has little influence on POZ geometry.

For each addition pathway, the two TSs leading to different POZ conformers have very similar energies, such that channels essentially contribute equally to POZ formation. Furthermore, the chemically activated POZs face low interconversion barriers of 9.7/10.2 kJ mol⁻¹ (TS12) for POZ1a and POZ1b and 11.9/13.8 kJ mol⁻¹ (TS34) for POZ2a and POZ2b, such that the adduct populations will interconvert rapidly, readily assuming a microcanonical equilibrium independent of their initial formation ratios.

The addition process is highly exothermic with POZs lying over 166 kJ mol⁻¹ lower in energy compared to the free reactants (Table 1). The nascent energy is retained in the POZ ring structure, resulting in prompt decomposition through homolytic cleavage of the C–C and one of the O–O bonds which forms, in the case of asymmetrically substituted α-phellanderne, pairs of CI products. Ring opening occurs in competition with collisional stabilisation with the bath gas, however, the high nascent energy content combined with low barriers for POZ decomposition (<70 kJ mol⁻¹) leads to near-complete prompt POZ decomposition.

Ring opening of POZ1a proceeds via TS1a and TS2a, the former lying 19.5 kJ mol⁻¹ lower in energy such that CI1a is likely the only relevant reaction product. Despite negligible contributions from CI2a to the product distribution, discussion of its degradation is included in this paper for mechanistic completion and interest. Ring breaking of POZ1b goes through either TS1b or TS2b, with the two TSs separated by 4.5 kJ mol⁻¹. Therefore CI1b will be the favoured Criegee structure, although CI1b will also contribute to the product distribution.

Ring opening of POZ2a and POZ2b yields pairs of TSs that are quite similar in energy, a result of similar (mono-)substitution present on either side of the ozonide moiety. POZ2a decomposes through either TS3a (−109.8 kJ mol⁻¹) or TS4a (−112.0 kJ mol⁻¹), producing the Criegees CI3a and CI4a respectively. The energy difference between these two TSs is within the error threshold of the theoretical methods used in this study, and so no comment is made on the relative formation ratios of these two CIs. Ring opening of POZ2b proceeds through either TS3b (−97.8 kJ mol⁻¹) or TS4b (−97.8 kJ mol⁻¹) to yield equivalent amounts of CI3b and CI4b. Overall similar formation rates of CI3 and CI4 are expected, indicating that the adjacent π-bond has little impact on POZ2a and POZ2b decomposition.

For the eight CIs investigated, energies ranged from 210.0–233.0 kJ mol⁻¹ below that of the starting reactants. Given that ring-opening reactions in the POZ does not segment the molecule as a whole, all nascent energy is retained in the structure resulting in highly chemically activated CIs. As found for other CIs, the interconversion of CIs between conformers (e.g. CI1a and CI1b) is slow, with barriers for (pseudo)rotating the terminal oxygen in excess of 150 kJ mol⁻¹. Geometries show that these high barriers are the result of a double bond existing between carbon and oxygen in the dominant wavefunction for the substitute CIs; with these structures better described as closed-shell, charge-separated zwitterions rather than biradical species. When compared to the unimolecular decomposition pathways in Fig. 5–8, conversion between CI conformers is extremely uncompetitive and can be safely neglected.

Thus far, the entire discussion has focussed on the singlet PES. However decomposition of POZs results in highly energetic CI biradicals forming, thus the possibility of inter-system crossings (ISCs) must be considered. Ozone’s ground state wavefunction is known to show singlet character, with the lowest lying triplet state located around 100 kJ mol⁻¹ above the ground state. CIs are isoelectronic to ozone, with an analogous singlet ground state. However the vibrationally excited POZs can migrate onto the triplet PES and form stable minima through cleavage of an O–O bond (S.4, ESI†), with the ISC induced by strong spin-orbit coupling effects. It is then possible to form triplet CIs through
CHAPTER 2. COMPUTATIONAL STUDY

Fig. 5 Schematic Gibbs-free energy profile ($\Delta G_{298}^\circ$, G4(MP2), in kJ mol$^{-1}$) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of CI$_1$.

Fig. 6 Schematic Gibbs-free energy profile ($\Delta G_{298}^\circ$, G4(MP2), in kJ mol$^{-1}$) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of CI$_2$.

Fig. 7 Schematic Gibbs-free energy profile ($\Delta G_{298}^\circ$, G4(MP2), in kJ mol$^{-1}$) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of CI$_3$.
subsequent decomposition on the triplet PES. Such a pathway was found to be energetically unfavourable. Whilst an initial ISC onto the triplet surface may occur, as it is competitive with forming a singlet TS, upon cleavage of the C–C bond migration back onto the singlet surface is energetically favoured. In this sense, the triplet surface may act as an alternative pathway to forming singlet TSs. Nevertheless for the chemically activated POZs, the energy difference between the singlet TS and the triplet POZ is unlikely to have a large influence on the relative state density of these two kinetically critical points, resulting in a low probability of transition onto the triplet surface. Subsequent unimolecular reactions of the CIs is well-described using a restricted, closed-shell formalism, with only the bis(oxy) biradicals formed during dioxirane dissociation thought able to undergo an ISC onto the triplet PES. Such a transition is not investigated in this work, although results are expected to be similar to the findings of Nguyen et al.\textsuperscript{25,63} for β-pinene and β-caryophyllene, to which the reader is referred for further discussion.

3.2 Unimolecular reactions of the CIs

The fate of chemically activated CIs depends on their incipient energy, with unimolecular reactions occurring in competition with collisional stabilisation. For endocyclic alkenes such as α-phellandrene, where all of the nascent energy is retained in the tethered products, stabilisation requires multiple collisions.\textsuperscript{70} The CIs, stabilised or chemically activated, can undergo unimolecular decomposition through pathways well established in the literature\textsuperscript{5,19} including H-migration to form unsaturated hydroperoxides (hydroperoxide channel), cyclisation to dioxirane intermediates (ester or ‘hot’ acid channel), and internal ring-closure reactions to yield secondary ozonides (SOZs) or cyclic peroxides (Fig. 5–8). Stabilised CIs can additionally partake in bimolecular reactions with available atmospheric species (e.g. H$_2$O, NO$_2$, SO$_2$, aldehydes, carboxylic acids), which is uncompetitive for chemically activated CIs.\textsuperscript{19,70,71}

3.2.1 SOZ formation. Energetically, internal ring closure with the adjacent carbonyl group to yield a SOZ is the most favourable unimolecular reaction for all CIs derived from α-phellandrene, with barriers ranging from 17.6–60.0 kJ mol$^{-1}$. These values are consistent with the low barriers calculated for the sesquiterpene β-caryophyllene,\textsuperscript{64} demonstrating that ring strain for monoterpenes with 6 carbons in the product ring is not detrimental to internal cyclization. However entropically SOZ formation is unfavourable. This is because a linear precursor forms a bicyclic TS, reducing the degrees of freedom for internal rotation into vibrational modes.\textsuperscript{62,63} For chemically activated CIs, entropic hindrance reduces the competitiveness of SOZ formation with respect to other unimolecular pathways, with high energy content enabling significantly looser TSs to dominate the chemistry. However the low energy barrier likely makes SOZ formation important, if not the dominant unimolecular channel for stabilised CIs formed from α-phellandrene ozonolysis.

For the CIs derived from POZ1, Fig. 5 and 6 show both CI1a and CI2b cyclize to SOZ1c, facing barriers of 56.8 and 24.2 kJ mol$^{-1}$ through TS1e and TS2f respectively, whilst CI1b and CI2b rearrange to SOZ1f through TS1f and TS2c, facing barriers of 27.0 and 17.6 kJ mol$^{-1}$ respectively. Meanwhile for CIs derived from POZ2 decomposition, Fig. 7 and 8 show both CI3a and CI4b rearrange to SOZ3c, overcoming barriers of 60.1 (TS3c) and 31.3 kJ mol$^{-1}$ (TS4f) respectively, whilst CI3b and CI4a cyclize to SOZ3e through TS3e and TS4c, facing barriers of 39.0 and 27.9 kJ mol$^{-1}$ respectively. The barriers for SOZ formation from CI1a, CI2a, CI2b, CI4a and CI4b are significantly lower in energy compared to other accessible unimolecular decomposition channels (≥ 20 kJ mol$^{-1}$), indicating that SOZ formation likely dominates when these CIs are thermalised. For CI1b, CI3a and CI3b, other competitive pathways exist which are discussed in later sections. The pairs of SOZs formed are conformational isomers, and can interconvert rapidly through low barriers (TS1k, TS3i, 9–16 kJ mol$^{-1}$) such that a microcanonical equilibrium will likely be established independent of their nascent ratios.

The atmospheric fate of SOZs is largely unknown, with decomposition to acids and esters through simultaneous C–C
and C–O bond cleavage investigated. The decomposition product is found to be dependent on the orientation of the bridging peroxide group, with SOZ1e rearranging to ESTER1b and ACID1 through barriers of 127.5 (TSi1) and 165.9 kJ mol$^{-1}$ (TSi1m), while SOZ1f decomposes to ESTER1a and ESTER1c over barriers of 191.1 (TSioj) and 178.0 kJ mol$^{-1}$ (TSi1) respectively (Fig. 5). Given the low barrier of interconversion between the two SOZs (TSi1k), it is likely that the majority of decomposition will occur through the lowest barrier channel, yielding ESTER1b.

For the other set of SOZs, SOZ3e was found to decompose to ACID3b and ESTER3a through TSs3j and TSs3k, facing barriers of 169.5 and 127.4 kJ mol$^{-1}$ respectively, whilst SOZ3e decomposes through barriers of 169.2 (TS3l) and 137.8 kJ mol$^{-1}$ (TS3m) to yield ACID3a and ESTER3b respectively (Fig. 7). The barriers for ester and acid formation are significantly different for both conformers of SOZ3 (>30 kJ mol$^{-1}$), with ester formation again the likely unimolecular decomposition product.

The high barriers of decomposition observed for $z$-phellandrene derived SOZs are consistent with what has been reported in the literature for ethylene$^{27}$ and $\beta$-caryophyllene,$^{63}$ confirming the stability of SOZs as first-generation products. Bimolecular reactions are therefore likely to be rate limiting due to the stability of the SOZ intermediates in the atmosphere, predominantly occurring through addition of OH radicals, NO$_3$ radicals, or O$_3$ to the remaining double bond.$^5$

3.2.2 Hydroperoxide channel. The hydroperoxide channel is thought to be the major source of OH radicals in the ozonolysis mechanism of alkenes,$^{2,19}$ and, when available, the major decomposition route for chemically activated CIs.$^{70}$ The conventional hydroperoxide channel is accessible for CI1a, CI1b, CI2b and CI4b, with barriers of 71.0–90.5 kJ mol$^{-1}$ observed for 1,4-H shifts through transition states TSi1d, TSi1g, TS2g and TS4g, yielding the vinylhydroperoxide intermediates HP1d, HP1g, HP2g and HP4g respectively.$^{73}$ The chemically activated intermediates dissociate promptly through a barrierless reaction channel, forming OH radicals, along with resonance-stabilised vinoxy-like radicals RAD1d, RAD1g, RAD2g and RAD4g. The chemically activated intermediates dissociate promptly through a barrierless reaction channel, forming OH radicals, along with resonance-stabilised vinoxy-like radicals RAD1d, RAD1g, RAD2g and RAD4g. Nevertheless, when the radical electron is still involved in the TS active site, allyl resonance is not in full effect until after the barrier has been cleared, at which point it drives the barrier down through the products HP1h and HP3f, with resultant loss of OH forming the resonance stabilised radicals RAD1h and RAD3f. Geometry in the radical products suggests a mixture of all canonical structures. The newly proposed hydroperoxide pathway is recognisably akin to the alternative 1,6-H migration channels found for alkenyloxy radicals, where allyl-resonance stabilisation significantly lowers barrier heights compared to other abstraction pathways.$^{76–78}$ The energetic advantage provided by the allyl-resonance stabilised 1,6-H migration channel results in it being the only hydroperoxide channel accessed by CI1b and CI3b. The reduction in energy also makes the hydroperoxide channel for these CIs competitive with SOZ formation, such that a 1,6-H migration may additionally be a competitive pathway for thermalised CI1b and CI3b biradicals. These results are likely to extend to other structurally similar terpenes (e.g. $z$-terpinene, ocimene, safanral).

For the anti-CIs, CI2a, CI3a and CI4a, a 1,4-H shift is geometrically not possible, with 1,3-H migrations found to have high barriers in excess of 120 kJ mol$^{-1}$ (S.5, ESI†), making these reactions negligibly slow. The high barriers are consistent with what has been calculated for other alkenes in the literature.$^{63,78–81}$ In order to explain the formation of pinonic acid from the ozonolysis of $z$-pinene, Ma et al.$^{11}$ proposed an alternate mechanism whereby the CI isomerises through an aldehydic hydrogen abstraction. Whilst uncompetitive with competing hydroperoxide pathways in CI1a and CI3b (S.5, ESI†), the mechanism was found to provide an alternative hydroperoxide pathway with a lower barrier than 1,3-H migration for CI4a (Fig. 8). The mechanism proceeds through a 1,8-H shift with the acyl hydrogen, over a barrier of 95.5 kJ mol$^{-1}$ through TS4d. Post-transfer, the product rearranges into a relatively stable, 6-membered ring containing species HP4d. Driven by overall reaction exothermicity, decomposition through barrierless loss of OH proceeds, yielding the alkoy radical RAD4d. Subsequent decay can occur through

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![Fig. 9](image-url) Newly proposed hydroperoxide channel for CI1b through a 1–6 hydrogen shift, producing HP1h and RAD1h.
breaking adjacent C–C σ-bonds, rupturing the ring to form radicals RAD1j and RAD4k, along with OH radicals. The TSs lie 27.1 kJ mol$^{-1}$ apart however, with formation of the acyl radical RAD4k through TS4k overwhelmingly favoured, due to superior stability of the acyl radical compared to the alkyl radical$^{82,83}$ and resonance stabilisation with the adjacent π-bond.

The principle of acyl abstraction was applied to CI2a, where there is no adjacent aldehyde group, with a 1.9-H transition from the methyl group (CI1) found to have a barrier of 102.2 kJ mol$^{-1}$ through TS2d. Such a reaction has no precedent in the literature, with the structure of α-phellandrene enabling re-arrangement into a stable 7-membered ring HP2d to occur. Driven by overall reaction exothermicity, decomposition through barrierless loss of OH proceeds, yielding the alkoxyl radical RAD2d. Subsequent decay can occur through ring-breaking of either adjacent C–C σ-bond, with transition states TS2j and TS2k energetically indiscernible at 64(MP2) resolution. Consequently similar yields of radicals Rad2j and Rad2k are expected though this mechanism.

The radicals formed through the various hydroperoxide channels are rapidly stabilised by the addition of an oxygen molecule in the atmosphere, and can further decompose to a large number of low volatility products.$^{35,84}$

### 3.2.3 Ester or 'hot' acid channel

The ester or 'hot' acid channel first involves the formation of a dioxirane through cyclisation of the CIS, after clearing barriers of 71–98 kJ mol$^{-1}$ for the syn-conformers through TS2h, TS3g and TS4h, and 62–70 kJ mol$^{-1}$ for the anti-conformers through TS2e, TS3d and TS4e. For CI1 where conformational distinction is ambiguous; CI1a and CI1b had barriers of 87.2 (TS1e) and 74.0 kJ mol$^{-1}$ (TS1i) to overcome respectively. The large difference in observed barrier heights is due to steric hindrance in the syn-conformers. Indeed the largest differences between conformer barriers (>24 kJ mol$^{-1}$) are found in CI2 and CI4, where the Criegee moiety is adjacent to the isopropyl group. For terminal CIS, it has widely been discussed in the literature that syn-CISs favour the hydroperoxide channel, whilst anti-CISs (which cannot access the traditional hydroperoxide channel) favour the ester or 'hot' acid channel (Vereecken and Francisco$^{40}$ and references therein). It therefore appears that the availability of a 1,4-hydrogen is not the sole reason why the hydroperoxide channel is favoured in the syn-conformer; rather it is that the ester or 'hot' acid channel is significantly hindered, rendering it uncompetitive. Indeed this is the trend observed for CI2, CI3 and CI4, where the hydroperoxide channel is strongly favoured for the syn-conformer (CI2b, CI3b and CI4b) and ester or 'hot' acid channel for the anti-conformer (CI2a, CI3a and CI4a).

The ester or 'hot' acid channel for CI2a, CI3a and CI4a yields DIO2, DIO3 and DIO4 respectively. Interestingly dioxirane formation from CI3a is competitive with SOZ formation, with thermalised CI3a biradicals expected to contribute non-negligibly to the DIO3 budget. The hydroperoxide channel is favoured for both conformers of CI1, with trivial amounts of DIO1 expected through the ester or 'hot' acid channel.

The dioxiranes formed are comparatively stable, lying 75–105 kJ mol$^{-1}$ lower on the PES than the starting CIS. The general chemistry of dioxiranes is well described in the literature,$^{65,86}$ and in non-atmospheric applications they are known as strong epoxidising agents. Chemically activated dioxiranes rupture the O–O bond, forming a singlet bis(oxy) biradical, which readily displaces a neighbouring substituent to form an acid or ester. In their systematic computational study on bis(oxy) biradical isomerisation reactions, Nguyen et al.$^{63}$ found that with two different alkyl substituents, both ester-forming channels could be competitive, whilst for terminal bis(oxy) biradicals, H-atom migration would be dominant. Cremers et al.$^{86}$ also showed loss of CO$_2$ from smaller dioxiranes to be energetically favourable, however this process is thought to be insignificant in the larger α-phellandrene system, with the aforementioned isomerisations taken as the sole channel for dioxirane decomposition.

Migration of either substituent group in DIO1 yields an ester, facing barriers of 149.6 (TS1q) and 108.9 kJ mol$^{-1}$ (TS1p) for ESTER1a and ESTER1b respectively. Meanwhile DIO3 can promptly rearrange through TS3n, facing a barrier of 72.1 kJ mol$^{-1}$ to form ESTER3a, with the corresponding TS to ACID3a unable to be located on the B3LYP/6-31G(2df,p) PES. IRC calculations for each channel connected the TSs to both reactants and products, with no singlet bis(oxy) intermediate observed, contrary to other studies.$^{25,63,86}$ Nevertheless high level CASPT2/CASSCF calculations by Nguyen et al.$^{63}$ have shown the singlet bis(oxy) intermediate to be thermally unstable, with a very low or negligible barrier to isomerization. The barriers for ester formation suggest that the neighbouring vinyl groups make better migrating groups than either methyl or hydrogen atoms, implying that electron density in the adjacent π-bond is able to stabilise the TS more effectively. Indeed the effect of olefin substituents was not considered in the investigation of Nguyen et al.$^{63}$ It is therefore tentatively proposed that when α-phellandrene is adjacent to a vinyl group, ester formation involving the vinyl moiety is favoured.

Conventional TSs yielding acids and esters from DIO2 and DIO4 could not be located on the B3LYP/6-31G(2df,p) PES. Instead, re-arrangement into epoxides EPOX2 and EPOX4 was found to occur through TS2i and TS4i respectively, facing barriers of 75.7 and 63.6 kJ mol$^{-1}$. Epoxide formation from dioxiranes has precedence in the organic literature (Murray$^{85}$ and references therein), with bimolecular epoxidation having been subject to computational investigation.$^{87-90}$ However this is the first time that unimolecular epoxidation by a dioxirane has been proposed as a decomposition pathway. As shown in Fig. 10, with further discussion in the ESL,$^9 (S.6), the TSs show the characteristic concerted spiro-type structure that is observed in bimolecular dioxirane epoxidation reactions.$^{87-90}$ This spiro approach allows modest back bonding of the oxygen lonepair with the olefin π* orbital. The conformations of both CI2b and CI4b allow attainment of the advantageous spiro TS without excessive ring strain or steric hindrance. Such a process is believed to be unfavourable for smaller conjugated systems such as isoprene, or systems where the olefin group is too far separated in space from the dioxirane such as in β-caryophyllene, as ring strain to achieve a spiro TS would be too high. Indeed the barriers for epoxidation are favourable with respect to the other dioxirane decomposition channels investigated in this study.
The non-radical first generation products formed through SOZ and ester or ‘hot’ acid channels have very high energy content, with overall reaction exothermicity in excess of 540 kJ mol\textsuperscript{-1}. If formed through excited channels, such high internal energy is sufficient for chemically activated unimolecular reactions to occur; with elimination of a CO molecule facing barriers of over 290 kJ mol\textsuperscript{-1} for the various acid and ester products (S7, ESIF\textsuperscript{1}). The high barrier heights for CO elimination are consistent with what has been computed for smaller alkenes\textsuperscript{91,92} $\beta$-pinene\textsuperscript{25} and $\beta$-caryophyllene.\textsuperscript{63} Nevertheless the size and stability of the acid and ester products make it highly likely that they will be collisionally stabilised, preventing further unimolecular decomposition. The dioxiranes can also be collisionally stabilised but, under atmospheric conditions, thermal decomposition and rearrangement into esters/acid ultimately results.\textsuperscript{70} The two epoxides formed are expected to be stable, with formation saturating the molecule thus slowing the rate of bimolecular decomposition. EPOX\textsubscript{2} and EPOX\textsubscript{4} are therefore likely to be thermalised by collisions with the bath gas, with relatively long lifetimes compared to other unsaturated first generation degradation products.

The thermalised high-molecular weight oxygenated products, including SOZs, acids, esters and epoxides, are all formed without loss of carbon from the $\alpha$-phellandrene backbone, resulting in a significant reduction in species vapour pressure. The first generation products are therefore expected to partially condense in the atmosphere, contributing to SOA formation. The product distribution developed in this work can therefore go someway to explaining the high SOA yields that have been observed experimentally from $\alpha$-phellandrene ozonolysis.\textsuperscript{35}

3.2.4 Cyclic peroxide formation. The residual double bond in $\alpha$-phellandrene CIs enables another possible cyclisation reaction to occur for CI\textsubscript{1b} and CI\textsubscript{3b}, namely a 1,5-electrocyclisation reaction to a cyclic peroxide. The mechanism was first reported in Kuwata et al.,\textsuperscript{60} who found a barrier for methyl vinyl carbonyl oxide cyclisation of 46 kJ mol\textsuperscript{-1}, with yields of 40–45% predicted. Low barriers of 47.3 and 42.5 kJ mol\textsuperscript{-1} are similarly calculated for CI\textsubscript{1b} and CI\textsubscript{3b} respectively, through transition states TS\textsubscript{3j} and TS\textsubscript{3h}. Indeed geometries for the transition states TS\textsubscript{1j} and TS\textsubscript{3h}, and the products CP\textsubscript{1j} and CP\textsubscript{3h}, are akin to the isoprene analogues in Kuwata et al.,\textsuperscript{60} with the reaction showing all the same hallmarks of a monocrotatory pericyclic process; that being significant rotation of the vinyl group out of its original plane (torsional angles of 137.0° and –72.2° for TS\textsubscript{1j}, and 65.5° and –140.9° for TS\textsubscript{3h}), significant lengthening of the double bonds (increases of 0.05 Å, 0.02 Å, 0.04 Å and 0.03 Å for the C—C and C—O double bond in TS\textsubscript{1j} and TS\textsubscript{3h}), and significant shortening of the single bond (decrease of 0.05 Å and 0.06 Å for TS\textsubscript{1j} and TS\textsubscript{3h}) compared to the starting CIs. This suggests that given the right configuration of functional groups, the process is independent of parent species – with a pair of conjugated double bonds the only prerequisite.

Compared to other unimolecular decomposition routes, the barriers observed for 1,5-electrocyclisation are low. However, as is the case for SOZ formation, cyclisation of a CI to a 5-membered ring is entropically unfavourable, with the reaction only likely to be competitive for thermalised CIs. For CI\textsubscript{1b}, both a hydroperoxide (TS\textsubscript{1h}) and SOZ forming channel (TS\textsubscript{1f}) lie approximately 20 kJ mol\textsuperscript{-1} lower in energy (Fig. 5), such that 1,5-electrocyclisation into CP\textsubscript{1j} is unlikely to be a major channel. Meanwhile 1,5-electrocyclisation of CI\textsubscript{3b} through TS\textsubscript{3h} lies 3.6 kJ mol\textsuperscript{-1} higher than the SOZ forming channel (TS\textsubscript{3e}), and 4.1 kJ mol\textsuperscript{-1} lower than the hydroperoxide forming channel (TS\textsubscript{3f}) (Fig. 7). These values are within the uncertainty of the computational methods used, with all three channels likely competitive during CI\textsubscript{3b} decomposition.

The high yields of cyclic peroxides predicted during the decomposition of isoprene\textsuperscript{60} stems from a lack of competitive pathways. For $\alpha$-phellandrene CIs both SOZ formation, which as an intramolecular pathway is unavailable for isoprene, and a resonance stabilised hydrogen shift, for which isoprene CIs do not have the necessary size, are competitive. Consequently the high yields of cyclic peroxides reported in Kuwata et al.,\textsuperscript{60} for isoprene are not expected to be replicated in the ozonolysis of $\alpha$-phellandrene. The decomposition of CP\textsubscript{1j} and CP\textsubscript{3h} was not investigated in this work but, given the similarities observed with isoprene analogues, it is expected that they will undergo similar unimolecular decomposition pathways to form epoxides and dicarbonyls.\textsuperscript{60}

4. Conclusion

The gas-phase ozonolysis of $\alpha$-phellandrene is studied theoretically for the first time using the high-level \textit{ab initio} G4(MP2)
thermochemical protocol. The eight addition channels of $\mathrm{O}_3$ to the two double bonds in $\zeta$-phellandrene were examined, with the lowest barriers existing for addition to the least substituted double bond. Subsequent decomposition of four primary ozonides to form eight distinct Criegee intermediates were studied, with the hydroperoxide and ester or ‘hot’ acid channels accessible for these chemically activated CIs, and internal ring closure reactions to form secondary ozonides and cyclic peroxides investigated. In general, entropically unfavourable reactions had the lowest barriers for reaction, with considerable SOZ formation expected for thermalised CIs. The chemically activated CIs showed significant differences in their chemistries, however in general $\text{syn}$-CIs favoured the hydroperoxide channel and $\text{anti}$-CIs the ester or ‘hot’ acid channel. Interestingly, the cyclic conjugation present in $\zeta$-phellandrene enables an allyl-resonance stabilised 1,6-H migration to occur in CI1b and CI3b and unimolecular epoxide formation in the ester or ‘hot’ acid channel of CI2 and CI4. These novel processes are competitive with conventional mechanisms, and are thus expected to be important in the ozonolysis of structurally similar compounds (e.g. $\zeta$-terpinene, ocimene, safranal). Given the lack of attention $\zeta$-phellandrene has received in the literature, the pathways and first generation products characterised in this study can be used to assist in the analysis of future laboratory studies, and guide mechanism development.

Acknowledgements

This research was undertaken with the assistance of resources from the National Computational Infrastructure (NCI), which is supported by the Australian Government. We gratefully acknowledge the system administration support provided by the Faculty of Science at the University of Western Australia to the Linux cluster of the Karton group and an Australian Research Council (ARC) Discovery Early Career Researcher Award [to A. K., project number: DE140100311]. The authors would also like to thank Dr Andrew Rickard for helpful discussions.

References

2.1. COMPUTATIONAL INVESTIGATION INTO THE OZONOLYSIS OF α-PHELLANDRENE.

2.1.2 Article Supplementary Information

The supplementary information for the published article, ‘Computational investigation into the gas-phase ozonolysis of the conjugated monoterpene \( \alpha \)-phellandrene’, consists of 9 sections, as listed below. The last two sections, S.8 and S.9, are considerably large and do not provide any new information to the study with; S.8 representing output in an easy to understand non-graphical format and; S.9 providing textual Gaussian output for each reaction considered in the study. Consequently S.8 and S.9 are not included in this thesis, with an interested reader invited to view these supplementary entries on the PCCP website through use of the article’s DOI. The remaining Supplementary sections, S.1 – S.7, are now provided in their published form.

S.1 Effect of Chirality

S.2 Energies for \( \text{O}_3 \) addition to \( \alpha \)-phellandrene

S.3 Geometry of \( \text{O}_3 \) Addition

S.4 Triplet Surface Analysis

S.5 Uncompetitive Hydroperoxide Channels

S.6 Geometry of Epoxidation Reactions

S.7 \( \text{CO}_2 \) Elimination from First Generation Products

S.8 \( \alpha \)-phellandrene Reaction Equations

S.9 G4(MP2) Cartesian Coordinates and Energies for all Reactants, Transition States and Products on the \( \text{O}_3 \) addition to \( \alpha \)-phellandrene Potential Energy Surface
**Electronic Supplementary Information**

**Computational investigation into the gas-phase ozonolysis of the conjugated monoterpane α-phellandrene**

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School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA 6009, Australia.

**S.1 Effect of Chirality**

α-phellandrene is a chiral molecule, with C5 a stereocenter. The effect of chirality was investigated for the transition of **POZ1a** to **CI1a**. Table S.1 shows the two enantiomers of α-phellandrene are energetically identical, lying within the noise resolution of G4(MP2). This is not surprising given the chiral centre’s distance from the reactive site, with the respective orientation of the hydrogen atom having little to no influence on chemical kinetics or energetics. As such the effects of chirality are ignored in this study.

<table>
<thead>
<tr>
<th></th>
<th>ΔE_e</th>
<th>ΔE_0</th>
<th>ΔH_{298}</th>
<th>ΔG_{298}</th>
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<tr>
<td><strong>POZ1a</strong></td>
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<td>0</td>
<td>2.63 x 10^{-3}</td>
<td>5.25 x 10^{-3}</td>
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<tr>
<td><strong>TS2a</strong></td>
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<td>0</td>
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</tr>
<tr>
<td><strong>CI1a</strong></td>
<td>7.88 x 10^{-3}</td>
<td>7.88 x 10^{-3}</td>
<td>1.05 x 10^{-2}</td>
<td>7.88 x 10^{-3}</td>
</tr>
</tbody>
</table>

**Table S.1.** Absolute difference in energies (ΔG_{298}, G4(MP2), in kJ mol^{-1}) for the two enantiomers in going from **POZ1a** to **CI1a**.
### S.2 Energies for O₃ addition to α-phellandrene

<table>
<thead>
<tr>
<th>Addition Pathway</th>
<th>ΔEₑ (kJ mol⁻¹)</th>
<th>ΔE₀ (kJ mol⁻¹)</th>
<th>ΔH₂₉₈ (kJ mol⁻¹)</th>
<th>ΔG₂₉₈ (kJ mol⁻¹)</th>
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<td>-10.3</td>
<td>-8.5</td>
<td>28.8</td>
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<tr>
<td>DB1a TS1</td>
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<td>-0.6</td>
<td>-2.3</td>
<td>46.8</td>
</tr>
<tr>
<td>POZ1a</td>
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<td>-223.5</td>
<td>-228.4</td>
<td>-171.5</td>
</tr>
<tr>
<td>vDW2</td>
<td>-13.3</td>
<td>-9.6</td>
<td>-8.1</td>
<td>30.3</td>
</tr>
<tr>
<td>DB1b TS2</td>
<td>-6.5</td>
<td>-1.7</td>
<td>-2.6</td>
<td>45.7</td>
</tr>
<tr>
<td>POZ1b</td>
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<td>-224.3</td>
<td>-229.4</td>
<td>-171.1</td>
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<tr>
<td>vDW3</td>
<td>-12.7</td>
<td>-8.6</td>
<td>-7.5</td>
<td>32.5</td>
</tr>
<tr>
<td>DB2a TS3</td>
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<td>-6.8</td>
<td>-8.2</td>
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</tr>
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<td>POZ2a</td>
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<tr>
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<td>-217.8</td>
<td>-222.6</td>
<td>-166.0</td>
</tr>
</tbody>
</table>

**Table S.2.** Change in total electronic energy (Eₑ), total electronic energy including zero-point energy correction (E₀), enthalpy and Gibbs free energy with respect to free reactants for the van der Waals complex (vdW), transition state (TS) and primary ozonide (POZ) for the addition of ozone to α-phellandrene.
S.3 Geometry of O$_3$ Addition

As an example for all addition reactions in this study, the geometries for ozone addition to DB1 is shown below in Figure S.3.

Figure S.3. A set of optimised geometries for a van der Waals complex (vdW1), concerted transition state (TS1) and POZ (POZ1).
S.4 Triplet Surface Analysis

The CIs, being biradicals, can exist as either singlets or triplets. It is therefore important to know on which PES the reaction is occurring. Consequently an analysis of the reaction from POZ’s leading to CI formation was undertaken. For computational efficiency, the isopropyl group was replaced by a methyl group, and analysis completed at the B3LYP/6-31+G(d) level of theory. The results from this study were conclusive enough to warrant no further analysis at higher levels of theory. Ozone, α-phellandrene (and its surrogate), and the POZ’s all have singlet ground state. Figure S.4 shows that on this singlet surface the POZ can pass through a TS (TS1-4-s) and form a singlet Criegee biradical (CI1-4-s). Alternatively the POZ can migrate onto the triplet surface, where a stable minima is formed via cleavage of an oxygen-oxygen bond (POZ1-4-t). Research by Minaev and Kozlo68 showed the ISC of Criegee biradicals to be induced by large spin-orbit coupling effects involving the terminal oxygen, with similar effects expected to prompt POZ1-4-t formation. POZ1-4-t can then pass through TS-1-4-t, to form triplet Criegee biradicals CI1-4-t. It is evident in Figure S.4 that energetically this is an unlikely pathway, with the singlet surfaces lying at significantly lower energies. Whilst an initial intersystem crossing (ISC) onto the triplet surface may occur, as it is competitive with forming a singlet TS, migration back onto the singlet surface through the singlet TS is more favourable than proceeding through the triplet TS. The triplet surface may therefore act as an alternative pathway to forming the singlet TS’s. Nevertheless for the chemically activated POZ’s, the energy difference between the singlet TS and the triplet POZ is unlikely to have a large influence on the relative state density of
these two kinetically critical points, resulting in a low probability of transition onto the triplet surface.

![Graph]

**Figure S.4.** Comparison of the singlet and triplet PES ($\Delta G_{298}$, G4(MP2), in kJ mol$^{-1}$) for the transition of POZ’s to CIs. $\Delta G$ is with respect to **POZ1-s**.
S.5  **Uncompetitive Hydroperoxide Channels**

The following hydroperoxide channels were found to be uncompetitive with other possible hydroperoxide pathways available for the given Criegee intermediate. Note that in all cases a 1,3-hydrogen migration was uncompetitive.

<table>
<thead>
<tr>
<th></th>
<th>Barrier (kJ mol(^{-1}))</th>
<th>Mechanism</th>
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<tbody>
<tr>
<td>CI1a</td>
<td>106.0</td>
<td>1,8-H acyl migration</td>
</tr>
<tr>
<td>CI2a</td>
<td>121.7</td>
<td>1,3-H migrations</td>
</tr>
<tr>
<td>CI3a</td>
<td>130.1</td>
<td>1,3-H migrations</td>
</tr>
<tr>
<td>CI3b</td>
<td>120.3</td>
<td>1,8-H acyl migration</td>
</tr>
<tr>
<td>CI4a</td>
<td>121.3</td>
<td>1,3-H migrations</td>
</tr>
</tbody>
</table>

**Table S.5.** Barrier heights (\(\Delta G_{298}, G4(MP2)\)) for hydroperoxide channels not included in the primary analysis.
S.6  Geometry of Epoxidation Reactions

**DIO2:** Epoxidation proceeds through cleavage of the weak peroxide bond which stretches from 1.496 to 1.843 Å in going from **DIO2** to **TS2i**, followed by breaking of one of the dioxirane C–O and ethylenic π bonds which are both elongated in the **TS2i**. The approach of oxygen to the olefin is close to perpendicular, first bonding with C6 followed by C7 in a concerted fashion. Meanwhile a carbonyl π-bond is formed with the residual oxygen from the dioxirane moiety to form **EPOX2**. Labelling the epoxide forming oxygen as O1, and the other oxygen in the dioxirane moiety as O2, whilst keeping the carbon labels the same as in Figure 1 in the main text, then the C7-O1-C6-C3 and C7-O1-C6-O2 torsion angles in **TS2i** are −127.1° and −163.0° respectively, indicating a spiro transition type.

**DIO4:** Epoxidation proceeds through cleavage of the weak peroxide bond which stretches from 1.496 to 1.835 Å in going from **DIO4** to **TS4i**, followed by breaking of one of the dioxirane C–O and ethylenic π-bonds which are both elongated in the TS. The approach of oxygen to the olefin is close to perpendicular, first bonding with C3 followed by C2 in a concerted fashion. Meanwhile a carbonyl π-bond is formed with the residual oxygen from the dioxirane moiety to form **EPOX4**. Labelling the epoxide forming oxygen as O1, and the other oxygen in the dioxirane moiety as O2, whilst keeping the carbon labels the same as in Figure 1 in the main text, then the C2-O1-C3-C6 and C2-O1-C3-O2 torsion angles in **TS4i** are 124.5° and 159.3° respectively, indicating a spiro transition type.
S.7  CO₂ Elimination from First Generation Products

Chemically activated products can have sufficient energy to eliminate a CO₂ molecule directly, generating a shorter alkyl chain. The barriers for this channel for some products formed in this study are listed below.

<table>
<thead>
<tr>
<th></th>
<th>Barrier (kJ mol⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>ESTER₁a</td>
<td>389.4</td>
</tr>
<tr>
<td>ESTER₁b</td>
<td>308.9</td>
</tr>
<tr>
<td>ACID₁</td>
<td>290.8</td>
</tr>
<tr>
<td>ESTER₃a</td>
<td>291.4</td>
</tr>
<tr>
<td>ACID₃b</td>
<td>289.5</td>
</tr>
</tbody>
</table>

*Table S.7.* Barrier heights ($ΔG_{298}^0$, G₄(MP2)) for CO₂ elimination from first generation products.
2.2 Kinetic Calculations

2.2.1 Method

To quantify branching ratios, and hence relative importance of the different initial reaction channels of ozone to α-phellandrene, transition state theory (TST) is employed to calculate bimolecular, temperature-dependent rate coefficients from computational output (Eyring, 1935; Truhlar et al., 1996; Fernández-Ramos et al., 2006). Conventional TST assumes that the reactants and TS exist in a quasi-equilibrium, and requires very little knowledge of the PES; namely the TS activation energy and partition functions of the reactants and TS. The sole focus of TST is therefore the saddle point, with the mechanism by which reactants evolve into products being irrelevant. TST calculations are performed using the KiSThelP software package (Canneaux et al., 2014), which has been developed to estimate molecular and reaction properties from electronic structure output. KiSThelP is theoretically less advanced than other programs available on the market, such as MultiWell (Barker, 2001, 2009; Barker et al., 2016) and polyRate (Zheng et al., 2017), and is not intended to predict highly accurate rate coefficients, but rather provide cheap and useful insight into a given system using first-principles. The inputs required for KiSThelP are mass of the system (amu), vibrational frequency numbers (cm$^{-1}$), electronic degeneracy, moment of inertia (amu $a_0^2$), rotational symmetry number, linearity and electronic potential energy (Ha). These inputs are used in KiSThelP to calculate the rate coefficient through the thermodynamic interpretation of TST:

\[ k_{TST}(T) = \sigma \frac{k_b T}{h} \left( \frac{RT}{P_0} \right)^{\Delta n} e^{-\frac{\Delta G^{0,\dagger}(T)}{k_b T}} \]

(2.1)

where $\sigma$ is the reaction pathway degeneracy, $k_b$ is the Boltzmann constant, $T$ is the temperature, $h$ is Planck’s constant, $R$ is the ideal gas-constant, $P_0$ is the standard pressure, $\Delta G^{0,\dagger}(T)$ is the standard Gibbs free energy of activation for the considered reaction and $\Delta n$ is the change in moles, being 0 or 1 for gas-phase uni- or bi-molecular reactions respectively. In this work, quantum mechanical tunnelling effects are not corrected for, although sensitivity testing reveals corrections are minor and of similar magnitude for each initiation channel. The neglect of tunneling therefore has little impact on the outcome of this study. All calculations are computed at 1 bar, with a reaction path degeneracy of 2, corresponding to $C_{2v}$ symmetry present in ozone. The overall thermal rate is computed as a sum of the fluxes of the different product-forming channels, as given by:
where \( \gamma_i \) is the fraction of redissociation back into the initial reactants, which is assumed to be zero for the addition of ozone to \( \alpha \)-phellandrene (Nguyen et al., 2009a).

### 2.2.2 Results and Discussion

As discussed in Section 2.1.1, the addition of ozone to the two double bonds in \( \alpha \)-phellandrene can occur through eight distinct reaction channels. TST thermal rate coefficients, computed using G4(MP2) quantum chemical data obtained for each of these channels, is given in Table 2.2 for conditions typical of the troposphere (298 K, 1 bar). Addition to the more substituted double bond, DB1, is predicted to occur at a rate of \( 7.76 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), while addition to the less substituted double bond, DB2, is calculated to occur at a rate of \( 2.70 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Overall, a total rate coefficient of \( 3.47 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) is predicted for the addition of ozone to \( \alpha \)-phellandrene, which is over an order of magnitude faster than the recommended literature rate coefficient (Calvert et al., 2000). The result obtained is considered reasonable given limitations of the KiSThelP software, and that inherent errors in G4(MP2) methodology (\( \sim 4.4 \text{ kJ mol}^{-1} \)) are expected to lead to discrepancies in TST rate coefficients ordering an order of magnitude (Curtiss et al., 2007b; Wheeler et al., 2008; Baptista et al., 2011). Such discrepancies in predicted rate coefficients with experimental data are not uncommon in literature studying the ozonolysis of monoterpenees (Zhang and Zhang, 2005; Baptista et al., 2011; Oliveira and Bauerfeldt, 2015).

The temperature dependence of rate coefficients are plotted in Figure 2.1 using Arrhenius expressions\(^2\) and are additionally compared with experimentally measured values (Grimsrud et al. (1975); Atkinson (1990); Shu and Atkinson (1994). A small negative temperature dependency is predicted for the addition of ozone to both double bonds, indicative of overall barrierless processes (Nguyen et al., 2009b). The small magnitude of the temperature dependency suggests that the rate coefficient can more or less be considered constant over all relevant \( \alpha \)-phellandrene atmospheric emission and destruction sites. As shown in the Supplement (S.2, Section 2.1.2), the total energy of the system (\( E_e, E_0, H_{298} \)) is highest in the van der Waals prereactive complex, not the TS, suggesting that an association bottleneck could be relevant. If this were true, then the notionally ignored van der Waals complex may

---

\(^2\) Arrhenius’ equation gives the temperature dependence of a rate coefficient based on a pre-exponential factor (A) and an activation energy (\( E_a \)), and has the general form: 
\[ k = Ae^{-E_a/(RT)} \]

where R is the ideal gas constant and T the temperature.
2.2. KINETIC CALCULATIONS

### Table 2.2: TST predicted site-specific rate coefficients for the gas-phase ozonolysis of α-phellandrene at 298 K and 1 bar.

<table>
<thead>
<tr>
<th>Addition Pathway</th>
<th>$k \text{ (cm}^3\text{ molecule}^{-1}\text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DB1a</td>
<td>$1.48 \times 10^{-15}$</td>
</tr>
<tr>
<td>DB1b</td>
<td>$2.34 \times 10^{-15}$</td>
</tr>
<tr>
<td>DB2a</td>
<td>$3.88 \times 10^{-14}$</td>
</tr>
<tr>
<td>DB2b</td>
<td>$6.14 \times 10^{-14}$</td>
</tr>
<tr>
<td>DB1a$^a$</td>
<td>$1.35 \times 10^{-14}$</td>
</tr>
<tr>
<td>DB1b$^a$</td>
<td>$1.37 \times 10^{-14}$</td>
</tr>
<tr>
<td>DB2a$^a$</td>
<td>$5.78 \times 10^{-15}$</td>
</tr>
<tr>
<td>DB2b$^a$</td>
<td>$1.99 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

$^a$ Denotes attack from the face with the dashed red line in Figure 2 in the PCCP paper (Section 2.1.1).

play an important role in determining kinetics, with variational TST thus required for accurate assessment of rate coefficients (Nguyen et al., 2009b; Vereecken and Francisco, 2012).

Despite over-prediction of the thermal rate coefficients, any errors in theory or method are likely to cancel out through comparison, such that results can be qualitatively compared to gain insight into the system. Addition to DB2 is therefore predicted to occur around 3.5 times faster than addition to DB1 at 298 K, due to steric hindrance from the methyl group. This prediction is slightly higher than the ratio of $\sim 2.5$ for addition to the more substituted compared to the less substituted double bond observed in isoprene, based on experimental yields of the major first-generation carbonyls methacrolein and methylvinyl ketone (Paulson et al., 1992a; Aschmann and Atkinson, 1994; Rickard et al., 1999). Nonetheless, a more pronounced steric differential arises due to buckling of the 6-member ring, with the side that ozone approaches more or less determining which addition site is more reactive. This effect is evident in Table 2.2, whereby addition to DB2 is favoured 26:1 for the assessed approach face (solid red line in Figure 2 of the PCCP paper, Section 2.1.1), whilst addition to DB1 dominates 7:2 when ozone approaches from the opposing side (dashed red line). Syn- and anti-conformers are predicted to be formed in a 4:3 ratio, however nascent differences are rapidly negated by the low barriers for interconversion (TS12, TS34) between different POZ forms.

Further TST calculations on the PES were not conducted due to unquantified uncertainties in the methodology and time-constraints. The primary aim of the simple kinetic study was to provide tangible results from quantum chemical output. A more detailed variational TST analysis of the initiation reactions, followed by a complete
Figure 2.1: Predicted TST overall and site-specific thermal rate coefficients for the gas-phase ozonolysis of \( \alpha \)-phellandrene over atmospherically relevant temperatures, compared with experimental data.

RRKM (Rice–Ramsperger–Kassel–Marcus) master equation analysis (Forst, 2003; Miller and Klippenstein, 2006) of the entire PES to predict first-generation product yields, provides a clear avenue for future investigation (Zhang and Zhang, 2005; Nguyen et al., 2009a; Baptista et al., 2011).
Chapter 3
Experimental

All experiments in this thesis were conducted at the GIG-CAS smog chamber facility, over 4 separate campaigns from 2013 – 2016, with filter analysis conducted during a 6-week visit to the University of York, UK, in 2016.

3.1 GIG-CAS Smog Chamber

The GIG-CAS smog chamber is a state-of-the-art indoor smog chamber designed for studying atmospheric gas-phase and aerosol chemistry (Wang et al., 2014). The reactor is constructed from FEP Teflon film (FEP 100, Type 200A; DuPont, USA), shaped around two external rectangular stainless steel frames, as shown in Figure 3.1. The FEP reactor is self-made using a heat sealing laminator, with all seams reinforced by a polyester film tape with a silicone adhesive (polyester tape 8403; 3M, USA). The maximum chamber dimensions are $5.0 \text{ m} \times 3.0 \text{ m} \times 2.0 \text{ m}$, giving a maximum volume of $30.0 \text{ m}^3$, surface area of $62 \text{ m}^2$ and a surface-to-volume ratio of $2.07 \text{ m}^{-1}$. The reactor is housed in a thermally insulated room, with inner walls lined with polished stainless steel sheets to maximise light intensity and homogeneity. The floor is lined with less reflective, but more durable stainless steel sheets. The chamber is illuminated by 135 black lamps (1.2 m long, 60 W Phillips/10-R; Royal Dutch Electronics Ltd) separated into two banks (55 and 80 lamps each) mounted on opposing sides of the chamber, external to the reactor walls. Temperature is controlled inside the enclosure by three air-conditioning units (40 kW total power), capable of producing temperatures over the range 263 to 313 K. Eight thermocouples are distributed around the enclosure, placed approximately 1 metre above the floor. The enclosure temperature is maintained by an electronic control system which adjusts power to the air-conditioning units according to the difference between the eight thermocouples and the set temperature. A Siemens QFM2160 sensor measures temperature and relative humidity (RH) inside the reactor. The top rectangular frame of the reactor is connected to a mechanical step-motor, enabling the chamber
Figure 3.1: The GIG-CAS smog chamber. Several features including metal frame, FEP reactor walls, Teflon-coated fans, injection and sampling ports, polished room walls and a bank of blacklamps are visible.

to collapse during experiments (compensating for losses due to sampling, leaks and permeation) and expand whilst filling, and maintain a slight positive pressure inside the reactor to minimise contamination from ambient air. The experiment stops when the reactor lowers to around one third of its maximum height. Two Teflon coated, 3-winged stainless steel fans are incorporated into the reactor from the floor, to enhance mixing of gas- and particle-species inside the reactor. Four ports are incorporated into the base of the reactor, each containing bundles of 0.635 cm I.D. Teflon tubes. One port located in the center of the chamber has 12 tubes used for injection purposes (e.g. purified air, gaseous samples, water vapour, aerosol seeds). The remaining ports, two containing 4 and one containing 12 tubes, provide sampling lines for the various instruments.

The matrix gas used in experiments is prepared by passing compressed laboratory air through a combustion chamber filled with Hopcalite, followed by passing through the following series of scrubbers; Purafil, activated charcoal, Hopcalite, allochroic silica gel and a PTFE filter. The set-up is able to supply purified dry air ($< 5$ ppb non-methane hydrocarbons) with a maximum flow rate of 200 L min$^{-1}$. The reactor is flushed between experiments with purified dry air at a flow rate of 100 L min$^{-1}$ for at least 48 hours until no residual hydrocarbons, $O_3$, NO$\_x$ or particles are detected.

Liquid reactants, such as $\alpha$-phellandrene, acetonitrile and cyclohexane, are intro-
duced into the chamber by injecting known volumes, using microlitre syringes, into a heating system with an injection port similar to that used in gas-chromatography. The temperature of the injection port is varied according to the boiling point of the sample, with 180–190°C used for α-phellandrene and 150°C for acetonitrile and cyclohexane. NO\textsubscript{x} (NO 99.9%; NO\textsubscript{2} 99.5%; Foshan KODI Gas Chemical Industry Co., Ltd.) are injected through a septum, installed to a union tee, using gas-tight syringes, with the outflow connected to one of the reactor injection ports. Both liquid reactants and NO\textsubscript{x} are flushed into the chamber by nitrogen gas (≥ 99.999%, Foshan KODI Gas Chemical Industry Co., Ltd.). Ozone is generated by a commercial ozone generator (VMUS-4; Azco Industries Ltd, Canada), using pure oxygen feed gas (≥ 99.999%, Foshan KODI Gas Chemical Industry Co., Ltd.) to prevent the unwanted generation of NO\textsubscript{x}. Ozone introduction is moderated by generation time and O\textsubscript{2} flow rate. Humidification is achieved by passing purified dry air over boiling Milli-Q ultra-pure water contained in a 0.5 L Florence flask.

### 3.2 Analytical Instruments

The GIG-CAS chamber facility is fitted with a comprehensive suite of analytical instruments for monitoring the gas- and particle-phases inside the reactor. The specific instruments and related measurement parameters are listed in Table 3.1. The instruments are connected to the chamber by FEP Teflon tubes, with the end of the tube being placed inside the reactor as part of one of the bundled sampling ports. The instruments themselves are all located in a room adjacent to the reactor, as shown in Figure 3.2. Residence times in the sampling lines are on the order of seconds, with the influence of the sampling process on the homogeneity of air reaching instruments thought negligible (Wang et al., 2014).

#### 3.2.1 Gas-Phase Inorganics

An EC9841T chemiluminescence analyser (Ecotech, Australia) is used to measure NO and NO\textsubscript{2} inside the reactor. The analyser operates by detecting luminescence from chemically activated NO\textsubscript{2} molecules, which are produced by the reaction between NO and O\textsubscript{3} (Equation 1.4) inside the analyser. Excited NO\textsubscript{2} is formed in a 1:1 molar ratio, thus the intensity of chemiluminescence is directly proportional to the NO concentration in the sample. An additional sample channel passes through a NO\textsubscript{2} to NO converter (molybdenum, 325°C), with the difference between the NO\textsubscript{x} and NO channels representing the original NO\textsubscript{2} concentration. The detection limit and accuracy of the NO\textsubscript{x} analyser are 50 ppt and ±0.5% respectively.

Ozone is measured by an EC9810 UV photometric gas detector (Ecotech, Aus-
Table 3.1: Instrument suite at the GIG-CAS chamber facility used to analyse experiments discussed in this thesis.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measured Parameters</th>
<th>Detection Limit/Range</th>
<th>Accuracy(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siemens QFM2160</td>
<td>Temperature</td>
<td>0 – 50°C</td>
<td>±0.8°C</td>
</tr>
<tr>
<td></td>
<td>Relative humidity</td>
<td>0 – 100%</td>
<td>±3%</td>
</tr>
<tr>
<td>Ecotech 9810</td>
<td>O(_3)</td>
<td>0.5 ppb</td>
<td>0.5 ppb or ±0.5%(^b)</td>
</tr>
<tr>
<td>Ecotech 9841T</td>
<td>NO/NO(_2)/NO(_x)</td>
<td>50 ppt</td>
<td>100 ppt or ±0.5%(^b)</td>
</tr>
<tr>
<td>Agilent GC-MSD/FID</td>
<td>VOCs</td>
<td>&lt; 10 ppt</td>
<td>±5%</td>
</tr>
<tr>
<td>Ionicon PTR-TOF-MS 2000</td>
<td>VOCs</td>
<td>0.1 – 5000 ppb</td>
<td>±(5 – 30)%</td>
</tr>
<tr>
<td>TSI SMPS</td>
<td>Particle number</td>
<td>1 – 10(^7) cm(^{-3})</td>
<td>±10%</td>
</tr>
<tr>
<td></td>
<td>Particle size</td>
<td>10 – 1000 nm</td>
<td>±(3 – 3.5)%</td>
</tr>
<tr>
<td>Aerodyne HR-TOF-AMS</td>
<td>Particle composition</td>
<td>22 ng m(^{-3}).(^c)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\) Claimed by manufacturers.
\(^b\) Whichever is greater.
\(^c\) For organics.

The analyser detects ozone using a mercury vapour lamp, which has a strong emission at 254 nm, close to the centre of the ozone absorption band. The analyser utilises a MnO\(_2\) ozone scrubber, which is periodically switched in and out of the measuring stream, removing ozone whilst allowing other common absorbers such as SO\(_2\) to pass. Since absorbances add, the resulting difference between the scrubbed and non-scrubbed cycles is a function of ozone concentration. The detection limit and accuracy for the ozone analyser are 0.5 ppb and ±0.5% respectively. Both the ozone and NO\(_x\) analysers are regularly calibrated during smog chamber campaigns, using a Thermo Scientific Model 146i multi-gas calibrator.

During experiments, it was noted that α-phellandrene induces a false positive bias in the ozone analyser. This is because α-phellandrene, due to its conjugation, is optically active in the ultraviolet region, with an absorbance maximum at 263 nm (de Kock et al., 1960; Arruda et al., 2013). This implies that α-phellandrene is somewhat removed by the MnO\(_2\) scrubber. This phenomena has been noted in the literature, with chamber studies showing interference to be extremely prevalent for aromatic compounds and their derivatives (Huntzicker and Johnson, 1979; Grosjean and Harrison, 1985; Leston et al., 2005; Spicer et al., 2010; Riva et al., 2017). Initial attempts were made to remove α-phellandrene from the sample stream, however it was difficult to find a scrubber that would remove α-phellandrene without perturbing O\(_3\). A liquid nitrogen/hexane cold trap (−94°C) was also trialled, as theoretically this would remove α-phellandrene whilst allowing ozone (boiling point = −112°C) to pass. In addition to α-phellandrene however, a large number of organics also condensed, rapidly inhibiting flow through the trap and into the O\(_3\) analyser.
Ultimately a method of ozone detection other than UV photometry should be employed. For the final campaign, an Aeroqual Series 500 portable gas monitor, fitted with a semiconductor oxide O₃ sensor (OZL, 0 – 0.50 ppm) (Auckland, New Zealand), was purchased for use in chamber experiments. Inside the sensor, a metal oxide semiconductor is heated to around 300°C, at which point it exhibits a change in resistance that is very sensitive to the amount of ozone in contact with its surface; a technology that is not anticipated to experience major, direct, interference from α-phellandrene. Multiple studies have shown the Aeroqual ozone sensor to be reliable with respect to traditional ozone analysers (Lee and Tsai, 2008; Lin et al., 2015). Nonetheless, the sensor broke immediately once fitted to the GIG-CAS chamber due to a manufacturing error. A replacement sensor was not able to be shipped in time for the campaign, with ozone measurements once again reliant on the EC9810 analyser.

Given the inability to negate interference on the ozone analyser, the effect was instead calibrated by comparing proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF, Section 3.2.2) α-phellandrene readings, with those on the ozone analyser. Interference could then be corrected for during post-processing of data. Calibration results from all experiments are shown in Figure 3.3, which shows high variability. Based on Beer-Lambert’s law, a linear calibration curve is expected, which is approximately observed during specific calibration experiments (which had aliquots of α-phellandrene added to the reactor). However, when com-

3.2. ANALYTICAL INSTRUMENTS

![Diagram of Instrument Suite](image)

Figure 3.2: Instrument suite at the GIG-CAS smog chamber. The reactor, shown in Figure 3.1, is housed behind the back, temporary white wall.
Figure 3.3: Calibration of α-phellandrene’s interference on the ozone analyser. Data are from both designated calibration experiments and chamber simulations, collected upon introduction of α-phellandrene into the reactor up until commencement of the given reaction. Grey lines act as visuals, constraining data belonging to the two separate responses observed.

pared with data from individual chamber simulations, recorded after the addition of α-phellandrene up until commencement of the given chamber reaction, significant variability is observed. Results are relatively insensitive to physical and chemical conditions inside the reactor (e.g. temperature, relative humidity and addition of reactants including NO$_x$, cyclohexane and inorganic acids). Some consistency is observed between campaigns conducted in 2013, 2014 and 2016, whilst the O$_3$ analyser response in 2015 shows a significantly different trend. Given calibration procedures of both the ozone analyser and PTR-TOF were consistent across all campaigns, changes in sensitivity of the ozone analyser with respect to α-phellandrene are attributed to the MnO$_2$ scrubber. If, for whatever reason, MnO$_2$ scrubbing of α-phellandrene were to become more/less efficient, then the respective reading on the ozone analyser would also change. The impact of unknown variables however cannot be ruled out. Despite some consistency being observed during individual campaigns, it is insufficient for construction of reliable calibration curves. Ozone concentrations were therefore corrected separately for each individual experiment using an ad hoc method; determining the magnitude of the α-phellandrene bias at the start of each experiment and assuming it scales linearly throughout. Such a method introduces a large amount of uncertainty into reported ozone readings. The optical activity of α-phellandrene in the UV region is derived from conjugation, with degradation products not expected to bias ozone readings. Indeed α-phellandrene
readings on the ozone analyser and PTR-TOF scaled linearly during the reaction of α-phellandrene with NO2, showing degradation products to have a negligible impact on ozone readings.

3.2.2 Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer

The proton-transfer-reaction mass spectrometer (PTR-MS) was first-developed in the mid-1990’s (Hansel et al., 1995; Lindinger et al., 1998), with the technique shown to be a fast and reliable tool for online organic trace gas monitoring with widespread application, including food and flavour chemistry, medicinal sciences and environmental research (Hewitt et al., 2003; de Gouw and Warneke, 2007; Blake et al., 2009). Earlier instruments relied on quadrupole mass spectrometers as mass analysers, however Blake et al. (2004) showed the feasibility of utilising a time-of-flight mass spectrometer (TOF-MS) in a PTR-MS system for the first time. Initially these systems were challenged by poor sensitivity and low ion count rates (Blake et al., 2004; Ennis et al., 2005), which was largely solved by Jordan et al. (2009), who coupled the ion source and drift tube with a Tofwerk orthogonal acceleration reflection TOF-MS, leading to the development of a new generation of high mass resolution PTR-TOF-MS (referred to as PTR-TOF throughout this thesis). The newly developed PTR-TOF instrument retains all the advantageous features of conventional PTR-MS instruments, including wide applicability to different classes of VOCs, high sensitivity and fast response time, as well as having the added advantage of being able to capture the whole mass spectrum at once and separate nominally isobaric ions (Jordan et al., 2009; Cappellin et al., 2010; Graus et al., 2010). Commercially available through Ionicon Analytik GmbH, a PTR-TOF 2000 is utilised at the GIG-CAS chamber to measure VOCs at ultra-low concentrations, with a high mass resolution in real-time.

Principle of Operation

Figure 3.4 shows the basic construction of the PTR-TOF, consisting of four major components: an ion source, a drift tube, a transfer lens and the time-of-flight system. Whilst having the potential to operate in different ionisation modes, in this work, the hydronium ion (H3O+) was used exclusively as the primary ion source. H3O+ is produced from water vapour using a hollow cathode ion source. Nascent H3O+ ions are drawn into the drift tube by an electric field, where the analyte sample is continuously injected. Inside the drift tube a proton transfer from H3O+ to the
Reaction 3.1 will be thermodynamically spontaneous if the change in Gibbs free energy is negative. However, proton affinities are more commonly used to assess if a given proton transfer reaction is likely to occur, with it generally true that species with proton affinities greater than that of water (691 kJ mol\(^{-1}\)) undergo an exothermic proton transfer reaction (Blake et al., 2009). Proton affinities have been tabulated for a large number of molecules (Hunter and Lias, 1998). Most non-alkane VOCs have proton affinities higher than that of water, whilst most common inorganic constituents of air possess proton affinities lower than that of water. The PTR-TOF is therefore effectively transparent to all but trace organic species. Most VOCs have proton affinities \(\leq 900\) kJ mol\(^{-1}\), so only a relatively small amount of excess energy is released upon reaction with the hydronium ion. In this regard, chemical ionisation by proton transfer is considered a ‘soft’ technique, yielding ions with little to no fragmentation when compared with ‘harder’ methods such as electron impact ionisation. The product RH\(^+\) is therefore ideally a singly charged, non-fragmented, positive ion of molecular weight one atomic mass unit larger than the neutral precursor molecule. During chamber simulation experiments, the PTR-TOF operating conditions are such that \(H_3O^+ \gg RH^+\), making reaction 3.1 soluble through first-order kinetics.

\[
\Delta[RH^+] \approx k_i [H_3O^+]_0 [R] \Delta t
\]

Consequently, the product ion is linearly dependent on the neutral reagent concentration. Proton-transfer reaction rate coefficients have been experimentally measured and/or predicted through computational chemistry techniques for a wide range of molecules of atmospheric interest (Anicich, 2003; Tani et al., 2003; Smith and Španěl, 2005; Cappellin et al., 2012).

After protonation, charged species traverse through a 9.1 cm long drift tube consisting of a series of stainless-steel ring electrodes interspersed with insulating Teflon O-rings. The potential difference applied across the drift tube was varied from 484 to 600 V in this work, with an extraction voltage of 35 V used. Temperature and pressure inside the drift tube were held constant at 60°C and 2.2 mbar respectively. These conditions provide an electric field strength (E) of 57 to 70 V cm\(^{-1}\), and a reduced electric field (E/N) of 112 to 136 Td, where N is the gas number density in molecules cm\(^{-3}\). Such conditions are considered within the standard operating regime, providing a compromise between ion hydration and product ion fragmentation (Lindinger et al., 1998; Hewitt et al., 2003).
Outgoing protonated VOCs travel through a specially designed transfer lens into the pulse extraction region of the time-of-flight mass spectrometer. Pulsing of ions into the TOF occurs every 32 µs. Flight time through the TOF-MS determines the ions mass-to-charge ratio, with each extraction pulse generating a complete mass spectrum. A Multichannel Plate (MCP, PHOTONIS, Sturbridge, MA, USA) detects ions with the signal preprocessed by an amplifier/discriminator unit (Ionwerks XCD; Ionwerks Inc., Houston, TX, USA) to generate individual ion counting events. This signal is processed by a time-to-digital converter with arrival times of pulsed ions detected with a 0.2 ns time resolution, resulting in 160 000 bins per spectrum. The spectral information of 62 500 pulse cycles are co-added to produce two second time series of full PTR-TOF spectra. Acquisition software TOF-DAQ v1.72 (Tofwerk AG, Switzerland) is used to capture and store the data. The PTR-TOF Data Analyzer developed by Müller et al. (2013) is used for post-experimental analysis. The data analyser features inbuilt corrections for dead time, baseline and mass discrimination effects. For the majority of experiments in this thesis, 30 spectra were averaged to generate 1-minute averages which, especially for trace species, improved signal counts. Ion signals up to \( m/z \) 350 were analysed, using a discriminator of 1 count per second (cps). Intrinsic \( \text{H}_3^{18}\text{O}^+ \) \( (m/z \ 21.022) \) and \( \text{H}_3^{18}\text{O}^+(\text{H}_2\text{O}) \) \( (m/z \ 39.033) \) signals along with acetonitrile \( (m/z \ 42.034) \) were consistently used for mass axis calibration and peak shape determination, along with other injected reactants or prominent products, where applicable.
Determination of Mixing Ratios

The PTR-TOF Data Analyzer exports data as normalised counts per second (ncps), which standardises ion count rates relative to a combined $\text{H}_3\text{O}^+$ and $(\text{H}_2\text{O})_2\text{H}^+$ count rate of one million counts per second.

$$
(RH^+)_{\text{ncps}} = \frac{RH^+}{H_3\text{O}^+ + (H_2\text{O})_2\text{H}^+} \times 10^6
$$

(3.3)

The use of normalised counts ensures instrument response is invariant to minor perturbations in the ion source signal. Major $\text{H}_2\text{O}$ and $(\text{H}_2\text{O})_2\text{H}^+$ signals at $m/z$ 19 and $m/z$ 37 exceed the saturation threshold of the PTR-TOF, with minor isotopic signals at $m/z$ 21 and $m/z$ 39 used instead, scaled by factors of 500 and 250 respectively to reflect total abundance. Volume mixing ratios in ppb are calculated for each signal from detected counts using Equation 3.4, the derivation of which is given in Appendix B (House, 2008).

$$
[R_a] = \frac{10^9 \mu_0 (U_d + U_{dx})}{k_a L_d^2} \frac{(R_a H^+)_{\text{det}} R T_d^2 P_0 T_{H_3O^+}}{(H_3O^+)_{\text{det}} N_A T_0 P_d^2 T_{R_a H^+}}
$$

(3.4)

where,

$\mu_0$ Reduced ion mobility for $\text{H}_3\text{O}^+$ (2.76 cm$^2$ V$^{-1}$ s$^{-1}$ in a N$_2$ buffer gas (Dotan et al., 1976))

$U_d$ Drift tube voltage (V)

$U_{dx}$ Drift tube extraction voltage (V)

$k_a$ Rate coefficient of $R_a$ with $\text{H}_3\text{O}^+$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)

$L_d$ Length of drift tube (9.1 cm)

$(R_a H^+)$ Detected counts for the protonated VOC (cps)

$(H_3O^+)$ Detected counts for $\text{H}_3\text{O}^+$ (cps)

$R$ Ideal gas constant ($8.314 \times 10^6$ cm$^3$ Pa K$^{-1}$ mol$^{-1}$)

$N_A$ Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$)

$T_d$ Temperature inside the drift tube (K)

$P_d$ Pressure inside the drift tube (Pa)

$T_0$ Standard temperature (273.15 K)

$P_0$ Standard pressure ($1.0 \times 10^5$ Pa)
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$T_{H_3O^+}$ PTR-TOF transmission coefficient for $H_3O^+$ ions

$T_{R_aH^+}$ PTR-TOF transmission coefficient for a given product ion

By including all constants and device specific values, and adjusting for use of ncps, Equation 3.4 is reduced to:

$$[R_a] = 3.86 \times 10^{-13}(U_d + U_{dx})\frac{(RH^+)^{ncps}T_{H_3O^+}}{k_aT_{H_3O^+}}$$

(3.5)

The transmission efficiency of an ion through the PTR-TOF system is dependent on its $m/z$, with efficiency increasing as the mass increases (Jordan et al., 2009). The effect is primarily the result of the sampling duty cycle in the orthogonal-acceleration region of the TOF. Smaller ions coming from the drift tube have a large velocity, and so a higher proportion of them reach the end of the orthogonal accelerator and are lost compared to heavier ions (Müller et al., 2014). This effect is largely corrected for by the PTR-TOF Data Analyzer (Müller et al., 2013), with detected ions multiplied by the factor $[(m/z)_{max}/(m/z)]^{1/2}$, where $m/z_{max}$ corresponds to an ion with a flight time equal to the TOF pulsing period. However, additional instrument specific mass discrimination effects, such as extraction efficiency from the drift tube into the TOF and mass dependent detection efficiency of the electron multiplier (de Gouw and Warneke, 2007; Müller et al., 2014), are important and need to be characterised using appropriate gas-standards. Ideally, one would calibrate each compound of interest, however the majority of compound ions identified in this study were previously unknown. Instead, transmission curves were constructed from sensitivity testing (Graus et al., 2010), during which a standard calibration gas mixture was dynamically diluted using two calibrated mass flow controllers to introduce VOCs with mixing ratios of 0 to 100 ppb. The sensitivity of the PTR-TOF for each given VOC in the gas mixture is then determined from the slope of signal intensity versus concentration, using linear regression. Where identified, fragmentation effects are explicitly corrected for by summing identified fragments. The sensitivity results can then be used to construct a transmission curve, with an example shown in Figure 3.5.

Finally, fragmentation effects inside the PTR-TOF must be established for quantification of uncalibrated VOCs. The fragmentation pattern of α-phellandrene upon protonation has been studied twice in the literature (Misztal et al., 2012; Tani, 2013). Both studies showed fragmentation of α-phellandrene to be significant across the drift tube voltages used in this work, with fragmentation having a greater impact as the drift tube voltage, and hence energy of the system, is increased. Nonetheless, increasing the drift tube energy is advantageous as it limits the degree of water cluster-ion formation ($H_3O^+(H_2O)_n$) (Hewitt et al., 2003; Brown et al., 2010). Clus-
Figure 3.5: Results from a sensitivity test using a calibration gas standard and corresponding transmission curve construction. Gas mixture contained methanol, acetonitrile, acetaldehyde, acrolein, acetone, isoprene, crotonaldehyde, 2-butanone, benzene, toluene, o-xylene, chlorobenzene, α-pinene and 1,2-dichlorobenzene. As an example, inset is the result from the sensitivity testing of acetone. Calibration conducted on 15th August 2016.

Cluster ions can act as reagent ions, with suppression therefore simplifying interpretation of mass spectra (Hewitt et al., 2003). Drift tube operating conditions must therefore represent a compromise between reagent ion hydration and product ion fragmentation. Cluster ion formation for different drift tube voltages for the PTR-TOF used in this study is shown in Figure 3.6. The cluster $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ was found to begin to significantly contribute (> 10%) at drift tube energies less than 110 Td. Also evident is the presence of impurity ions (e.g. $\text{O}_2^+$, $\text{NO}^+$) formed from air molecules in the hollow cathode and source drift region; however these are relatively impervious to drift tube energetics.

The fragmentation studies of both Misztal et al. (2012) and Tani (2013) used a PTR-MS fitted with a quadrupole mass spectrometer. Transmission is known to be significantly different between quadrupole and time-of-flight systems (Jordan et al., 2009), with results unlikely to directly translate into the PTR-TOF system used in this study. The fragmentation of α-phellandrene in the PTR-TOF, under pertinent experimental conditions, was therefore extensively investigated.

On the advice of fellow students at the GIG-CAS, the PTR-TOF was initially operated using a drift tube voltage of 600 V, the logic being that, at this energy, the impact of water cluster ion formation is effectively removed. However, extensive fragmentation of α-phellandrene under this regime was noted. To accurately characterise the fragmentation pattern, five equal aliquots of α-phellandrene were
Figure 3.6: Abundance of primary ions in the PTR-TOF whilst sampling purified, dry air at different drift tube energies. Data for \( \text{H}_3\text{O}^+\text{H}_2\text{O} \) lies underneath \( \text{NO}^+ \). Pink line denotes best compromise between fragmentation and water cluster formation.

 added step-wise to a clean reactor which was continually sampled by the PTR-TOF. Fragments were then identified as those ions having a correlation with the parent \( \alpha\)-phellandrene ion \( (\text{C}_{10}\text{H}_{17}, \text{m/z} \ 137) \) of \( R^2 > 0.95 \) across all five additions (Figure 3.7). All other detected ions represent background contaminants inside the reactor. Transmission corrected counts of identified fragment ions were plotted against the parent ion, with the gradient from linear regression determining the contribution of the respective fragment, relative to the parent ion. The contribution of a given fragment ion to the total \( \alpha\)-phellandrene signal is therefore calculated by:

\[
F_i^+ = \frac{s_i}{\sum_i s_i} \times 100
\]

where \( s_i \) is the slope of fragment ‘i’, and \( F_i^+ \) is the percentage contribution of fragment ‘i’ to the total \( \alpha\)-phellandrene signal, with index ‘i’ run over all fragments satisfying \( R^2 > 0.95 \). Ions satisfying this condition are listed in Table 3.2, along with their contribution to the \( \alpha\)-phellandrene signal.

Ionisation of \( \alpha\)-phellandrene through proton transfer in the PTR-TOF, using a drift tube energy of 136 Td, was found to yield 21 fragment ions. The observed fragmentation pattern is similar to the PTR-MS results of Misztal et al. (2012) and Tani (2013), although with slightly varying fragment ratios. The major signals observed are the parent ion and the fragments \( \text{C}_6\text{H}_9^+ (\text{m/z} \ 81) \) and \( \text{H}_7\text{H}_9^+ (\text{m/z} \ 93) \), which together make up over 80% of the signal. Indeed, these two ions are commonly observed fragments from monoterpenes (Steeghs et al., 2007; Maleknia et al., 2007; Misztal et al., 2012; Tani et al., 2003; Tani, 2013). The ion \( \text{C}_9\text{H}_{13}\text{O}_2^+ \)
is thought to be produced by reaction with $O_2^+$ in the drift tube, leading to the loss of a CH$_4$ group. This process is only minor under the drift tube conditions investigated in this work, with all other fragments the result of conventional H$_3$O$^+$ protonation, confirming that $O_2^+$ reactions are subsidiary. Nevertheless the PTR-TOF enables users to switch operation to an $O_2^+$ primary ion mode, with it thought that C$_9$H$_{13}$O$_2^+$ would be the major $\alpha$-phellandrene fragment under this operating regime.

Given the large fragmentation of $\alpha$-phellandrene observed at 600 V, the effect of changing the drift tube voltage over 350 – 660 V was investigated for a single addition of $\alpha$-phellandrene to the reactor. Assuming the same fragment ions are yielded, fragment contributions are now calculated as a ratio of counts for each drift tube setting investigated. Naturally, this method is not as accurate, however it does allow for a qualitative assessment of the impact of drift tube energetics on $\alpha$-phellandrene fragmentation. As expected, the amount of mass located at the parent signal increases as the drift tube energy is lowered, with Figure 3.8 showing response of major ions. The signals at $m/z$ 135 and 119 were observed to decrease as the drift tube energy was increased, suggesting that they may be derived from primary species present as contaminants in the $\alpha$-phellandrene sample (Aldrich Chemical Company, Inc., USA). GC-MS evidence provides support for the presence of $p$-cymene (see Section 3.6). Comparing fragmentation with water cluster formation results (Figure 3.6), a PTR-TOF drift tube of 112 Td was selected as the optimal operating condition.

The fragmentation of $\alpha$-phellandrene was therefore accurately quantified at 112
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Figure 3.8: Abundance of major α-phellandrene fragment ions in the PTR-TOF at different drift tube energies.

Td using 9 aliquots, with results plotted in Figure 3.7 and listed in Table 3.2. Based on the observed fragmentation patterns, fragmentation scaling factors of 3.16 ± 0.04 and 2.62 ± 0.02 are used to correct the α-phellandrene parent signal (m/z 137) in experiments with a PTR-TOF drift tube operating at E/N = 136 Td and E/N = 112 Td respectively. Nevertheless results show that molecules inside the drift tube cannot effectively remove their excess energy through collisional thermalisation under the low pressures of the drift tube, with fragmentation expected to be problematic when analysing α-phellandrene oxidation products. Varying degrees of fragmentation have been observed when analysing primary C1 to C10 oxygenates in the literature (e.g. Smith and Španěl, 2005; Maleknia et al., 2007; Brown et al., 2010; Tani, 2013; Pang, 2015).

A similar analysis methodology was used to determine the fragmentation pattern of formic acid (98%, J&K Scientific Ltd., China), acetic acid (glacial, TEDIA Company, Inc., USA) and cyclohexanone (99.8%, Sigma Aldrich, USA), through individual injection and sampling of each in 5 litre FEP Teflon bags. Formic acid was primarily detected at m/z 47, with minor fragments at m/z 48, 49 and 65 contribution less than 2% at either of the drift tube energies used in this study. Acetic acid had 88% of mass residing at m/z 61 for both E/N = 136 Td and 112 Td, with the remaining mass distributed over m/z 43, 62 and 79, corresponding to dehydration to the acylium ion, the 13C isotope and protonation by a water cluster respectively. Meanwhile 98% and 85% of cyclohexanone was found at its parent mass of m/z 99 at respective drift tube energies of 112 and 136 Td, with the minor dehydrated and cluster peaks detected at m/z 81, 116 and 117. These fragmentation patterns
Table 3.2: Contribution of identified α-phellandrene PTR-TOF fragment ions at E/N = 136 and 112 Td.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion</th>
<th>R²</th>
<th>Contribution (%)</th>
<th>m/z</th>
<th>Ion</th>
<th>R²</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.1</td>
<td>C₅H₇⁺</td>
<td>0.995</td>
<td>0.47 ± 0.01</td>
<td>69.1</td>
<td>C₅H₉⁺</td>
<td>0.982</td>
<td>0.21 ± 0.01</td>
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<tr>
<td>79.2</td>
<td>C₆H₇⁺</td>
<td>0.975</td>
<td>0.09 ± 0.004</td>
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<td></td>
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<tr>
<td>81.1</td>
<td>C₁₀H₉⁺</td>
<td>0.999</td>
<td>37 ± 0.3</td>
<td>0.999</td>
<td>31 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82.1</td>
<td>¹³CC₅H₇⁺</td>
<td>0.999</td>
<td>2.2 ± 0.03</td>
<td>0.994</td>
<td>2.0 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91.1</td>
<td>C₇H₇⁺</td>
<td>0.956</td>
<td>0.18 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>92.1</td>
<td>C₇H₈⁺</td>
<td>0.999</td>
<td>1.6 ± 0.01</td>
<td>0.993</td>
<td>1.6 ± 0.04</td>
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<tr>
<td>93.1</td>
<td>C₇H₉⁺</td>
<td>0.979</td>
<td>15 ± 0.3</td>
<td>0.994</td>
<td>10 ± 0.1</td>
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</tr>
<tr>
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<td>¹³CC₆H₇⁺</td>
<td>0.97</td>
<td>1.2 ± 0.03</td>
<td>0.991</td>
<td>0.92 ± 0.03</td>
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<tr>
<td>95.1</td>
<td>C₇H₁₁⁺</td>
<td>0.996</td>
<td>2.0 ± 0.02</td>
<td>0.991</td>
<td>1.3 ± 0.04</td>
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<td></td>
</tr>
<tr>
<td>119.1</td>
<td>C₉H₁₁⁺</td>
<td>0.952</td>
<td>0.97 ± 0.02</td>
<td>0.988</td>
<td>1.1 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>121.1</td>
<td>C₁₀H₁₃⁺</td>
<td>0.984</td>
<td>0.19 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>135.1</td>
<td>C₁₀H₁₅⁺</td>
<td>0.969</td>
<td>2.1 ± 0.08</td>
<td>0.992</td>
<td>7.6 ± 0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>136.2</td>
<td>¹³CC₉H₁₅⁺</td>
<td>0.981</td>
<td>0.38 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>137.2</td>
<td>C₁₀H₁₇⁺</td>
<td>1.00</td>
<td>32 ± 0.2</td>
<td>1.00</td>
<td>38 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>138.2</td>
<td>¹³CC₉H₁₇⁺</td>
<td>0.999</td>
<td>3.3 ± 0.04</td>
<td>0.997</td>
<td>4.1 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>139.2</td>
<td>¹³C₁₂C₆H₁₇⁺</td>
<td>0.990</td>
<td>0.23 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>153.2</td>
<td>C₁₀H₁₃O₂⁺</td>
<td>0.969</td>
<td>0.91 ± 0.02</td>
<td>0.996</td>
<td>1.3 ± 0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

are consistent with reported values in the literature (Lindinger et al., 1998; Christian et al., 2004; Wang et al., 2009; Haase et al., 2012), with corrections made for fragmentation of these species in this work when necessary.

PTR-TOF error estimates are derived from uncertainty in reaction time, which is estimated to be 10% (Keck et al., 2007), reaction rate, transmission (10%), signal counts, which are described by Poisson statistics with a standard error of √N in a measurement of N ions (de Gouw and Warneke, 2007), and applied fragmentation factors. Where possible, proton transfer reaction rate coefficients are taken from experimental literature (Anicich, 2003; Smith and Španèl, 2005), followed by theoretical calculations (Cappellin et al., 2012). For example, a rate coefficient of 2.3 × 10⁻⁹ cm³ s⁻¹ is used for the proton transfer reaction of α-phellandrene, based on the experimental study by Tani (2013), a value which has theoretical support (Zhao and Zhang, 2004). However, for the vast majority of species identified in this work, no information exists, with a nominal value of 2 × 10⁻⁹ cm³ s⁻¹ ± 30% used (Brilli et al., 2014).
3.2.3 Canister Based Monitoring

The canister based monitoring method for VOCs has proven to be a reliable approach, able to capture, store and measure VOCs at the ppb level using conventional analytical detectors (United States Environmental Protection Agency (EPA), 1999; Wang and Austin, 2006). Indeed hundreds of different VOCs have been measured using the technique, with diverse applications. Analysis occurs offline after sample capture, resulting in poor time resolution when compared with the PTR-TOF. However, canisters allow for enhanced analytical analysis. For example, when analysed by gas-chromatography, coupled with detection techniques including flame ionisation (FID), mass spectrometry (MS) and electron capture (ECD), canisters provide isotopic resolution and valuable structural information, possibly resulting in product identification. Coupled with online PTR-TOF measurements, offline analysis provides a more complete and detailed analysis of the gas-phase composition inside the reactor.
Samples were collected in 2 L evacuated (< 3 Pa), electropolished stainless steel canisters. Prior to use, each canister was cleaned a minimum of three times by sequential filling to 300 kPa with nitrogen gas and evacuation down to 3 Pa. During experiments, air from the reactor was drawn through a FEP Teflon sample line for one minute by an external pump, before the canister was attached. Drawing air through the line not only ensures a current air mass is sampled, but also passivates the sample line walls. Once attached, the canister is opened, with the resulting pressure differential causing air from the reactor to rapidly flow into the canister, filling it in less than 30 seconds.

Radical chemistry rapidly terminates inside the dark canister. In general, polar and non-polar primary VOCs store well up to around 14 days even with reactive species present (e.g. NO, NO$_2$) (Batterman et al., 1998; Wang and Austin, 2006). Nevertheless, when possible, canisters were analysed on the day of sampling. Whilst true for most of the canisters discussed in this work, analytical instrument demand at the GIG-CAS did result in waiting times of up to two weeks for some of the samples collected. Canisters were unavailable for use during the 2013 and 2014 experimental campaigns, with canisters used to a limited extent during 2015 and 2016 campaigns. The principle of analysis was fundamentally the same during both campaigns: VOCs are concentrated by collection in a cryogenically-cooled trap, the cryogen is removed and VOCs revolatised, introduced into a GC column and then fed into a detector. Nevertheless, performance of the described tasks differed between the two years.

**2015 Canister Analysis Method**

The 2015 canister analysis set-up is shown in Figure 3.10. Approximately 700 Torr of air from the canister was introduced into the system manifold, passing over glass beads (1/8 inch diameter, washed with acetone and heated at 350°C overnight) and trapped in a U-tube submersed in liquid nitrogen. This procedure corresponds to a roughly 1500 cm$^3$ sample aliquot at standard temperature and pressure (STP). A Brooks Instruments mass flow controller (model 5850E) was used to regulate the flow, which was kept below 500 cm$^3$ min$^{-1}$ to ensure complete trapping of VOCs and prevent freeze-up. This procedure preconcentrates the relatively less volatile compounds in the sample (e.g. hydrocarbons), while allowing volatile components (e.g. N$_2$, O$_2$ and Ar) to be pumped away. Trapped compounds were re-volatilised by immersing the U-tube trap in hot water (~80°C) and flushed into a helium carrier flow (head pressure, 48 psi). The sample flow was then reproducibly split into three streams at a 1-to-6-port union (Valco Instruments, 1/16 inch manifold 1 to 6 ports, 0.75 mm inlet bore, 0.25 mm outlet bore, with three outlet ports capped off). Each stream was chromatographically separated and sensed by a single detector.

The first stream was passed through a J&W DB-1 column (60 m; I.D., 0.32 mm;
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Figure 3.10: 2015 canister analysis set-up. The canister being sampled is attached to the system on the left of the picture. The U-tube is shown near the bottom centre of the frame, submersed in hot water.

film, 1 µm) in an Agilent Technologies 7890A GC system and detected by an Agilent Technologies 5975C inert XL MSD. The GC oven temperature was programmed to initially be at -50°C, holding for a minute; increasing to 10°C at 10°C min⁻¹; followed by 5°C min⁻¹ to 120°C; then 10°C min⁻¹ to 250°C, before finally holding for 7 minutes. MSD is employed for unambiguous compound identification and select ion monitoring. The second stream is sent through a HP-PLOT Q column (30 m × 0.32 mm × 2.0 µm, Agilent Technologies, USA) in a ThermoScientific Trace 1300 Gas Chromatography with FID detection. Here, the GC oven starts at 10°C, holding for a minute, before increasing at 5°C min⁻¹ to 120°C and finally 10°C min⁻¹ to 250°C, at which the temperature is held constant for 10 minutes. FID analysis allows for sensitive detection of hydrocarbons. The final stream is carried by a J&W DB-1 column (60 m; I.D., 0.32 mm; film, 1 µm) in a SHIMADZU GC-2010 Plus for ECD detection using a ⁶³Ni source. ECD is sensitive to halocarbons and alkyl nitrates, however the output was not analysed in this study.
2016 Canister Analysis Method

Canisters were analysed using an Entech Model 7100 Preconcentrator (Entech Instruments Inc., USA), coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionisation detector (GC-MSD/FID, Agilent Technologies, USA). To each sample, a fixed volume (100 mL) of internal standard spiking mixture (bromochloromethane, chlorobenzene-d5, 1,4-difluorobenzene and 4-bromofluorobenzene) was added to the airstream, to monitor both system performance and enable target compound quantification. There are three stages to trapping and concentrating VOCs in the Entech preconcentrator. Firstly, 100 mL (1 atm, 0°C) air samples are drawn through a liquid nitrogen cryogenic trap at -180°C, concentrating VOCs whilst N₂, O₂ and other sample components pass through to the pump. The first-stage trap is then heated to 10°C and trapped gases transferred by 40 mL of helium at a flow of 10 mL min⁻¹ to a secondary trap with Tenax-TA adsorbents at -50°C. The majority of H₂O and CO₂ has been removed by this stage. The secondary trap is then heated to 180°C, thermally desorbing gases which are transferred by 30 mL of helium at a flow rate of 10 mL min⁻¹ to a third cryo-focussing trap at -170°C. This last cryogenic focussing stage is necessary to improve separation and peak shapes of samples exiting the GC column. The trap is then rapidly heated and VOCs transferred to the GC-MSD/FID system. The mixture is first separated by an HP-1 capillary column (60 m x 0.32 mm x 1.0µm, Agilent Technologies, USA) with a helium carrier gas, before being split into two streams: a HP-PLOT Q column (30 m x 0.32 mm x 2.0µm, Agilent Technologies, USA) followed by FID detection, and a 65 cm x 0.10 mm I.D. stainless steel line followed by MSD detection. The GC oven temperature was programmed to be initially at -50°C, holding for 3 minutes; increasing to 10°C at 15°C min⁻¹ and holding for a further 3 minutes, then to 120°C at 5°C min⁻¹, then to 250°C at 10°C min⁻¹, before finally holding for 7 min. The MSD was used in selected ion monitoring (SIM) mode and the ionisation method was electron impacting (EI).

In both 2015 and 2016, a combined Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 non-methane hydrocarbons (NMHCs)) and TO-14 standard mixture (39 compounds, Spectra Gases Inc., USA) was analysed prior to each batch of canisters to calibrate instrument performance and response. The contents of this calibration mixture is given in Table 3.3.

CO and CH₄ Analysis

In both 2015 and 2016, CH₄ and CO in canister samples were analysed separately to the main system through gas chromatography (Agilent 6890N) equipped with FID and a packed column (5A Molecular Sieve 60/80 mesh, 3 m x 1/8 inch). The starting
<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (ppt)</th>
<th>Compound</th>
<th>Conc. (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>8638</td>
<td>benzene</td>
<td>10656</td>
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<tr>
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<td>12175</td>
<td>cyclohexane</td>
<td>10378</td>
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<tr>
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<td>10430</td>
<td>2-methyl-hexane</td>
<td>10601</td>
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<tr>
<td>propene&lt;sup&gt;1&lt;/sup&gt;</td>
<td>7905</td>
<td>2,3-dimethyl-pentane</td>
<td>10834</td>
</tr>
<tr>
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<td>11263</td>
<td>3-methyl-hexane</td>
<td>10936</td>
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<tr>
<td>3-methyl-1-butene</td>
<td>7930</td>
<td>3-methyl-heptane</td>
<td>10718</td>
</tr>
<tr>
<td>isopentane</td>
<td>9574</td>
<td>n-octane</td>
<td>10949</td>
</tr>
<tr>
<td>1-pentene</td>
<td>9757</td>
<td>ethyl-benzene</td>
<td>10136</td>
</tr>
<tr>
<td>2-methyl-1-butene</td>
<td>10181</td>
<td>m/p-xylene</td>
<td>21821</td>
</tr>
<tr>
<td>n-pentane</td>
<td>11322</td>
<td>styrene</td>
<td>8067</td>
</tr>
<tr>
<td>isoprene</td>
<td>8859</td>
<td>o-xylene</td>
<td>10741</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>1496</td>
<td>n-nonane</td>
<td>40609</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>8768</td>
<td>isopropylbenzene</td>
<td>10029</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>8996</td>
<td>α-pinene</td>
<td>9408</td>
</tr>
<tr>
<td>2,2-dimethyl-butane</td>
<td>9267</td>
<td>n-propylbenzene</td>
<td>10029</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>10591</td>
<td>m-ethyltoluene</td>
<td>9047</td>
</tr>
<tr>
<td>4-methyl-1-pentene</td>
<td>9948</td>
<td>p-ethyltoluene</td>
<td>11402</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>10317</td>
<td>1,3,5-trimethyl-benzene</td>
<td>9996</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td>9560</td>
<td>o-ethyltoluene</td>
<td>10033</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>10477</td>
<td>1,2,4-trimethylbenzene</td>
<td>9970</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>10386</td>
<td>n-decane</td>
<td>10310</td>
</tr>
<tr>
<td>1-hexene</td>
<td>9905</td>
<td>1,2,3-trimethylbenzene</td>
<td>9223</td>
</tr>
<tr>
<td>n-hexane</td>
<td>11628</td>
<td>m-diethylbenzene</td>
<td>2894</td>
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<tr>
<td>2-hexene</td>
<td>9948</td>
<td>p-diethylbenzene</td>
<td>3478</td>
</tr>
<tr>
<td>3-hexene</td>
<td>9948</td>
<td>o-diethylbenzene</td>
<td>5854</td>
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<tr>
<td>methyl-cyclopentane</td>
<td>10337</td>
<td>n-undecane</td>
<td>1026</td>
</tr>
<tr>
<td>2,4-dimethylpentane</td>
<td>10856</td>
<td>n-dodecane</td>
<td>1026</td>
</tr>
</tbody>
</table>

<sup>1</sup> FID only.

Table 3.3: Combined PAMS and TO-14 standard mixtures used to calibrate the GC-MS/FID systems for canister analysis. Compounds are listed in order of retention time when read from top to bottom, left to right.
temperature was 120°C with a flow rate 40 mL min$^{-1}$ of helium. CH$_4$ was detected at a retention time (RT) of 0.60 minutes. CO was first converted by a Ni-based catalyst to CH$_4$, before separation by the packed column and detection by FID at 2.35 minutes. Samples were analysed a minimum of two times and compared to a 1.0 ppm reference gas for quantification. Neither species is detected by the PTR-TOF, owing to both having proton affinities lower than that of water.

### 3.2.4 Scanning Mobility Particle Sizer

Particle number size distribution inside the reactor is measured by a scanning mobility particle sizer (SMPS; TSI Incorporated, USA) (Wang and Flagan, 1990), consisting of an electrostatic classifier (TSI 3080), fitted with a TSI 3081 differential mobility analyser (DMA) and condensation particle counter (CPC, TSI 3775). The SMPS is connected to the reactor using a conductive silicon sampling line, to reduce electrostatic losses of particles. The particles are first introduced into the electrostatic classifier, where they are neutralised by a radioactive $^{85}$Kr source, creating a steady-state bipolar charge distribution. Both positive and negative ions are continuously produced, following the bipolar charge equilibrium described theoretically by Fuchs (1963). Polydisperse particles are then fed into the top of the DMA, which consists of a cylinder with a negatively charged rod at the center. The main flow through the DMA is laminar particle free sheath air. Particles with a positive charge move across the sheath flow towards the central rod at a rate governed by their electrical mobility, which is primarily determined by particle charge and diameter, electric field and sheath flow, but also depends on particle shape, gas viscosity and Cunningham correction factor, and therefore indirectly on temperature and pressure of the gas flow inside the DMA (Wiedensohler et al., 2012). Particles of monodisperse electric mobility exit the DMA through a sample slit and are fed into the CPC to be counted, while all other particles exit with the exhaust air. By exponentially scanning the voltage on the central rod, a full particle number size distribution is built up. In all experiments, the DMA was operated with a sheath flow of 3.0 L min$^{-1}$ and a sample flow rate of 0.3 L min$^{-1}$. Voltage inside the DMA was varied exponentially from -10 V to -9950 V every 240 seconds, providing a mobility spectrum over particle diameters ranging from 14 nm to 750 nm.

SMPS data are processed by the Aerosol Instrument Manager software (AIM, Version 9.0, TSI Inc.). The software calculates the gas viscosity, mean free path, the Cunningham slip correction and bipolar charge distribution using user-provided values for temperature and pressure. It then converts the measured electrical particle mobility distribution to a number size distribution (dN/dlog$D_p$), using an inversion routine based on the bipolar charge distribution (Hoppel, 1978; Hagen and Alofs, 1989).
Particles with a higher electrical mobility are drawn towards the inner rod at a faster rate than those with a lower electrical mobility. As seen in Figure 3, since the particles flow toward the bottom of the column at a constant rate, the electrical mobility of a particle together with the strength of the electric field determine where the particle will impact the center rod. For a given voltage, particles with a high electrical mobility will impact the rod sooner than those with a low electrical mobility. There is a slit near the base of the rod. Particles that would normally impact the rod in this location pass through the slit and exit the DMA; therefore, for a given voltage, only particles with a certain electrical mobility will pass through the slit.

Thus, a DMA is used to classify polydisperse aerosol particles based on electrical mobility since the voltage on the rod can be directly related to the electrical mobility of the particles exiting the DMA. In an SMPS system, a classifier scans across a voltage range while a CPC counts the classified particles, generating a size distribution.

Since electrical mobility depends on particle size and particle charge, for a classifier to accurately sort particles based on size, the charge of the particles must be controlled. A polydisperse aerosol can have any charge distribution. In the SMPS spectrometer system, the charge distribution of the polydisperse aerosol is standardized using an aerosol neutralizer (either radioactive or soft x-ray) prior to size classification the DMA.

Figure 3.11: Schematic showing working principle of the differential mobility analyser. Image adapted from TSI (2014).

1983; Wolfenbarger and Seinfeld, 1990; Wang and Flagan, 1990), where dN is a particle size bin from the DMA transfer function and dlogD_p is the difference in the base 10 logarithm of the maximum and minimum diameters comprising the bin. The size distribution is assumed to be constant across the width of the transfer function for all sizes, with a lognormal concentration distribution used to facilitate comparisons of different instruments operating at different resolutions. The SMPS inversion algorithm in AIM additionally accounts for flow rates of the CPC and DMA, measurement scan time, response time of the CPC and parameters of the working gas, whilst correcting for the DMA transfer function (Knutson and Whitby, 1975; Birmili et al., 1997; Collins et al., 2002), CPC counting efficiency (Agarwal and Sem, 1980; Stolzenburg and McMurry, 1991; Hermann et al., 2007) and losses of particles through diffusion.

Usually the SMPS additionally requires a pre-impactor upstream to the DMA, to remove all particles larger than the upper size limit of the mobility particle size spectrometer (Wiedensohler et al., 2012). This ensures that there is no interference to the electrical particle mobility distribution from multiply charged particles with
sizes larger than the measurement range, which is essential for a correct multiple charge inversion scheme. Nevertheless, the impactor was not utilised during this work to reduce particle losses, which is justified by the steep decline in particle number size distribution at larger diameters in fresh chamber experiments. Contributions of large (> 750 nm), multiply charged particles are therefore negligible (Wiedensohler et al., 2012). Error in the SMPS particle number size distribution is conservatively estimated at 10%, with higher moment size distributions (e.g. volume (dV/dlogD_p) and mass (dM/dlogD_p)) calculated from the number size distribution by assuming spherical particles (Wiedensohler et al., 2012).

**SMPS Size Calibration**

Governed by the physical principle that the ability of a particle to traverse an electric field (electrical mobility) is fundamentally related to particle size, the SMPS manufacturers claim that no size calibration is necessary after the first principle measurement. Nonetheless, the performance of the SMPS was tested twice in separate campaigns for quality control, using polystyrene latex spheres (PSLs) (Nanosphere™ Size Standards, Thermo Scientific, USA) (Vasiliou, 2005; Mulholland et al., 2006; Kidd et al., 2014). PSLs have a density of 1.05 g cm\(^{-3}\) and are perfectly spherical, such that they have a shape factor of 1. PSLs were added to nanopure water (6.1 MΩ cm), with each solution sonicated for 5 minutes to minimise coagulation of particles, prior to atomisation by an ATM 220 Atomizer Aerosol Generator (Topas-GmbH). Using conductive silicon tubing, the generated particles were passed through a silica gel to dry before sampling by the SMPS. The mean diameters of the PSLs used were 81 ± 3 nm, 203 ± 5 nm, 296 ± 6 nm, 498 ± 9 nm and 707 ± 9 nm.

The volume size distributions measured by the SMPS for the different PSLs solutions are shown in Figure 3.12 for both calibration studies. The voltage scan conditions used were consistent to that used during measurements of polydisperse aerosol in laboratory experiments, in order to obtain an appropriate assessment of SMPS-sizing accuracy under typical operating conditions. Unfortunately, the resolution of the voltage sweep likely resulted in the true peak being missed, with Gaussian functions fitted to the data to estimate peak centres. The results of peak fitting are given in Table 3.4. The operational size range of the SMPS prevented the use of data from the 707 nm PSLs solution from being used, with the peak unable to be accurately ascribed.

In their study harmonising technical standards, Wiedensohler et al. (2012) defined the maximum tolerable deviation of the SMPS from the nominal PSLs diameters to be the quoted PSLs size uncertainty, with an additional ±1% uncertainty for the sheath air flow rate. Using this definition, to pass the sizing quality test the deviation of the SMPS must be within ±4.7% for 81 nm, ±3.5% for 203 nm, ±3.0%
3.2. ANALYTICAL INSTRUMENTS

Figure 3.12: Volume size distributions measured by the SMPS for PSLs of diameters 81 nm (red), 203 nm (blue), 296 nm (green) and 498 nm (purple).

<table>
<thead>
<tr>
<th>Year</th>
<th>PSLs Size (nm)</th>
<th>SMPS Sizing(^1) (nm)</th>
<th>Deviation from nominal diameter(^2) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>81 ± 3</td>
<td>84.9 ± 0.08</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>81 ± 3</td>
<td>85.0 ± 0.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>203 ± 5</td>
<td>198 ± 1</td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td>203 ± 5</td>
<td>199 ± 0.3</td>
<td>-2.1</td>
</tr>
<tr>
<td></td>
<td>296 ± 6</td>
<td>324 ± 1</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>296 ± 6</td>
<td>324 ± 2</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>296 ± 6</td>
<td>324 ± 2</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>498 ± 9</td>
<td>481 ± 0.7</td>
<td>-3.3</td>
</tr>
<tr>
<td>2016</td>
<td>498 ± 9</td>
<td>478 ± 2</td>
<td>-4.0</td>
</tr>
<tr>
<td></td>
<td>498 ± 9</td>
<td>481 ± 1</td>
<td>-3.5</td>
</tr>
<tr>
<td></td>
<td>81 ± 3</td>
<td>83.8 ± 0.7</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>81 ± 3</td>
<td>83.7 ± 0.6</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>203 ± 5</td>
<td>197 ± 0.2</td>
<td>-2.7</td>
</tr>
<tr>
<td></td>
<td>203 ± 5</td>
<td>197 ± 0.2</td>
<td>-2.7</td>
</tr>
<tr>
<td></td>
<td>296 ± 6</td>
<td>294 ± 0.4</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>296 ± 6</td>
<td>293 ± 0.4</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>498 ± 9</td>
<td>491 ± 1</td>
<td>-1.4</td>
</tr>
<tr>
<td></td>
<td>498 ± 9</td>
<td>481 ± 0.7</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

1\(^1\) Determined from Gaussian fits.
2\(^2\) Calculated using (measured - actual)/actual

Table 3.4: Peak diameters of SMPS measured volume-size distributions and deviation from quoted PSLs diameters during particle sizing calibration experiments.
for 296 nm and ±2.8% for 498 nm PSLs solutions. Table 3.4 shows that 2016 passed the test, whilst 81 nm, 296 nm and 498 nm in 2015 had deviations greater than the acceptable values. Nonetheless, constructing a calibration curve of SMPS vs PSLs diameters for 2015 yields a gradient of 0.9969, with strong correlation ($R^2 = 0.987$), suggesting that over the entire size range the SMPS provides correct sizing with no systematic bias. Given this, the good calibration results from the final campaign in 2016, and that no changes were made to the SMPS or its operation throughout all GIG-CAS chamber campaigns, it is assumed that the sizing ability of the SMPS was accurate for all experiments conducted.

### 3.2.5 High-Resolution Time-of-Flight Aerosol Mass Spectrometer

Particle mass loading and chemical composition are measured on-line by a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS; referred to as AMS throughout this thesis; Aerodyne Research Incorporated, USA) (Jayne et al., 2000; DeCarlo et al., 2006). Particles are sampled through a 100 µm critical orifice at a flow rate of 1.0 to 1.2 cm$^3$ s$^{-1}$, before being accelerated through an aerodynamic lens. The lens system consists of a cylindrical barrel containing circular apertures of sequentially decreasing diameter (5 mm I.D. to 3 mm I.D.), which focus particles into a narrow collimated beam before accelerating them, supersonically, through a nozzle. Spherical particles with approximate sizes of 30 to 500 nm are transmitted with 100% efficiency (Jayne et al., 2000; Zhang et al., 2004; Liu et al., 2007). Particles are introduced into a 0.295 m long flight tube maintained at $10^{-5}$ Torr by turbo molecular pumps, where supersonic expansion of the aerosol on exiting the aerodynamic lens creates a size-dependent particle velocity distribution. The particle beam is then pulsed by a mechanical chopper wheel. Particles are flash vaporised by impact on a resistively heated tungsten surface (~600°C) and ionised by electron impact (70 eV). Transfer optics create a narrowly collimated beam from the ionisation source, with ions extracted orthogonally into a Tofwerk AG (H-TOF Series, Switzerland) high-resolution TOF-MS. The TOF contains ion optics for two modes of operation, referred to as V- and W-modes. In V-mode, ions are reflected once in the TOF by a reflectron, before detection by a MCP detector (effective ion path length = 1.3 m). Meanwhile, in W-mode, ions are directed into a hard mirror which focusses them back into a reflectron for a second pass, before detection by the MCP detector (length = 2.9 m). The longer flight path is associated with enhanced mass resolution in the TOF-MS, however lateral broadening of ions increases over the longer path, reducing total signal intensity. Therefore, operation in V-mode is more sensitive, whilst the W-mode provides higher mass resolution (DeCarlo et al., 2006).
Both modes are employed during chamber simulations, with the AMS switching between the high-sensitivity V-mode and high-resolution W-mode every 2 minutes.

The AMS produces two types of data: mass spectrum and particle time-of-flight. In recording mass spectrum data, the particle beam in the AMS is alternatively transmitted and blocked by the chopper every 5 (V-mode) or 10 seconds (W-mode), to allow independent particle and background gas measurements respectively. The difference between these spectra provides a mass spectrum of volatile and semi-volatile constituents of the aerosol mixture. The mass spectrum is recorded with no size information but with a high duty cycle. When operating in the particle time-of-flight (PTOF) mode, the particle beam in the flight tube is pulsed by the mechanical chopper, which operates at 145 Hz with a 0.5% duty cycle. Due to supersonic expansion, particle size becomes a function of flight time. The opening of the chopper slit defines the start time of the PTOF cycle, with the end being ion detection by the MCP. Fast particle vaporisation and detection is therefore essential. Because flight time is measured in a free-molecular regime, the AMS measures mass-weighted size distributions as a function of the vacuum aerodynamic diameter (dM/dlogDva). This can be related to classical aerodynamic diameters (in the continuum regime) via (DeCarlo et al., 2004):

\[
D_{va} = \frac{\rho_p}{\rho_0} \frac{D_v}{\chi_v}
\]  

(3.7)

where Dv is the classical volume-equivalent diameter, \(\rho_p\) is the density of the particle...
material, $\rho_0$ is the unit density (1 g cm$^{-3}$) and $\chi_v$ is the dynamic shape factor in the free-molecular regime. During V-mode measurements, the AMS switched between mass spectrum and PTOF measurement modes every 10 seconds, whilst in W-mode only the mass spectrum setting is active.

**General Calibrations**

A number of calibrations and checks were routinely performed during campaigns to ensure the AMS was operating optimally and producing reliable results. The AMS flow rate is derived from lens pressure (utilising a conversion factor) and is used to convert signal intensities into mass concentrations. Calibration of the flow rate was made by replacing the micro-metre sampling orifice with a fine metering valve (SS-SS4, Swagelok, USA). Flow rate through the system can then be manually changed, which is measured by a KOFLOC D8500 mass flow controller/meter. Flow rates started at approximately 0.3 cm$^3$ s$^{-1}$ and were increased incrementally up to around 1.7 cm$^3$ s$^{-1}$, thereby covering the working range of the AMS. For each point, flow rates recorded by the AMS and flow meter were recorded. All testing showed satisfactory agreement between the two readings over AMS flow rates used in experiments, such that no post-corrections were employed.

The mass scale was routinely calibrated before each experimental measurement to establish the relationship between recorded ion flight times and $m/z$. The calibration is based on a 3-point, linear least square regression in time-of-flight space using $\text{N}^+$ ($m/z$ 14.00307), $\text{N}_2^+$ ($m/z$ 28.00615) and $^{184}\text{W}^+$ ($m/z$ 183.9509). These three ions are selected because they are easily recognisable, ubiquitous in the AMS system, have strong signal intensities, are dominated by a single elemental composition and span the $m/z$ range of interest. The calibration is used to calculate the displayed and saved stick values. Nonetheless, post-processing of data includes a higher order calibration routine that is generally more accurate and thus supersedes the initial data acquisition $m/z$ calibration.

Similarly, the baseline, that is the voltage from which all signals originate, is set prior to conducting each experiment, using an inbuilt routine in the data acquisition software. Raw electronic noise is recorded for an extended period of time, with the baseline then determined from the average value of this recorded data. Repeat measurements are made until the baseline is stable to within 0.1 bit for W-mode and 0.05 bit for V-mode of the menu value for baseline bits. This baseline is applied to the whole experiment, with post-processing enabling fine-tuning of the recorded baseline.
Figure 3.14: Results from an AMS flow rate calibration experiment conducted on 19/08/2015. Open and closed circles are data measured by the AMS and KOFLOC flow meter respectively, with the line fitted to the latter data.

Particle Velocity Calibration

The relationship between particle velocity and vacuum aerodynamic diameter can be described by an empirical sizing equation developed by Jayne et al. (2000) and modified by Allan et al. (2003):

\[ v = \frac{\text{flightlength}}{\text{flighttime}} = v_l + \frac{v_g - v_l}{1 + \left( \frac{D_v}{D^*} \right)^b} \]

(3.8)

where \( v \) is the particle velocity (m s\(^{-1}\)), \( v_l \) is the axial gas velocity in the aerodynamic lens (m s\(^{-1}\)), \( v_g \) is the gas velocity at the exit nozzle of the lens (m s\(^{-1}\)), \( D_v \) is the particle vacuum aerodynamic diameter (nm) and \( D^* \) (nm) and \( b \) are empirical fitting parameters.

To calibrate the PTOF, the PSLs solutions are used. Being perfectly spherical, the PSLs have vacuum aerodynamic diameters equal to the product of their density and diameters (DeCarlo et al., 2004).

\[ D_v = D \times \rho \times S \]

(3.9)

where \( D \) is the geometric diameter, \( \rho \) the density and \( S \) is a shape factor which is equal to 1 for perfect spheres. The vaporiser temperature in the AMS was increased to 800°C to ensure rapid evaporation of PSLs. Particle flight time in the flight tube is on the order of milliseconds, whilst vaporisation, ionisation, ion flight time in the TOF and detection occurs in microseconds. This enables time to essentially be recorded as being from opening of the chopper to final detection. PTOF
Figure 3.15: Results from an AMS velocity calibration experiment conducted on 14th August 2015. Inset are the raw spectrums, with flight times calculated using Equation 3.10, averaged, and then used to obtain data points. Optimised fitting parameters (Equation 3.8) are given with line of best fit shown.

spectra were recorded for 2 to 3 minutes, to yield a good PTOF peak shape. Between measurements of different sized solutions, the system was flushed by atomising nanopure water for approximately 10 minutes, until residual particle concentrations had dropped below 3 \( \mu g \text{ m}^{-3} \).

A particle velocity calibration was conducted twice during the 2015 campaign and once in 2016. Despite the vaporiser operating at 800°C, evaporation of PSLs still requires a non-negligible time with respect to particle time-of-flight. Evaporative broadening therefore ‘smears’ the signal to longer retention times. Consequently, in calculations, the leading edge of the signal was used with a small correction to adjust the time to the middle of the chopper opening.

\[
T = T_{\text{edge}} + 0.5 \times \frac{\text{chopper duty cycle}}{\text{chopper frequency}} \tag{3.10}
\]

where \( T \) is the PTOF and \( T_{\text{edge}} \) is the time of the leading edge of the signal. Results from one of the experiments conducted in 2015 are shown in Figure 3.15.

The empirical relationship described in Equation 3.8 has four fitting parameters. Meanwhile, data collected lie on a line in log space (Allan et al., 2003) and so can be adequately described with two parameters, with many solutions possible if all four parameters are held free. Instead, \( v_g \) is calculated from the PTOF of N\(_2\) (m/z 28), which is determined to be 500 ± 30 m s\(^{-1}\). Gas velocity in the aerodynamic lens can be calculated through fluid dynamics. Flow rate (Q) is equal to area (A) times
velocity ($v$).

$$Q = Av$$  \hspace{1cm} (3.11)$$

In order to conserve mass:

$$v_1 P_1 = v_2 P_2$$  \hspace{1cm} (3.12)$$

where $P$ is pressure. Velocity after the orifice is therefore given by:

$$v_2 = \frac{P_1}{P_2} \left( \frac{Q_1}{\pi r^2} \right)$$  \hspace{1cm} (3.13)$$

The flow rate and pressure are recorded by the AMS, which has an inner lens diameter of 10 mm (Liu et al., 2007). Ambient pressure was assumed as 760 Torr in all calculations. Superfluous parameters are now removed, such that only $D^*$ and $b$ are fit. Revised values were implemented into the AMS toolbox for analysis. Where no calibration experiment was conducted (2013 and 2014), results from a 2012 calibration study were used, namely $v_l = 28.04$ m s$^{-1}$, $v_g = 508.29$ m s$^{-1}$, $D^* = 14.04$ nm and $b = 0.5496$. Since being set-up at the GIG-CAS, the AMS has never physically been moved, nor have operating conditions been altered. For this reason, prolonged use of the initial calibration values are thought to have minimal effect, as evidenced by consistency with the latter measured values (e.g. Figure 3.15).

### Ionisation Efficiency Calibration

Ionisation efficiency is defined as the ratio of the number of ions produced for a given number of parent molecules vaporised (e.g. if the ionisation efficiency is $1 \times 10^{-6}$, then 1 in a million molecules is ionised), and is an essential component for accurate signal to mass conversion in the AMS (Jimenez et al., 2003; Allan et al., 2003). To calibrate the ionisation efficiency in the AMS, a method known as Brute Force Single Particle was implemented using aqueous ammonium nitrate. Solutions were prepared by adding a few drops of 0.5 mol L$^{-1}$ ammonium nitrate solution (Sigma Aldrich, > 99.0%) to nanopure water. Ammonium nitrate is used as a primary calibration material because of its volatility, ensuring near 100% particle vaporisation with little residual interference, and because it is easily generated from aqueous solution. The solution was atomised with the resulting sample stream passed through silica gel to dry, before being introduced into the DMA of the SMPS. The DMA was held at a fixed voltage, such that all particles were removed except for those of the desired size. Particles of mobility diameters somewhere in the 300 to 400 nm range were selected. Whilst larger particles produce more ions and therefore make detection easier, the number of particles produced by the atomiser and size-selected by the DMA decreases strongly with size, with 300 to 400 nm diameter particles providing a good compromise. The monodisperse output was then fed into
the AMS for analysis. The number of cycles having particles detected was kept below 7%, to minimise the probability of 2 particles being detected in the same chopper cycle. The same pulsing period was used on the AMS as in chamber experiments to make calibration results directly translatable.

The experimental data generated were analysed using the software ‘ToF-AMS Ionization Efficiency Calibration Using the BFSP v3.1.5’, which is available at http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html. Under experimental conditions of single particle events, the number of molecules per particle (MPP) is easily calculated in the software using geometry and known physical characteristics of ammonium nitrate particles. Meanwhile, the number of ions produced per particle (IPP) is determined from a duty cycle corrected sum of ion intensities of the fragment ions, namely \( \text{NH}_3^+ \), \( \text{NH}_2^+ \), \( \text{NH}^+ \) for ammonium and \( \text{NO}_2^+ \) and \( \text{NO}^+ \) for nitrate. The single ion threshold was defined as 20 bit ns\(^{-1}\). Ionisation efficiency (IE) is then calculated from the following formula:

\[
IE = \frac{IPP}{MPP} = \frac{IPP}{\frac{\pi}{6} \times d_m^3 \times \rho \times \chi_v \times f \times \frac{N_A}{MW}}
\]  

(3.14)

where \( d_m \) is the mobility diameter size selected by the DMA, \( \rho \) is the density of \( \text{NH}_4\text{NO}_3 \) particles (1.72 g cm\(^{-3}\)), \( \chi_v \) is an empirically derived shape factor (0.8, Jayne et al. (2000)), \( f \) is the weight fraction of the anion or cation in the parent molecule (e.g. 0.775 for \( \text{NO}_3^- \) in \( \text{NH}_4\text{NO}_3 \)), \( N_A \) is Avogadro’s number and MW is the molecular weight of the specific cation or anion.

The majority of aerosol particles selected by a DMA will be singly charged with the desired diameter, however by way of Boltzmann’s statistics a small percentage is made up of multiply charged, larger particles with the same mobility diameter. However, vacuum aerodynamic diameter differs and so these particles are size-resolved by the AMS and removed by selecting relevant particle arrival and background regions. AMS ionisation efficiency studies were conducted in 2015 and 2016, with the ionisation efficiency of \( \text{NO}_3^- \) found to range from 6.16 to 7.58 \( \times 10^{-8} \). The ionisation efficiency measured when the AMS was first purchased in 2012 was 6.36 \( \times 10^{-8} \), and therefore falls within the measured calibration results.

**Data Analysis and Fragmentation Table**

AMS data were analysed in Igor Pro 6.37 (Wavemetrics), using the standard TOF-AMS data analysis toolkits Sequential Igor Data Retrieval (SQUIRREL, version 1.51H) for unit mass resolution data and Peak Integration by Key Analysis (PIKA, version 1.10H) for high-resolution peak fitting (http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html). The software allows imple-
mentation of corrections for the mass scale, baseline, particle velocity and ionisation efficiency, in addition to a number of other user-defined corrections.

An essential aspect of the software is the fragmentation table, which is constructed to de-convolute spectra to enable identification and quantification of specific aerosol components (Allan et al., 2004; Aiken et al., 2008; Canagaratna et al., 2015). In essence, the fragmentation table is a mathematical formulation of the apportionment of TOF-AMS signals amongst different chemical species (e.g. air, organics, nitrates, sulphates, ammonium and chlorides) accounting for isotopic abundance, interference from several contributing species and loss of signal through fragmentation. For each ion, this is achieved either through using cross-references to other entries in the table, scaling factors or a combination of both. For example, $m/z$ 44 has contributions from both gas and particle derived CO$_2$. Because gas phase atmospheric composition is well known, the gas phase contribution to the total signal can be subtracted to get the particle-only measurement. The $m/z$ 44 gas phase contribution in the fragmentation table is therefore taken as $\text{frag}_{\text{air}[44]} = 0.0004 \times 1.36 \times 1.28 \times 1.14 \times \text{frag}_{\text{air}[28]}$, where 0.0004 corresponds to the expected ambient gas phase CO$_2$ concentration (400 ppm) (Monastersky, 2013), 1.36 is the literature relative ionisation efficiency (RIE) of CO$_2$, 1.28 is the reciprocal of the fraction of N$_2$ in the air, 1.14 is an empirical correction to account for differences in focussing and transmission of CO$_2$ with respect to N$_2$, and $\text{frag}_{\text{air}[28]}$ is the N$_2$ signal in the table. The contribution of organics to the $m/z$ 44 signal is then taken as the total $m/z$ 44 signal minus $\text{frag}_{\text{air}[44]}$. The fragmentation table is an important component in calculating constituent mass loadings and subsequently bulk elemental analysis. For this reason, attempts were made to fine-tune relationships between various fragments that exist under the current experimental conditions, to improve the default fragmentation table (Chen et al., 2011).

High-resolution analysis using PIKA is able to separate CO$^+$ and N$_2^+$ signals at $m/z$ 28. Nevertheless, the contribution of CO$^+$ can be buried by the much larger N$_2^+$ signal from air. The fragmentation table therefore estimates the CO$^+$ organic component at $m/z$ 28 empirically, using the organic component of the CO$_2$$^+$ signal at $m/z$ 44 with a default scaling factor of 1.00 (Aiken et al., 2008). Measurements from multifunctional systems show relative consistency with the value of 1 (Zhang et al., 2005; Takegawa et al., 2007), however differences are noted in the literature, especially among systems that contain products that are rich in hydroxyl functional groups and poor in carboxyl groups (Chhabra et al., 2010, 2011; Chen et al., 2011; Canagaratna et al., 2015). The contribution of organics to CO$^+$, relative to CO$_2$$^+$, is therefore directly obtained in this work by analysing experiments with sufficient SOA loading, such that high-resolution analysis can distinguish between CO$^+$ and N$_2^+$ peaks (Chhabra et al., 2010; Chen et al., 2011). The difference in $m/z$ 28
peak resolution between V- and W-mode is shown in Figure 3.16. Four ozonolysis experiments were sufficient for analysis, with \( \text{(CO}^{+})_{\text{org}}:\text{(CO}_2^{+})_{\text{org}} \) ranging from 0.93 – 1.25, with an average ratio of 1.10 ± 0.13. These results are consistent with ratios from ozonolysis studies on α-pinene (0.98 – 1.08) and β-caryophyllene (1.22 ± 0.21) (Chhabra et al., 2010; Chen et al., 2011). Meanwhile, an average value of 1.38 ± 0.3 is obtained for SOA derived from the photooxidation of α-phellandrene. These \( \text{(CO}^{+})_{\text{org}}:\text{(CO}_2^{+})_{\text{org}} \) ratios are then used in the fragmentation table of experiments with lower aerosol mass loadings.

The total signal intensity at \( m/z \) 18 contains contributions from molecular water (\( \text{H}_2\text{O}^{+} \)), atomic oxygen \( ^{18}\text{O}^{+} \), ammonia \( ^{15}\text{NH}_3^{+} \) and ammonium \( \text{NH}_4^{+} \). The latter two can be resolved by the high-resolution spectra, whilst the air term \( ^{18}\text{O}^{+} \) is observed to be minor by measuring particle free spectra. For molecular water, sources include humidity in the air, molecular water in the particle phase and water produced by the decomposition of inorganic and organic particulate species.

To quantify the different sources of molecular water at the \( m/z \) 18 signal, experiments were conducted whereby aerosol was generated in the chamber either through a typical ozonolysis or photooxidation study, before being exposed to a gradual increase in relative humidity. Aerosol was allowed between 75 to 90 minutes to form and stabilise, before any changes in humidity were made. After a baseline measurement, the humidity was gradually increased by passing a stream of pure \( \text{N}_2 \) gas over boiling nanopure water and into the chamber at a flow rate of 12 L min\(^{-1} \). Whilst doing so dilutes the concentration of aerosol inside the chamber, it is the composition, not concentration, that is of primary interest in this calibration experiment. Humid air was introduced for either 3.5 hours (ozonolysis) or 4.5 hours (photooxidation).
3.2. ANALYTICAL INSTRUMENTS

Figure 3.17: Plot of $\left(\text{H}_2\text{O}^+\right)_{\text{humidity}}:\left(\text{N}_2^+\right)_{\text{air}}$ against relative humidity for measurements recorded with HEPA filter in place. Each dot corresponds to a single V-mode measurement, with filled circles from aerosol generated during a dark ozonolysis experiment and open circles for aerosol formed through a photooxidation experiment. Lines of best fit ($\times 10^{-4}$) of 2.75 ± 0.09 and 2.3 ± 0.1 for ozonolysis (solid) and photooxidation (dashed) data respectively are shown.

During the experiment, during which time the relative humidity inside the chamber changed from 5 to 90%. Throughout the measurements, the sample stream was periodically diverted to pass through an in-line HEPA capture filter (TSI Incorporated, USA) prior to AMS injection, creating two datasets: those with and without particles.

The only source contribution to the $m/z$ 18 signal for data collected with the HEPA filter in-line is molecular water from humidity. The default setting in the fragmentation table sets, $\text{frag}_{\text{RH}[18]} = 0.01*\text{frag}_{\text{air}[28]}$ (Allan et al., 2004), that is relative humidity is set as a ratio of the measured $(\text{N}_2^+)^{\text{air}}$ signal. For the filtered dataset, Figure 3.17 shows the ratio $(\text{H}_2\text{O}^+)^{\text{humidity}}:((\text{N}_2^+)^{\text{air}})$ plotted against RH. Slopes ($\times 10^{-4}$) of 2.75 ± 0.09 and 2.3 ± 0.1 were fit to the ozonolysis and photooxidation data respectively. These findings are consistent with the values of 2.39 – 3.01 reported by Chen et al. (2011) for the photooxidation of isoprene and ozonolysis of α-pinene and β-caryophyllene.

Results show that at the humidities used during chamber experiments in this study (∼5%), the contribution of molecular water from humidity to the $m/z$ 18 signal is considerably less than the default fragmentation table setting. Consequently, when analysing chamber experiments, the following change is made to the fragmentation table; $\text{frag}_{\text{RH}[18]} = 0.0014*\text{frag}_{\text{air}[28]}$ for ozonolysis experiments and $\text{frag}_{\text{RH}[18]} = 0.0012*\text{frag}_{\text{air}[28]}$ for photooxidation experiments.

For data collected without a filter, water can come from both the gas- and particle-phases, the latter including unevaporated water sourced from the decom-
Figure 3.18: Plot of \((\text{H}_2\text{O}^+)_{\text{humidity}} + (\text{H}_2\text{O}^+)_{\text{org}}\) against relative humidity for data collected without a filter. Each filled circle corresponds to a V-mode measurement taken from the ozonolysis experiment, with open circles corresponding to photooxidation data. Lines of best fit for the ozonolysis (solid) and photooxidation (dashed) data are shown.

position of organic species. As no inorganic aerosol seed was added, the inorganic particle contribution is taken as zero. The gas-phase contribution and molecular water existing in the aerosol are both assumed to be zero at 0% relative humidity, as the air is taken to be dry and all particle-phase water to evaporate. Therefore, plotting \((\text{H}_2\text{O}^+)\) against relative humidity yields the value of \((\text{H}_2\text{O}^+)_{\text{org}}\) at the intercept of 0% relative humidity, with results shown in Figure 3.18.

The fragmentation table defines \text{frag	extsubscript{organic}[18]} = 0.225*\text{frag	extsubscript{organic}[44]}, that is, it assumes the contribution water makes to the organic aerosol is 22.5% that of \text{CO}_2 (Aiken et al., 2008). Using the already discussed method of determining the organic contribution to \text{CO}_2, the ratio of \((\text{H}_2\text{O}^+)_{\text{org}}:(\text{CO}_2^+)_{\text{org}}\) is found to be 1.41 ± 0.09 and 1.65 ± 0.03 for ozonolysis and photooxidation SOA respectively. For implementation into the AMS, the results need to be corrected for the differing relative ionisation efficiencies (RIE) of \text{CO}_2 and \text{H}_2\text{O}. For \text{CO}_2, the RIE\textsubscript{org} value of 1.4 recommended by Alfarra et al. (2004) is used, whilst a RIE value of 2 is used for water, based on the work of Mensah et al. (2011). As a result, the value of \((\text{H}_2\text{O}^+)_{\text{org}}:(\text{CO}_2^+)_{\text{org}}\) becomes 0.99 ± 0.06 for ozonolysis and 1.16 ± 0.02 for photooxidation, with these values then input into the respective fragmentation tables. These findings are considerably higher than the default value suggested by Aiken et al. (2008), with multifunctional organic hydroperoxides prevalent in terpene oxidation systems a potential explaining factor (Chen et al., 2011). Interestingly, the results are similar to the value of 1 proposed by Allan et al. (2004), which Aiken et al. (2008) superseded.
In addition to systematic adjustments, corrections were also made to each experiment individually through the Frag check routine in SQUIRREL, to account for subtle changes in experimental conditions. For example, the background concentration of CO$_2$ in Guangzhou, a megacity, is likely to differ from the global average, with fluctuations due to variation in meteorology and local activity expected (Verma et al., 2010). To account for this, the purely organic signal Org43 (C$_2$H$_3$O) is used to scale the Org44 (CO$_2$) signal. The ratio of the organic signals should go through the origin, with the CO$_2$ gas-phase contribution adjusted to enforce this. An example is shown in Figure 3.19, which required implementation of a scaling factor of magnitude 1.2 for the y-intercept to be zero, implying that the average background CO$_2$ concentration is $\sim$480 ppm. Similar fragmentation checks and adjustments against Org43 are also made to calibrate the organic contributions of Org15 and Org29, respectively caused by $^{15}$N and $^{15}$NN being slightly different to what may be predicted isotopically. Filtered datasets were collected during the last 20 minutes of 2016 experiments. During this time, all main peaks were found to go to zero, indicating that the fragmentation table was operating correctly, at least for the 2016 campaign.

3.2.6 Filter Based Sampling and Analysis

Sampling

Aerosol samples were collected on pre-fired Whatman quartz microfiber filters (47 mm) using the set-up shown in Figure 3.2. Blank filter papers were secured inside an
inline polycarbonate filter holder (Savillex, USA), which had one end connected to
the chamber through an FEP Teflon sample line and the other to a pump, operating
at 16 to 25 slpm. The pump draws air from the chamber through the filter, which
captures the aerosol mixture. Filter samples were collected for at least 2 hours, with
collection starting once conditions inside the chamber had stabilised; that is when all
\( \alpha \)-phellandrene was consumed, gaseous time profiles were steady and aerosol mass
had reached its peak. Post collection filters were wrapped in aluminium foil and
dried in a desiccator for 24 hours before storage in a fridge at 4°C at the GIG-CAS.
Samples were transported under dry ice to the University of York, where they were
stored in a freezer at -20°C before analysis.

Preparation and Analysis

Filter samples were cut into small pieces and suspended in 4 mL of Optima™ LC/MS
grade water (Fisher Scientific, USA) for 2 hours (Hamilton et al., 2008). Extraction
was aided by two 15 minute periods of sonication, separated by 5 minutes to avoid
excessive heating. The sample solution was then filtered through a 0.45 µm pore
syringe (Milllex-HA, Millipore, USA), with a further 1 mL of Optima™ water added
to the dry residue for a subsequent extraction, following the same method. Combined
extraction samples were then evaporated to dryness using a V-10 vacuum solvent
evaporator (Biotage®, 36°C, 8 mbar). The residual residue was re-suspended in
500 µL of 50:50 methanol:water (Optima LC-MS grade, Fischer Scientific) solution,
with dissolution aided by the Biotage® evaporator (4000 rpm). Pre-conditioned
filters, prepared by heating blank filter papers (Whatman Quartz microfiber filters,
47 mm) in a furnace at 550°C for 5 hours, were analysed as a procedural blank following the same method.

Samples were analysed using reversed-phase high-performance liquid chromatog-
raphy (HPLC) (Agilent 1100 series, Berkshire, UK), coupled to a Q-Exactive™ Hy-
brid Quadrupole-Orbitrap™ Mass Spectrometer (Thermo Scientific, USA). Samples
(30 µL) were injected into the HPLC system using an auto-sampler, and were sep-
arated using a reversed phase Pinnacle DB C\(_{18}\) column (150 × 6 mm) with 5 µm
particle size (Thames Restek, UK). The starting mobile phase consisted of 85% Optima water, mixed with 0.1% formic acid (Sigma Aldrich), and 15% Optima
methanol (Sigma Aldrich), graduating to 10% of the water/formic acid solution and
90% methanol over 13 minutes, before holding this ratio for a further minute. The
flow rate was set to 1.3 mL min\(^{-1}\).

The Q-Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer includes an
atmospheric pressure ion source, a stacked-ring ion guide (S-lens) in the source

\(^{1}\)In hindsight a ‘chamber blank’ would have been preferred; that is identical analysis of a filter
which had sampled air from a clean chamber.
region, a quadrupole mass filter, a curved linear ion trap (C-trap), a Higher energy Collisional Dissociation (HCD) cell and an Orbitrap mass analyser (Michalski et al., 2011). A schematic is shown in Figure 3.21. Molecules are charged at atmospheric pressure using electrospray ionisation (ESI, 35 eV), in both positive and negative ionisation modes. These ions then pass through a transfer tube to an S-lens (Olsen et al., 2009), and then via an injection multipole into a bent flatapole in which ions are collisionally cooled. Ions are then transmitted via a lens into a hyperbolic quadrupole ($r_0 = 4$ mm). Following an exit lens, a short octapole brings ions into the C-trap which is interfaced with a HCD cell. The Q-Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer has two modes of operation; MS and MS/MS. In MS mode, the entire mass range produced by the ion source passes through the quadrupole mass filter. Ions are then collected in a C-trap, which stores and compresses ions into small packets. While in MS/MS mode, the quadrupole only transmits a defined mass window around a precursor ion of choice. Ions are then activated using HCD with high-pressure N$_2$ gas, producing mass fragments which are interfaced into the C-trap. The MS/MS mode is also known as tandem mass spectrometry and allows for structural elucidation. In either mode, ions from the C-trap are ejected into the Orbitrap™ mass analyser and analysed in a single Orbitrap™ detection cycle. The Orbitrap™ itself is a small electrostatic device containing a central, spindle-shaped electrode which the injected high energy ion packets orbit around (Makarov, 2000; Hardman and Makarov, 2003). The electrostatic attraction of ions towards the central electrode is compensated by a centrifugal force arising.
from the initial tangential velocity of ions, resulting in ions moving in a complex spiral pattern (Scigelova and Makarov, 2006). The axial component of these oscillations can be detected as an image current on the two halves of an electrode encapsulating the Orbitrap, and is independent of initial energy, angle and position. The signal is Fourier transformed to obtain oscillation frequencies of ions, resulting in an accurate reading of their $m/z$. The technique achieves very high resolution, surpassing that obtainable through use an orthogonal time-of-flight system (such as that found in the PTR-TOF and AMS) (Scigelova and Makarov, 2006; Zubarev and Makarov, 2013).

Full mass spectra scans were acquired in the Orbitrap™ mass analyser over $m/z$ 50 – 750 range, with a resolution of 70 000 at $m/z$ 200. A capillary temperature of 320°C, spray voltage of 4.0 kV, N$_2$ auxiliary gas temperature of 320°C and N$_2$ flow rate of 30 arbitrary units were used. The Orbitrap™ was frequently mass calibrated using ESI positive and negative ion calibration solutions (Pierce®, Thermo Scientific). Data analysis were conducted using Xcalibur™ mass spectrometry software, assuming the only atoms present are $^{12}$C, $^{13}$C, $^1$H and $^{16}$O in the negative ionisation mode, in addition to $^{23}$Na in the positive ionisation mode. Analysis of the pre-conditioned filters consistently showed only baseline noise, confirming that peaks in chromatograms were not due to artefacts of sample preparation.
3.3 Chamber Experiment Methodology

Conducting a smog chamber experiment is a structured process that involves:

1. Connecting online instruments discussed in Section 3.2 to the clean reactor.

2. Recording stable background readings on all instruments.

3. Injecting relevant reactants.

4. Initiating the reaction.

5. Periodically lowering the reactor roof to maintain a positive differential pressure.

6. Taking samples for offline measurements.

7. Disconnecting all instruments and re-introduce clean airflow to flush reactor.

These basic steps were followed in all chamber experiments. Experimental timelines from an ozonolysis and photooxidation experiment are now provided, serving as a template for analogous experiments discussed in this thesis. For brevity, the times at which the reactor roof was lowered are not included. α-Phellandrene concentrations were chosen to be high enough to allow sufficient detection and analysis of the system, whilst still maintaining a somewhat accurate representation of ambient conditions.

3.3.1 Ozonolysis Experiment

Ozonolysis experiment conducted on 19th August 2014. Note that this experiment included the addition of formic acid to the reactor, a species not included in the majority of ozonolysis experiments.

12:20 Clean air flow into reactor disconnected. Fans (40.10 and 36.54 rpm) and temperature control (25°C) switched on.

12:21 O₃ and NOₓ instruments connected.

12:23 SMPS connected.

12:24 PTR-TOF connected.

12:25 AMS connected.

12:34 Injection box switched on and flushed with N₂ gas.
12:35 2 μL of acetonitrile injected at 150°C.

12:37 First of 6 × 1000 μL cyclohexane injections at 150°C.

12:54 Cyclohexane injections stopped.

12:58 10 μL of α-phellandrene injected at 190°C.

13:04 50 μL of formic acid injected at 150°C.

13:20 O₃ generated by introducing pure oxygen feed gas at 0.8 L min⁻¹ for 24.8 seconds into the ozone generator.

14:36 Start filter sampling with flow rates of 20.90 and 16.28 L min⁻¹.

16:40 Stop filter sampling.

16:41 O₃, NOₓ, SMPS, PTR-TOF and AMS all disconnected.

16:42 Temperature control and fans switched off.

16:43 Clean air re-introduced into reactor.

### 3.3.2 Photooxidation Experiment

Photooxidation experiment conducted on 26th August 2016. Note that this experiment only had NO added, whereas other photooxidation experiments conducted instead had NO₂ added or a combination of both. Additionally this experiment included an hour of dark measurements at the end to parameterise the SOA wall loss rate.

14:21 Temperature control (25°C) and fans (40.87 and 31.25 rpm) switched on.

14:22 Clean air supply disconnected.

14:23 O₃ and NOₓ instruments connected.

14:41 PTR-TOF connected.

14:43 AMS connected.

14:55 Background canister taken.

15:20 Injection system switched on and flushed with N₂ at a flow rate of 0.3 L min⁻¹.

15:22 29 μL of α-phellandrene injected at 170°C.

15:30 2 μL of acetonitrile injected at 150°C.
3.4 Chamber Characterisation Experiments

The impact of chamber auxiliary processes varies between smog chambers and over

15:35 N₂ flow through injection line stopped.

15:38 Starting canister taken.

15:42 20 mL of NO injected.

15:50 UV lights switched on.

16:13 Third canister taken.

17:21 Fourth canister taken.

18:32 Fifth canister taken.

19:32 Sixth canister taken.

19:40 UV lights switched off.

20:42 O₃, NOₓ, SMPS and PTR-TOF all stopped.

20:44 Filter placed in front of AMS.

20:58 AMS, temperature control and fans switched off.

20:59 Clean air re-introduced into reactor.

It is therefore crucial to regularly characterise the GIG-CAS chamber auxiliary

3.4 Chamber Characterisation Experiments

mechanism, so that differences between chamber studies and the atmosphere are quantified and justly accounted for. Only afterwards can chamber results be correctly interpreted. For this reason, GIG-CAS chamber auxiliary processes were

regularly parameterised. Important auxiliary processes are listed in Section 1.5 and include non-representative lighting, O₃, NO, NO₂ and particle losses to the reactor walls, background offgassing of NOₓ, and other reactive species and heterogeneous reactions that result in chamber radical sources upon irradiation. The impact of auxiliary processes are assessed through various characterisation experiments that either directly measure the parameter of interest, or are highly sensitive to the process being assessed (Carter et al., 2005; Hynes et al., 2005). For dark chamber experiments, only the relevant wall losses were considered important whilst, for photooxidation studies, the entire suite of auxiliary processes are considered.
3.4.1 Actinometry

The artificial light produced by the black lamps inside the chamber is not representative of the entire ground-level solar light spectrum, with the ultraviolet irradiation produced corresponding to the wavelengths for maximum NO\textsubscript{2} photolysis. Indeed very little light is irradiated at longer wavelengths (> 400 nm); a region that photolyses some organic species including peroxy radicals and methylglyoxal (Cocker et al., 2001b). Nonetheless, the majority of photolysis reactions in the troposphere occur at wavelengths below 400 nm (Carter et al., 1995), which is why black lamps, along with their low-cost and efficient irradiation, are widely implemented in smog chambers (Cocker et al., 2001b; Carter et al., 2005; Hynes et al., 2005; Presto et al., 2005a; Boyd et al., 2015).

The 135 black lamps housed inside the chamber are divided into four separately controlled groups, allowing light intensity to be regulated. However, in all photooxidation experiments, the entire suite of black lamps was used. The light spectrum emitted by these lamps was measured by an EPP2000CXR-50 concave grating spectrometer (StellarNet Inc., USA), and is shown in Figure 3.22. The black lamps primarily irradiate over the range 340 to 400 nm, with peak intensity at 369 nm.

Light intensity and photolysis rates were first characterised in 2012 when the chamber was constructed, with results discussed in Wang et al. (2014). These results are used when analysing data from the 2013 photooxidation experiments. Additional chemical actinometry experiments\textsuperscript{2} were conducted prior to the 2016 campaign to update photolysis frequencies.

Photolysis frequencies are first-order rate coefficients that quantify the rate of photolysis in terms of a relative concentration change of a precursor molecule or photo-product (Bohn et al., 2005). For example in the photolysis of NO\textsubscript{2}:

\[
\text{NO}_2 \xrightarrow{hv} \text{NO} + \text{O}^3\text{P}, \quad J(\text{NO}_2) = -\frac{1}{[\text{NO}_2]} \frac{d[\text{NO}_2]}{dt}
\]  

(3.15)

The photolysis rate of NO\textsubscript{2} in the GIG-CAS chamber is determined using steady-state actinometry by using the chamber as a chemical actinometer (Shetter et al., 2003; Bohn et al., 2005; Hynes et al., 2005). This involves injecting NO\textsubscript{2} into the reactor, irradiating it with the black lamps and continually measuring the concentrations of NO, NO\textsubscript{2} and O\textsubscript{3}. Photochemical equilibrium is quickly established via Reactions 1.2 – 1.4. If loss and formation processes compensate one another then:

\[
\frac{d[\text{NO}_2]}{dt} = -J_{\text{NO}_2}[\text{NO}_2] + k_{\text{NO} + \text{O}_3}[\text{NO}][\text{O}_3] = 0
\]

(3.16)

\textsuperscript{2}Chemical actinometry is the measurement of photolysis frequencies by irradiating a species and monitoring the gas-phase concentration of the precursor and product species.
The rate coefficient $k_{\text{NO}+\text{O}_3}$ is known experimentally (Sander et al., 2003; Atkinson et al., 2004), and so $J_{\text{NO}_2}$ can be calculated from the equilibrium concentration of NO, NO$_2$ and O$_3$:

$$J_{\text{NO}_2} = \frac{k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3]}{[\text{NO}_2]}$$ (3.17)

In this photo-stationary approach, losses (e.g. wall losses, dilution) are neglected and $J_{\text{NO}_2}$ is assumed constant. Indeed, losses are too slow to significantly influence the photochemical equilibrium, with $J_{\text{NO}_2}$ more than an order of magnitude greater than measured wall loss rates reported in Section 3.4.2.

Three steady-state NO$_2$ actinometry experiments were conducted at the start of the 2016 campaign. Using $k_{\text{NO}+\text{O}_3} = 1.875 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, the average recommended value of Sander et al. (2003) and Atkinson et al. (2004), and correcting for the reaction of NO and O$_3$ during sampling, an average NO$_2$ photolysis rate of $0.25 \pm 0.01$ min$^{-1}$ at full light intensity is obtained. This result is roughly half the 2012 measurement, $0.49 \pm 0.01$ min$^{-1}$ (Wang et al., 2014), suggesting a gradual degradation in overall lamp performance over the four years. For comparison, a value of $0.58$ min$^{-1}$ is calculated for noon on a summers day in Guangzhou using the National Center for Atmospheric Research Tropospheric Ultraviolet and Visible (NCAR-TUV) model (Wang et al., 2014).

Photolysis rates for species other than NO$_2$ in the GIG-CAS chamber were then calculated relative to the measured $J_{\text{NO}_2}$ value. From Carter et al. (1995), the actinic
CHAPTER 3. EXPERIMENTAL

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</tbody>
</table>

Table 3.5: MCM photolysis rates calculated for the GIG-CAS chamber in 2012 and 2016. Reactions corresponding to each photolysis parameter number can be found in Saunders et al. (2003).

Flux \((F)\) was estimated using:

\[
F(\lambda) = F_{rel}(\lambda) \frac{J_{NO_2}}{\sum \lambda F_{rel}(\lambda) \sigma_{NO_2}(\lambda) \Phi_{NO_2}(\lambda)} \tag{3.18}
\]

where \(F_{rel}(\lambda)\) is the relative spectral distribution, calculated by taking the product of the lamp emission spectrum and transmittance of Teflon \((0.93, \text{Hynes et al., 2005})\), \(J_{NO_2}\) is the measured \(NO_2\) photolysis rate and \(\sigma_{NO_2}\) and \(\Phi_{NO_2}\) are the literature cross-sections and quantum yields for \(NO_2\) for a given wavelength \((\text{Atkinson et al., 2006})\). Actinic fluxes were then used to calculate photolysis rates for all MCM photolysis parameters using Equation 1.1, with cross-section and quantum yield data for each reaction taken from IUPAC datasheets \((\text{Atkinson et al., 2006})\). \(J\) values calculated using this method with 2012 and 2016 \(J_{NO_2}\) values are presented in Table 3.5.
3.4.2 Wall Loss Experiments

**Gaseous Wall Loss**

Wall loss rates of O\(_3\), NO and NO\(_2\) were measured by injecting a certain concentration of these gases into the reactor and continually monitoring their dark decay. Wall loss rates are then obtained by treating wall loss as a first-order process (Grosjean, 1985; Hynes et al., 2005). During initial calibration of the chamber, wall loss rates of O\(_3\), NO and NO\(_2\) were determined to be \(1.31 \times 10^{-4}\) min\(^{-1}\), \(1.41 \times 10^{-4}\) min\(^{-1}\) and \(1.39 \times 10^{-4}\) min\(^{-1}\) respectively (Wang et al., 2014). These values are then used when interpreting data from the 2013 campaign. Prior to dark ozonolysis and NO\(_2\) experiments, corresponding wall loss rates were measured. Meanwhile, wall loss rates of O\(_3\), NO and NO\(_2\) were measured prior to photooxidation studies in 2016. Experimental results are shown in Figure 3.23 with determined wall loss rates listed in Table 3.6. Wall loss rates are generally consistent, with unique values used when investigating results for each particular year. Nevertheless, measured values equate to half lives of over 25 hours, suggesting that wall losses of these inorganic species have minor implications during conducted chamber experiments, which generally run for less than 5 hours.

Propene was found to be stable during initial calibration of the GIG-CAS chamber (Wang et al., 2014), with this again confirmed in 2016. Similarly, acetonitrile and cyclohexane were both observed to be stable in the chamber under dark, dry conditions. Recent studies however have shown that gaseous organic compounds exist in equilibrium with Teflon walls, with the extent of partitioning driven by species volatility (Matsunaga and Ziemann, 2010; Zhang et al., 2014b; Yeh and Ziemann, 2015; Krechmer et al., 2016; La et al., 2016). The extent of this effect is yet to

![Figure 3.23](image_url)

**Figure 3.23**: Results from wall loss experiments of O\(_3\), NO and NO\(_2\) for different campaigns. Wall loss rates are assumed to be first-order, with natural logarithm of concentration plotted against time. Lines of best fit are shown.
Table 3.6: Measured wall loss rates of gaseous inorganic species in the GIG-CAS chamber for different experimental campaigns.

<table>
<thead>
<tr>
<th>Year</th>
<th>Species</th>
<th>Temp (K)</th>
<th>RH (%)</th>
<th>Wall Loss Rate ( \times 10^{-4} \text{ min}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>O(_3)</td>
<td>296.7</td>
<td>(\leq 10)</td>
<td>1.31 ± 0.24</td>
<td>Wang et al. (2014)</td>
</tr>
<tr>
<td>2012</td>
<td>NO</td>
<td>296.7</td>
<td>(\leq 10)</td>
<td>1.41 ± 0.40</td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>NO(_2)</td>
<td>296.7</td>
<td>(\leq 10)</td>
<td>1.39 ± 0.68</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>O(_3)</td>
<td>297.8 ± 0.4</td>
<td>2.1 ± 0.5</td>
<td>4.71 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>O(_3)</td>
<td>298.2 ± 0.3</td>
<td>5.2 ± 0.6</td>
<td>2.56 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>NO(_2)</td>
<td>298.0 ± 0.4</td>
<td>8.9 ± 0.2</td>
<td>0.23 ± 0.3</td>
<td>This Study</td>
</tr>
<tr>
<td>2016</td>
<td>O(_3)</td>
<td>297.8 ± 0.4</td>
<td>2.6 ± 0.3</td>
<td>1.58 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>NO</td>
<td>297.5 ± 0.3</td>
<td>2.1 ± 0.3</td>
<td>1.50 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>NO(_2)</td>
<td>298.0 ± 0.5</td>
<td>7.7 ± 0.8</td>
<td>2.45 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

be quantified in the GIG-CAS chamber, and indeed experimental methods for estimating vapour-wall loss rates in chambers are not yet well established, although some loss of low-volatility organic compounds to the Teflon walls is expected (Zhang et al., 2014b; Yeh and Ziemann, 2015; Krechmer et al., 2016). The impact of this on gas- and particle-phase results is discussed in depth in Section 3.5.1.

**Particle Wall Loss**

The principal process complicating interpretation of measured aerosol data is the loss of particles to the reactor walls. To quantify the total amount of aerosol mass generated, the amount of aerosol lost to the reactor walls for each time point must be estimated and then combined with the aerosol mass measured. Particle deposition onto the Teflon wall of the reactor is influenced by chamber geometry, static charge build-up on the Teflon media, and turbulent diffusion inside the reactor, with the loss rate proportional to particle concentration and to a lesser extent particle size (Cocker et al., 2001b). Detailed wall loss models have been constructed that incorporate these variables in parameterising particle wall loss rates (Crump and Seinfeld, 1981; Cocker et al., 2001b; Keywood et al., 2004; Verheggen and Mozurkewich, 2006; Pierce et al., 2008; Hildebrandt et al., 2009), however the net difference in wall-loss corrected loadings is less than 10% when compared with corrections based on simpler constructs (Pierce et al., 2008; Nah et al., 2017).

One such technique is that proposed by Pathak et al. (2007b), which assumes that the wall loss rate is first order and independent of particle size. This enables the particle wall loss rate to be determined uniquely for each experiment, by analysing data after aerosol growth processes have ceased. If it is assumed that no new par-
particle formation is occurring, then the particle mass decay rate can be taken as the particle loss rate. The correction method of Pathak et al. (2007b) has the advantage that day-to-day variations in particle-wall deposition rates are accounted for, however the method loses accuracy if the wall-loss rate changes throughout an experiment. Furthermore, a key assumption is that the particle-wall loss rate is not strongly dependent on particle size, allowing for the overall particle-wall loss rate to be represented by a single first-order decay rate coefficient. The impact of this assumption is still unclear, however the method has compared favourably with other techniques (Pierce et al., 2008; Nah et al., 2017). Coagulation effects can be ignored, since coagulation does not affect aerosol mass concentration on which the method is based (Nah et al., 2017).

Wall loss rates are therefore determined in each experiment individually by plotting the natural logarithm of the density corrected measurements of aerosol mass against time, using data after SOA production has stopped. The gradient then provides the wall loss rate coefficient (Pathak et al., 2007b). In general, data usually spanned at least the last hour, with excellent fits achieved ($R^2 \geq 0.98$), suggesting that the assumptions of Pathak et al. (2007b) were valid. Furthermore, geometric means of the number distribution varied by no more than 6 nm over the fitted time periods; a size variation which has negligible impacts on wall loss rates (McMurry and Rader, 1985). Aerosol wall loss rates during ozonolysis, dark NO$_2$ and photooxidation experiments are given in Sections 3.5.1, 3.7.2 and 3.8.2 respectively. Once the first-order wall loss rate coefficient has been determined, total SOA production
at a given time can be calculated by:

\[ SOA(t) = M(t) + k_{SOA} \int_0^t M(t)dt \]  

(3.19)

where \( M(t) \) is the aerosol mass measured in the reactor at time \( t \) and \( k_{SOA} \) is the SOA wall loss rate coefficient. The integral was calculated numerically using the measurements. The method and impact is shown for an example experiment in Figure 3.24.

### 3.4.3 Chamber Auxiliary Mechanism

Chamber auxiliary mechanisms are typically assessed indirectly through specific characterisation experiments that are sensitive to different chamber effects (Carter et al., 2005; Hynes et al., 2005; Bloss et al., 2005). Model simulations are then used to derive chamber characterisation parameters that best fit experimental data.

The GIG-CAS chamber auxiliary mechanism was thoroughly investigated upon construction of the chamber in 2012, by simulating clean air, low NO\(_x\), CO, CO–NO\(_x\) and propene–NO\(_x\) irradiation experiments (Wang et al., 2014). The purpose of these experiments is summarised in Table 3.7. Of these, only the propene–NO\(_x\) experiment is discussed in this thesis, with results discussed briefly in Appendix C. The resulting auxiliary mechanism is used when modelling 2013 experimental data.

The GIG-CAS reactor bag was replaced immediately prior to undertaking the 2016 campaign, necessitating completely new characterisation. Due to time constants however, only three characterisation experiments were conducted; low NO\(_x\), CO–NO\(_x\) and propene–NO\(_x\) irradiation experiments. Analysis of these experiments was carried out using the photolysis rates listed in Table 3.5, measured O\(_3\), NO and NO\(_2\) wall loss rates listed in Table 3.6, measured temperatures and relative humidities and mechanisms extracted from the MCM. Constructed models were evaluated using the online modelling tool AtChem, which is integrated with the MCM and freely available at https://atchem.leeds.ac.uk. Written in Fortran 90, AtChem utilises the open-source library CVODE to provide rapid solutions to non-linear ordinary differential equations.

Table 3.8 describes the reactions and associated parameters of the considered chamber-dependent auxiliary mechanism, which was adapted from the study of Bloss et al. (2005), with recommendations from Hynes et al. (2005). Background hydrocarbons found in the zero air used to fill the chamber are modelled explicitly (Hynes et al., 2005). This is particularly important when modelling air irradiations, where small changes in background VOCs have a significant impact on O\(_3\) formation. NO\(_x\) offgassing can be represented in the model through any species that rapidly forms
3.4. CHAMBER CHARACTERISATION EXPERIMENTS

<table>
<thead>
<tr>
<th>Run Type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean air</td>
<td>Useful for evaluating NO\textsubscript{x} offgassing rates and screening for background VOC effects.</td>
</tr>
<tr>
<td>Low NO\textsubscript{x}</td>
<td>O\textsubscript{3} formation and NO oxidation are very sensitive to chamber radical sources, whilst being somewhat sensitive to NO\textsubscript{x} offgassing parameters.</td>
</tr>
<tr>
<td>CO</td>
<td>O\textsubscript{3} formation is very sensitive to NO\textsubscript{x} offgassing rates, relatively insensitive to radical source parameters.</td>
</tr>
<tr>
<td>CO–NO\textsubscript{x}</td>
<td>O\textsubscript{3} formation and NO oxidation are very sensitive to chamber radical sources, but not to NO\textsubscript{x} offgassing parameters.</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}–NO\textsubscript{x}</td>
<td>O\textsubscript{3} formation and NO oxidation are very sensitive to chamber radical sources, but not to NO\textsubscript{x} offgassing parameters.</td>
</tr>
</tbody>
</table>

Table 3.7: Summary of characterisation experiments and derived parameters relevant to mechanism evaluation.

NO\textsubscript{x} in atmospheric irradiation systems, such as NO, NO\textsubscript{2} or HONO (Carter et al., 2005). In this study, a reaction representing the light-induced outgassing of NO\textsubscript{2} is included with a rate coefficient of \( f_1 \times J_{\text{NO}_2} \) (Carter and Lurmann, 1991; Bloss et al., 2005), where the scaling factor \( f_1 \) is determined by simulating the experimental data. Similarly, in lieu of a more definitive complex representation, a simple reaction for the continual light-induced production of OH radicals from the Teflon walls is included (Carter and Lurmann, 1991), having a rate coefficient \( f_2 \times J_{\text{NO}_2} \).

Dark hydrolysis of NO\textsubscript{2} to HONO and absorbed NO\textsubscript{x} can provide an alternative radical source inside the chamber, and was assigned a starting rate coefficient of \( 1 \times 10^{-6} \text{ s}^{-1} \), based on results from the CSIRO chamber (Hynes et al., 2005). Hydrolysis of N\textsubscript{2}O\textsubscript{5} to nitric acid can be an important NO\textsubscript{x} sink, which can affect maximum ozone yields. The reaction is assumed to proceed both heterogeneously and homogeneously (Carter and Lurmann, 1991), with rate coefficients of \( 1 \times 10^{-5} \text{ s}^{-1} \) and \( 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) assigned respectively, similar to the studies of Bloss et al. (2005) and Hynes et al. (2005). Similarly, the wall loss of HNO\textsubscript{3} is assumed to occur at a rate of \( 1 \times 10^{-4} \text{ s}^{-1} \), based on the work of Hynes et al. (2005). The light induced off-gassing of adsorbed HNO\textsubscript{3} to OH and NO\textsubscript{2} is included with a photolysis rate coefficient \( J_{\text{HNO}_3} \), which is equivalent to \( J_8 \) in the MCM (Bloss et al., 2005). HONO is expected to be present to varying extents at the beginning of experiments where NO\textsubscript{x} is a reactant, being formed through heterogeneous hydrolysis of NO\textsubscript{2} in the transfer lines or on the chamber walls, and represents a non-negligible source of radicals upon irradiation (Carter and Lurmann, 1991). It is not possible to measure starting HONO concentrations inside the GIG-CAS chamber, thus it is varied between 0 to 5 ppb for each experiment to optimise model performance.
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Table 3.8: Auxiliary mechanism for chamber dependent-reactions and associated rate parameters.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Parameter</th>
<th>Lower – Upper Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>$hv + \text{wall} \rightarrow \text{NO}_2$</td>
<td>$f_1 \times J_{\text{NO}_2} \times \text{ppb s}^{-1}$</td>
<td>0.0075 &lt; $f_1$ &lt; 0.03</td>
</tr>
<tr>
<td>$hv + \text{wall} \rightarrow \text{OH}$</td>
<td>$f_2 \times J_{\text{NO}_2} \times \text{ppb s}^{-1}$</td>
<td>0.0075 &lt; $f_2$ &lt; 0.03</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{wHNO}_3$</td>
<td>$1 \times 10^{-6} \text{ s}^{-1}$</td>
<td>(0.5 – 2.0) $\times 10^{-6} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_5 \rightarrow \text{wHNO}_3 + \text{wHNO}_3$</td>
<td>$1 \times 10^{-5} \text{ s}^{-1}$</td>
<td>(0.5 – 2.0) $\times 10^{-5} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{wHNO}_3 + \text{wHNO}_3$</td>
<td>$1 \times 10^{-20} \times [\text{H}_2\text{O}] \text{ s}^{-1}$</td>
<td>(0.1 – 10) $\times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\text{HNO}_3 \rightarrow \text{wHNO}_3$</td>
<td>$1 \times 10^{-4} \text{ s}^{-1}$</td>
<td>(0.5 – 2.0) $\times 10^{-4} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$hv + \text{wHNO}_3 \rightarrow \text{OH} + \text{NO}_2$</td>
<td>$J_{\text{HNO}_3}$</td>
<td>(0.5 – 2) $\times J_{\text{HNO}_3}$</td>
</tr>
<tr>
<td>$[\text{HONO}]_0$</td>
<td>Varied from 0 – 5 ppb</td>
<td></td>
</tr>
</tbody>
</table>

All starting parameters are assumed to be certain to within a factor of two, except for the gas-phase hydrolysis of $\text{N}_2\text{O}_5$, which is assumed to be uncertain by a factor of 10 (Hynes et al., 2005). Once optimised in the following sections, the auxiliary mechanism will be held constant for all future modelling of $\alpha$-phellandrene, with initial HONO concentration the only adjustable parameter. Confidence in the auxiliary mechanism will then enable mechanistic fine-tuning to take place exclusively on the constructed $\alpha$-phellandrene degradation scheme, to best simulate experimental data.

Low-NO\textsubscript{x} Characterisation Experiment

The main factor limiting the utility of chamber experiments conducted under low NO\textsubscript{x} conditions is the offgassing of NO\textsubscript{x}. While the impact can directly be assessed by measuring the increase in NO\textsubscript{x} during experiments where no initial NO\textsubscript{x} is injected, the more sensitive technique is to measure the formation of O\textsubscript{3} in irradiations of VOCs under low-NO\textsubscript{x} conditions (Carter et al., 2005). A characterisation experiment of a clean chamber with low-NO\textsubscript{x} was therefore performed. The magnitude of NO\textsubscript{x} offgassing rates are determined by optimising the chamber auxiliary mechanism through a model simulation, to best replicate experimentally observed data.

Table 3.9: Starting conditions for the low-NO\textsubscript{x}-air characterisation experiment.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RH</th>
<th>NMHCs</th>
<th>CO</th>
<th>NO</th>
<th>NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>(ppb)</td>
<td>(ppm)</td>
<td>(ppb)</td>
<td>(ppb)</td>
</tr>
<tr>
<td>Low NO\textsubscript{x}</td>
<td>298</td>
<td>8.0</td>
<td>9.6</td>
<td>0.3</td>
<td>5.7</td>
</tr>
</tbody>
</table>
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Analysis of the background zero air prior to irradiation using the canister sampling technique gave: C$_2$H$_6$ (1.7 ppb), C$_2$H$_4$ (0.2 ppb), C$_2$H$_2$ (0.2 ppb), C$_3$H$_8$ (2.8 ppb) and C$_3$H$_6$ (0.1 ppb) using GC-FID, and i-C$_4$H$_10$ (0.4 ppb) and n-C$_4$H$_10$ (0.7 ppb) using GC-MS detection. CH$_4$ and CO were found at concentrations of 2.0 ppm and 0.3 ppm respectively. A small amount of NO$_x$ was also injected prior to irradiation, with starting conditions listed in Table 3.9. Background measurements of formaldehyde and acetaldehyde in 2012, taken by sampling air through a Sep-Pak DNPH-Silica cartridge (Waters Corporation, USA) and subjecting the sample to HPLC (HP1200; Agilent Technologies, USA) with a 360 nm UV detector (Wang et al., 2014), provided concentrations of 3.3 ppb and 0.2 ppb respectively. Since neither the chamber location or zero-air generator were changed, and no new data are available, these background concentrations are used for analysis of 2016 experiments.

A base model was created using the auxiliary parameters listed in Table 3.8 with an initial HONO concentration of 1 ppb. The sensitivity of ozone production to each parameter in the auxiliary mechanism was then investigated by varying each parameter in turn to its upper and lower limits, while keeping all other parameters at their nominal value. The percentage change in maximum ozone concentration induced by different parameters, relative to the base case, is shown in Figure 3.25.

Of the parameters in the auxiliary mechanism, modelled O$_3$ was most sensitive to the light induced production of OH and NO$_2$ from chamber walls, which is typical of low-NO$_x$ experiments (Hynes et al., 2005). Varying the rate of NO$_2$ hydrolysis...
was found to have a minor effect, whilst the impact of N$_2$O$_5$ hydrolysis and the sorption/desorption of HNO$_3$ was found to be negligible. Varying the initial HONO concentration had a large influence, highlighting the importance of tuning its value for each experiment. Meanwhile, the model was found to be highly sensitive to the amount of background VOC, which was tested using HCHO as a surrogate species (Hynes et al., 2005). This highlights the importance of explicitly representing background VOCs in models with low hydrocarbon concentrations. The maximum impact of any individual parameter was ±13%. For comparison, the wall loss rate of ozone was changed by a factor of two either way, which impacted the maximum ozone concentration by a maximum of 3.5%.

The best simulation of data is shown in Figure 3.26, and was generated by adjusting the rate parameter scaling factors of NO$_2$ and OH offgassing to $f_1 = 0.017$ and $f_2 = 0.022$, and using an initial HONO concentration of 41 ppt. This model representation slightly over-predicts ozone formation during the initial stages of the experiment, with NO and NO$_2$ concentrations respectively over- and under-predicted throughout the entire simulation. These trends are indicative of an under-represented VOC source, although it is not possible in the current model system to cycle more NO into NO$_2$ without simultaneously increasing the O$_3$ concentration. A useful quantity in assessing the ability of a model to capture the oxidative capacity of a system is D(O$_3$ – NO), which is defined as (Carter and Lurmann, 1991; Pinho et al., 2005, 2007):

$$D(O_3 - NO) = [O_3]_t - [NO]_t - ([O_3]_0 - [NO]_0) \quad (3.20)$$

where $[O_3]_0$ and $[NO]_0$ are the initial concentrations of O$_3$ and NO, and $[O_3]_t$ and $[NO]_t$ their concentrations at a time ‘t’. D(O$_3$ – NO) is useful because it provides
3.4. CHAMBER CHARACTERISATION EXPERIMENTS

A measure of the ability of the mechanism to simulate O\textsubscript{3} forming processes, even when O\textsubscript{3} is suppressed by the presence of excess NO. As shown in Figure 3.26, the model provides a good fit for D(O\textsubscript{3} – NO) in the system. Considering inherent uncertainties in chamber simulations (Hynes et al., 2005; Carter et al., 2005), the 2016 chamber auxiliary mechanism is considered to be adequately described for the low-NO\textsubscript{x} scenario.

**CO + NO\textsubscript{x} Characterisation Experiment**

The most sensitive experiments to parameterise auxiliary radical sources are NO\textsubscript{x}–air irradiations of simple compounds, such as CO or alkanes, which are not radical initiators and only form radical initiating products to a limited extent (Carter and Lurmann, 1991; Carter et al., 2005). A CO–NO\textsubscript{x} irradiation was therefore performed with initial conditions described in Table 3.10. Background hydrocarbons were C\textsubscript{2}H\textsubscript{6} (1.3 ppb), C\textsubscript{2}H\textsubscript{4} (0.9 ppb), C\textsubscript{2}H\textsubscript{2} (0.5 ppb), C\textsubscript{3}H\textsubscript{8} (2.7 ppb), C\textsubscript{3}H\textsubscript{6} (0.9 ppb), i-C\textsubscript{4}H\textsubscript{10} (2.1 ppb), n-C\textsubscript{4}H\textsubscript{10} (4.4 ppb), 1-C\textsubscript{4}H\textsubscript{8} (0.1 ppb), i-C\textsubscript{5}H\textsubscript{12} (1.7 ppb), n-C\textsubscript{5}H\textsubscript{12} (0.4 ppb) and m-xylene (0.1 ppb), whilst starting CO and CH\textsubscript{4} concentrations were 63.5 ± 1.8 ppm and 2.20 ± 0.09 ppm respectively.

Ozone was found to be over-predicted by an order of magnitude using the optimised auxiliary mechanism from the blank chamber scenario. Setting this as the base case, ozone sensitivity to each of the auxiliary parameters listed in Table 3.8 were investigated, with results for the most influential parameters shown in Figure 3.27. Modelled O\textsubscript{3} was found to be highly sensitive to light induced OH production, whilst light induced NO\textsubscript{2} production was found to have little impact on O\textsubscript{3} production, thus supporting the simulation’s sensitivity to radical sources. This is why, in contrast to the blank chamber experiment, the hydrolysis of NO\textsubscript{2} was found to be important in the simulation, as it provides an alternative radical source. Given the relatively high NO\textsubscript{2} concentration, the model was much more sensitive to NO\textsubscript{2} hydrolysis than to light-induced NO\textsubscript{2} production. Varying the starting HONO concentration, and thus the initial radical concentration, also had a large impact on O\textsubscript{3} formation. Changing these auxiliary parameters was again found to have a larger impact on [O\textsubscript{3}]\textsubscript{max} than directly varying the ozone wall loss rate. The remaining

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RH</th>
<th>NMHCs</th>
<th>CO</th>
<th>NO</th>
<th>NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>(ppb)</td>
<td>(ppm)</td>
<td>(ppb)</td>
<td>(ppb)</td>
</tr>
<tr>
<td>CO–NO\textsubscript{x}</td>
<td>298</td>
<td>4.0</td>
<td>18.6\textsuperscript{a}</td>
<td>63.5</td>
<td>84</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Includes assumed background HCHO and CH\textsubscript{3}CHO concentrations.

Table 3.10: Starting conditions for the CO–NO\textsubscript{x} characterisation experiment.
auxiliary processes were all found to have a minor impact on $[O_3]_{max}$ in the system within their respective uncertainty limits. This includes the variation of HCHO, the hydrocarbon surrogate. Although variations were relatively small, being a factor of two of the starting HCHO concentration, the magnitudes are reflective of uncertainty in the total background VOC concentration. The large CO concentration therefore renders the model insensitive to background hydrocarbons (Hynes et al., 2005).

The best-fit model is shown in Figure 3.28. The model kept parameters the same as the base case, except radical production was reduced by lowering the rate of OH offgassing by setting $f_2 = 0.0075$, and reducing the rate of NO$_2$ hydrolysis to its lower limit of $5 \times 10^{-7}$ s$^{-1}$. Initial HONO concentration was set to 0.61 ppb. It was also necessary to incorporate a large O$_3$ sink into the model. In the mechanism downloaded from the MCM, the only removal process of CO is through its reaction with the hydroxyl radical.

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{HO}_2$$  \hspace{1cm} (3.21)

However, given its large concentration, it is possible that CO is reacting in a way that perturbs ozone concentration inside the reactor. Direct consumption of O$_3$ is possible:

$$\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$$  \hspace{1cm} (3.22)

although this reaction occurs at the decomposition rate of ozone at room temperature, which is too slow to affect chamber results (Harteck and Dondes, 1957; Arin and Warneck, 1972; Toby et al., 1984). Alternatively, CO can react with atomic
3.4. CHAMBER CHARACTERISATION EXPERIMENTS

(a) O₃, NO and NO₂

(b) D(O₃ – NO)

Figure 3.28: Time profiles from the CO–NOₓ characterisation experiment. Black lines show experimental measurements and open circles are modelled results.

Oxygen, thereby inhibiting ozone formation:

\[
\text{CO} + \text{O}^{(3P)} \xrightarrow{M} \text{CO}_2
\]  

(3.23)

This reaction was subsequently included in the model, with a rate coefficient of \(5.0 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}\) required to provide the optimal fit shown in Figure 3.28. This rate is 5 orders of magnitude larger than what has been reported in the literature (Donovan et al., 1971; Inn, 1973), making it unlikely that it is the dominant O₃ sink in the system. The current mechanism is thus incomplete. Nevertheless, guided by the CO–NOₓ study, it is tentatively suggested that the rate of hydrolysis of NO₂ in the auxiliary mechanism be reduced to its lower limit. This change will only impact those experiments which are sensitive to auxiliary radical formation, and so is not thought to affect modelling of the proposed α-phellandrene experiments.

Propene + NOₓ Characterisation Experiment

The propene–NOₓ system has been widely used as a reference system to evaluate the ability of constructed mechanisms to capture the intricacies of smog chambers, whilst modelling a VOC–NOₓ irradiation (Carter et al., 2005; Hynes et al., 2005). This is due to propene having a simple, well-characterised degradation mechanism; which in the MCMv3.3.1 consists of 61 species and 202 reactions (Jenkin et al., 1997; Saunders et al., 2003). Starting conditions for the propene–NOₓ irradiation experiment are listed in Table 3.11. NMHC background VOCs were; C₂H₆ (2.5 ppb), C₂H₄ (1.3 ppb), C₂H₂ (1.9 ppb), C₃H₈ (10.2 ppb), C₃H₆ (0.3 ppb), i-C₄H₁₀ (2.7 ppb), n-C₄H₁₀ (2.3 ppb), i-C₅H₁₂ (3.3 ppb) and n-C₅H₁₂ (0.8 ppb).

Both the canister sampling method and the PTR-TOF were used to monitor the concentration of propene. Analysis using the canister sampling method followed the
protocol discussed in Section 3.2.3, with propene detected using GC-FID at an RT of 18.51 minutes. PTR-TOF counts were converted into ppb using Equation 3.4, with a propene and $H_3O^+$ rate coefficient of $1.70 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Milligan et al., 2002). The parent peak at $m/z$ 43 was found to represent 90% of the propene signal when the drift tube is operated at $E/N = 112 \text{ Td}$, with fragments at $m/z$ 41 and $m/z$ 44 observed corresponding to loss of $H_2$ and the $^{13}C$ isotope respectively. The concentrations recorded using the two sampling methods are compared in Figure 3.29 with good agreement observed, having a strong correlation and slope close to unity. Whilst the GC-FID was calibrated directly with propene, it was only calibrated to 7.905 ppb, resulting in large extrapolations for the more concentrated samples. Meanwhile the PTR-TOF was not calibrated directly with propene, but rather relied on secondary calibration techniques for its accuracy. The agreement of the two techniques is therefore encouraging. The average of the two results measured immediately prior to irradiation is taken as the starting concentration of propene in the reactor, namely $1.53 \pm 0.2$ ppm. This provides an initial VOC/NO$_x$ ratio of 3.

Initiation reactions involving O($^{3P}$) have been shown to be important under chamber conditions (Pinho et al., 2005). Thus, on the recommendation of Hynes et al. (2005), the O($^{3P}$) initiation of propene was incorporated into the MCM propene mechanism. The following scheme from Atkinson (1997) is added, as expressed using MCM codenames:

$$C_3H_6 + O(3P) \xrightarrow{0.3k} C_3H_6EPOX \quad (3.24)$$

$$C_3H_6 + O(3P) \xrightarrow{0.3k} C_2H_5CHO \quad (3.25)$$

$$C_3H_6 + O(3P) \xrightarrow{0.2k} CH_3O_2 + HCOCH_2O_2 \quad (3.26)$$

$$C_3H_6 + O(3P) \xrightarrow{0.2k} C_2H_5O_2 + HO_2 + CO \quad (3.27)$$

$$C_3H_6EPOX + OH \longrightarrow CH_3COCH_2O_2 \quad (3.28)$$

As per MCM convention, the reaction with molecular oxygen is implicit. The rate coefficient for the reaction of propene and O($^{3P}$) is taken to be $4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997), with relevant branching ratios shown above the arrows in the

---

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RH</th>
<th>NMHCs</th>
<th>C$_3$H$_6$</th>
<th>NO</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>(ppb)</td>
<td>(ppm)</td>
<td>(ppb)</td>
<td>(ppb)</td>
</tr>
<tr>
<td>propene–NO$_x$</td>
<td>297.9</td>
<td>5.3</td>
<td>28.8$^a$</td>
<td>1.53</td>
<td>391</td>
</tr>
</tbody>
</table>

$^a$Includes assumed background HCHO and CH$_3$CHO concentrations.

Table 3.11: Starting conditions for the propene–NO$_x$ characterisation experiment.
reaction scheme. The only species not in the MCM is propylene oxide, which is given the codename C3H6EPOX. C3H6EPOX is assumed to react solely with OH radicals with a rate coefficient of $4.95 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wallington et al., 1988).

The starting model combines the updated MCM reaction mechanism with the auxiliary mechanism proposed from simulating the blank chamber experiment, with the rate of NO$_2$ hydrolysis reduced to its lower limit as recommended by the CO-NO$_x$ simulation. Due to the large NO$_x$ injection, initial HONO in the reactor is set to 1 ppb in the base case. However, sensitivity testing shows that varying the auxiliary parameters to their maximum and minimum values has less than a ±0.5% impact on maximum ozone production. The inclusion of the O(\(^3\)P) initiation reaction scheme was found to make a similarly minor difference, reducing the maximum amount of ozone formed by 0.06%.

Model performance for key species is shown in Figure 3.30. The model was found to accurately reproduce propene and NO consumption. O$_3$ was modelled well over the first 100 minutes, however the model under-predicts its formation at longer reaction times. Peak production of NO$_2$ is accurately modelled, however afterwards the model predicts rapid and complete consumption of NO$_2$, whilst experimentally a steady reduction in NO$_2$ concentration is observed. Simulated consumption of NO$_x$ explains why ozone is under-predicted in the model, and suggests some large nitrogen sink/s are overly represented. The most important of these was found to
be the production of nitric acid through the reaction of the nitrate radical with organics (Reaction 1.29). PAN formation was also found to be an important nitrogen sink. The NO₂ time profile could accurately be reproduced by blocking the major nitrogen sinks in the model, however this was at the expense of O₃ which was subsequently over-predicted by a factor of two. Nonetheless in the base case, model simulation of D(O₃ – NO) is 15% lower compared to experimental measurements at the end of the experiment, which is within the ±25% uncertainty reported for chemical mechanism evaluation in smog chambers (Stockwell et al., 1990; Carter et al., 2005). The auxiliary mechanism used in modelling propene will thus be used in simulating 2016 α-phellandrene photooxidation experiments. Given the simplicity of the propene system, the findings of this calibration experiment places constraints on the accuracy that can reasonably be expected to be achieved when modelling α-phellandrene photooxidation experiments in 2016. Additional differences between modelled and measured concentrations can then be attributed to shortcomings in the constructed degradation mechanism. Results from a similar propene–NOₓ calibration experiment conducted in 2012 are discussed in Appendix C.

Two propene photooxidation products were detected using GC-FID at RTs of 24.9 and 25.2 minutes. The peak area at 24.9 minutes was around 10 times larger than that at 25.2 minutes. Given the similar RTs, the peaks are assigned to the two isomeric products hydroxyacetone (ACETOL) and 2-hydroxypropanal (CH₃CHOHCHO). MCM codenames are given in brackets. Both species are predicted to be major products in the MCM propene degradation mechanism, with ACETOL concentrations predicted to be around 10 times larger than that of CH₃CHOHCHO. One major product was detected using the GC-MSD at an RT of 7.38
3.4. CHAMBER CHARACTERISATION EXPERIMENTS

minutes. The produced spectra did not match any of the compounds in the NIST spectral database, although was dominated by a peak at \( m/z \) 43, suggesting the presence of the \( \text{CH}_3\text{CHO} \) functional group.

Whilst detection and identification of propene photooxidation products is not the focus of this chamber characterisation experiment, the inability of the described canister-based sampling method to detect the large number of products predicted by the MCM is concerning prior to sampling and analysis of the relatively unstudied \( \alpha \)-phellandrene system, especially given the large concentration of propene used. There are several known issues with the canister sampling method, with canisters known to have stability issues with some polar and semi-volatile organic compounds (Ochiai et al., 2002; Kumar and Viden, 2012). Firstly, reactive species are not removed from the sample prior to capture and storage, such that reaction of VOCs containing a vinyl group with \( \text{O}_3 \) and \( \text{NO}_2 \) may be problematic (Wang and Austin, 2006). Potassium iodide has previously been used at the GIG-CAS to remove \( \text{O}_3 \) prior to canister capture and storage (Helmig, 1997; Wang and Austin, 2006), by placing a KI pellet in the sample line linking the chamber to the canister. Nonetheless, the inclusion of KI was found to have little impact on results. Instead, a quick capture to analysis turnaround was used to mitigate the impact of reactive species loss inside the canister. Agreement of PTR-TOF and canister propene measurements supports the notion that reactive species have a negligible impact. The gas-phase reaction and subsequent transformation of product species however cannot be ruled out (e.g. polymerisation, condensation into SOA) (Batterman et al., 1998). Furthermore, reactions are activated by cryogenic trapping, in which reactive gases are physically concentrated together with organic trace gases (Helmig, 1997). Given that the main constituents of air are not trapped, concentrations may increase by several orders of magnitude, amplifying reaction rates when the concentrate is re-heated for sample transfer. However, overall, the canisters failed to detect the volume of carbon that should be present in the sample, suggesting a more general species loss or removal process. Secondly, VOCs can heterogeneously adsorb onto the canister walls. This phenomenon is especially problematic in dry samples, such as the ones taken in this study, as limited water is present to compete with VOCs for somewhat active surfaces on the canister walls. For this reason, polar degradation products are expected to exhibit variable, and somewhat poor stability with the polished stainless-steel walls (Batterman et al., 1998). For example, Ochiai et al. (2002) found a \( \text{RH} > 8\% \) was required in canisters to ensure good recovery of non-polar VOCs, and an \( \text{RH} > 27\% \) for polar VOCs (ketones, esters, ethers, nitriles). Nonetheless, the authors reported poor recovery under all conditions for polar VOCs having a vapour pressure lower than that of water. Additional loss processes include heterogeneous reactions on the canister walls and secondary ad-
CHAPTER 3. EXPERIMENTAL

sorption, whereby compounds adsorbed on the wall surface act as new active sites and adsorb other compounds in the canister. Losses may additionally be occurring in the FEP sample line connecting the canister to the reactor. Recent studies have shown that Teflon walls are not inert, with functionalised organic species experiencing significant losses through gas-wall partitioning (Matsunaga and Ziemann, 2010; Zhang et al., 2014b; La et al., 2016). Measures were taken to reduce the impact of the sample line, with the tubing passivated by drawing chamber air through the line for at least a minute prior to sampling. Sample times were also kept short (< 30 seconds). Lastly, soluble compounds can dissolve into condensed water inside the canister. Due to the low humidities used in this experiment, and that canisters were not pressurised, condensation of water inside the canister is expected to be minor. However, if water is not effectively removed during analysis, then alcohols and other polar compounds will elute out of the chromatographic column with the moisture (Kumar and Viden, 2012). For the most part however, water is expected to be removed through the sample pre-concentration method described in Section 3.2.3.

A compounding factor is the analysis set-up, which is optimised for measuring primary VOCs in ambient samples; a major research focus of the GIG-CAS group. The columns have all been selected with the primary aim of separating hydrocarbons. A PLOT-Q (Porous Layer Open Tubular) column was used prior to FID detection, which is specifically designed for the separation of very volatile gases such as the light hydrocarbons found in the calibration mixture. In the propene–NOx calibration experiment it was useful for monitoring propene concentration. However, during α-phellandrene experiments, the column restricts the use of the FID to monitoring small hydrocarbons in the background gas. A HP-1 column was used to separate the sample prior to detection by MSD in the characterisation experiment, whilst in 2015 a DB-1 column is used. The two columns are equivalent, both being constructed from 100% dimethylpolysiloxane, and are regarded as having excellent general purpose applicability. The stationary phase of the columns are non-polar. With an inert carrier gas, the required separation of small polar products expected from the photooxidation of propene will not be achieved. Instead, separation will almost entirely be based on product boiling points. A more gradual temperature increase, or a more polar column such as the DB-35ms, DB-23, DB200, VF-23ms, VF-WAXms and CP-Sil 13 CB columns made by Agilent, is thought required for enhanced product resolution.

Nonetheless, over the last 20 years, the canister based sampling method has been superseded by online detection methods for monitoring VOC concentrations in smog chambers. The PTR-TOF detected a suite of product ions, which are plotted in Figure 3.31. Quantitative analysis however is restricted by a lack of standards,
with fragmentation expected to have a large impact on results (Španěl et al., 1997; Smith and Španěl, 2005; Blake et al., 2006; Duncianu et al., 2017). Similarly, a lack of reliable H$_3$O$^+$ rate coefficients for a number of species constrains the accuracy of analysis. Acetaldehyde concentrations are determined by using results from the sensitivity analysis, with fragmentation patterns of formic and acetic acid known from separate testing (Section 3.2.2). Rate coefficients of formaldehyde, formic acid and acetic acid with H$_3$O$^+$ are taken from theoretical calculations (Cappellin et al., 2012), whilst for the remaining products a generic rate coefficient of $2 \times 10^{-9}$ cm$^3$ s$^{-1}$ was used for conversion of counts into ppb (Brilli et al., 2014).

PTR-TOF measurements are compared to model output in Figure 3.31, with significant differences observed. Of the 7 products simulated, only acetic acid and hydroxyacetone/hydroxypropanal (m/z 75) showed acceptable agreement, having measured and modelled time profiles within ±25% of one another. Of the remaining products, formaldehyde was over-predicted by 44%, acetaldehyde was under-predicted by 36%, formic acid was under-predicted by 63%, propylene oxide/propionaldehyde (both contribute to the signal at m/z 59) were under-predicted by 70% and methyl glyoxal was under-predicted by over an order of magnitude.

Whilst propene’s MCM degradation mechanism is not infallible and would somewhat contribute to model-measurement disagreement, the simple nature of the mechanism, by virtue of propene’s small size, limits errors that are likely to be introduced either through simplifications made during construction or gaps in literature knowledge. Indeed, some of the aforementioned photooxidation products of propene have been simulated in the literature with success (Carter et al., 1979; Hynes et al., 2005; Pinho et al., 2006), although no in-depth modelling study extensively simulating propene photooxidation products can be found in the literature. Instead, the largest source of disagreement is believed to be the PTR-TOF measurements. Rate
coefficients of simple oxygenates reported in the literature vary from $1.35 \times 10^{-9}$ cm$^3$ s$^{-1}$ for glyoxal to $3.56 \times 10^{-9}$ cm$^3$ s$^{-1}$ for 1,3-propanediol (Cappellin et al., 2012), thus use of the generic rate coefficient may result in erroneous conversion into ppb concentrations for some products. Furthermore, despite efforts to reduce fragmentation and water cluster effects in the PTR-TOF, propene was observed to fragment at 10%, with higher rates of fragmentation expected for functionalised products. It is likely no coincidence that the model under-predicts PTR-TOF measurements for the majority of the detected species, with heavier, more functionalised products containing ester, peracid, hydroperoxide, nitrate and/or PAN functionality expected to somewhat fragment into simpler species such as acetaldehyde upon protonation (Španěl et al., 1997; Smith and Španěl, 2005; Blake et al., 2006; Duncianu et al., 2017).

Despite a wide variety of products being detected, analysis of the simple propene system suggests that products formed in the larger and more complex $\alpha$-phellandrene system are unlikely to be quantified accurately in the PTR-TOF without standards. It can therefore be concluded that comparison of PTR-TOF measurements with model predictions is not a reliable measure of mechanism performance, using the current analysis methodology.

3.5 $\alpha$-phellandrene Ozonolysis

Due to the importance of ozonolysis reactions in the consumption of unsaturated VOCs in the atmosphere, it is common in the literature for chamber studies to focus exclusively on investigating the reaction of a precursor unsaturated VOC with ozone (Calvert et al., 2000; Johnson and Marston, 2008). Ozonolysis studies are conducted in the dark to prevent photochemistry from occurring, and usually feature the addition of an OH radical scavenger, such as CO, cyclohexane or butanol, to ensure that reaction with ozone is the only consumption pathway. Because of this, ozonolysis systems are simpler to study and interpret. Nevertheless, the mechanism of the reaction of ozone with even simple unsaturated hydrocarbons is far from completely understood, making investigation of the ozonolysis of any unsaturated VOC an important part of its characterisation (Johnson and Marston, 2008). Indeed, ozonolysis reactions of all major monoterpenes have been studied in depth, including $\alpha$-pinene, $\beta$-pinene, limonene and $\Delta^3$-carene (Lee et al., 2006a; Herrmann et al., 2010; Camredon et al., 2010; Berndt et al., 2003; Griffin et al., 1999; Pathak et al., 2007b; Jonsson et al., 2008; Shilling et al., 2008; Saathoff et al., 2009; Draper et al., 2015; Zhao et al., 2015a), with experiments showing monoterpane ozonolysis to yield non-negligible amounts of OH radicals and SOA under a wide range of conditions, with important atmospheric implications. Furthermore, generated SOA
has been assessed using a range of online and offline techniques to parameterise the chemical composition and physical properties of the organic aerosol (Ma et al., 2007; Walser et al., 2008; Bateman et al., 2009; Shilling et al., 2009; Chhabra et al., 2010; Kristensen et al., 2014; Witkowski and Gierczak, 2017). Sophisticated methods have been used to identify major SOA constituents, with a variety of unique polyfunctional species having since been attributed to different monoterpenes.

Following the computational study characterising the PES for the reaction of ozone with α-phellandrene, the first set of chamber experiments focusses on the reaction of ozone with α-phellandrene. Ozonolysis experiments were conducted at the GIG-CAS chamber during campaigns in 2013, 2014 and 2015. The majority of experiments had cyclohexane added in large concentrations as an OH radical scavenger. The canister based methodology could not be used during these experiments, as the high concentration of cyclohexane posed a risk of blocking cryogen traps used to pre-concentrate VOCs, and would ultimately saturate the detector, suppressing the response of other eluted compounds. All other analytical techniques described in Section 3.2 were used.

The discussion of the ozonolysis of α-phellandrene is separated into two parts, published as separate journal articles in Atmospheric Chemistry and Physics (ACP) and Atmospheric Chemistry and Physics Discussions (ACPD, under review). The first part, published in ACP, focusses on the chamber experiments, detailing data gathered from the online instruments at the GIG-CAS chamber and discussing gas-phase chemistry and products, SOA formation and bulk SOA properties. The second part, submitted to ACPD, focusses on analysis of the collected filter samples, identifying the major molecular constituents of the SOA and discussing relevant gas-phase precursors and formation routes.

The two articles are now presented in their published forms.
3.5.1 Article Presentation: Part 1

**Title**
Ozonolysis of α-phellandrene – Part 1: Gas- and particle-phase characterisation

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**Candidate Contribution**
I have contributed at an overall level of about 85% to the published work. Contributions were made to all aspects of the study, including research design, conducting necessary experiments, analysing output and manuscript preparation and submission.

S. M. Saunders
(On behalf of all other co-authors)
Ozonolysis of α-phellandrene – Part 1: Gas- and particle-phase characterisation

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Abstract. The ozonolysis of α-phellandrene, a highly reactive conjugated monoterpene largely emitted by Eucalypt species, is characterised in detail for the first time using a smog chamber at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Gas-phase species were monitored by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF), with yields from a large number of products obtained, including formaldehyde (5–9 %), acetaldehyde (0.2–8 %), glyoxal (6–23 %), methyl glyoxal (2–9 %), formic acid (22–37 %) and acetic acid (9–22 %). Higher m/z second-generation oxidation products were also observed, with products tentatively identified according to a constructed degradation mechanism. OH yields from α-phellandrene and its first-generation products were found to be 35 ± 12 and 15 ± 7 %, respectively, indicative of prominent hydroperoxide channels. An average first-generation rate coefficient was determined as 1.0 ± 0.7 × 10^{-16} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} at 298 \text{ K}, showing ozonolysis as a dominant loss process for both α-phellandrene and its first-generation products in the atmosphere. Endocyclic conjugation in α-phellandrene was also found to be conducive to the formation of highly condensible products with a large fraction of the carbon mass partitioning into the aerosol phase, which was monitored with a scanning mobility particle sizer (SMPS) and a high-resolution time-of-flight aerosol mass spectrometer (AMS). Nucleation was observed almost instantaneously upon ozonolysis, indicating the rapid formation of extremely low-volatility compounds. Particle nucleation was found to be suppressed by the addition of either NO2 or a Criegee scavenger, with it being proposed that stabilised Criegee intermediates are important for new particle formation in the system. Aerosol yields ranged from 25 to 174 % depending on mass loadings, with both first- and second-generation products identified as large contributors to the aerosol mass. In short, with a high chemical reactivity and aerosol-forming propensity, α-phellandrene is expected to have an immediate impact on the local environment to which it is emitted, with ozonolysis likely to be an important contributor to the significant blue haze and frequent nocturnal nucleation events observed over Eucalypt forests.

1 Introduction

Biogenic sources dominate the global emission budget of volatile organic compounds into the atmosphere, with monoterpenes accounting for a significant fraction of non-methane hydrocarbons emitted (Guenther et al., 1995; Schurges et al., 2009; Guenther et al., 2012; Lathière et al., 2006; Sindelarova et al., 2014). Considering source strength, estimated to be 30–127 Tg C year−1, along with high chemi-
Ozonolysis is generally agreed to occur through a concerted cycloaddition of ozone to the olefin bond, forming a 1,2,3-trioxolane intermediate species referred to as a primary ozonide (POZ) (Calvert et al., 2000; Johnson and Marston, 2008). Addition of ozone is highly exothermic with excess energy retained in the POZ structure, resulting in rapid decomposition through homolytic cleavage of the C–C and one of the O–O bonds, which forms, in the case of asymmetrically substituted alkenes, a pair of products containing a carbonyl and a reactive Criegee intermediate (CI). Sufficient vibrational and rotational excitation exists in the CI to permit further unimolecular decomposition which typically occurs through one of two channels; firstly, excited CIs can cyclise to a dioxirane, which then decomposes to a carboxylic acid, ester or lactone, depending on neighbouring substituents, in what is known as the ester or “hot” acid channel, or secondly, when available, excited CIs can isomerise via a 1,5-hydrogen shift to form a vinyl hydroperoxide, which subsequently decomposes into a vinoxy radical and a hydroxyl radical in what is known as the hydroperoxide channel. Alternatively, excited CIs can be collisionally stabilised such that bimolecular reactions with trace species (e.g. H₂O, NO₂, CO, aldehydes, acids) become important (Johnson and Marston, 2008). The relative prevalence of these competing channels is strongly linked to the structure and conformation of the CI products, with the various mechanistic pathways summarised in Fig. 1.

When considered as a whole, research shows significant variability in gas-phase ozonolysis products and SOA yields between different monoterpenes due to their structural differences, highlighting the unique impact different monoterpenes can have on regional atmospheric chemistry. It is therefore important that individual monoterpene variability be accounted for in developing accurate gas- and particle-phase models. Nonetheless, current literature has predominantly focused on a small number of the more commonly emitted monoterpenes (e.g. α-pinene, β-pinene, limonene). One monoterpene for which relatively little is known is α-phellandrene (structure provided in Fig. 1). One of the most reactive monoterpenes, α-phellandrene has been identified as a major constituent of extracts (Li et al., 1995; Brophy and Southwell, 2002; Pavlova et al., 2015; Maghsoudlou et al., 2015) and in emissions (He et al., 2000; Maleknia et al., 2009) from various Eucalypt species, the world’s most widely planted hardwood tree (Myburg et al., 2014). During day-to-day activities and processes, Eucalypts, such as Eucalyptus microtheca, Eucalyptus viminalis and Eucalyptus dives, emit α-phellandrene into the atmosphere, with α-phellandrene likely contributing to the intense and frequent particle nucleation events observed over Eucalypt forests – a phenomenon already believed to be caused by monoterpene oxidation (Suni et al., 2008; Lee et al., 2008; Ortega et al., 2009, 2012). In the indoor environment, α-phellandrene can be found as an additive to household cleaning products, detergents and air fresheners (e.g. Eucalypt-themed products), with the European EPHECT project reporting α-phellandrene at a concentration of 16.7 μg m⁻³ in a study of a passive air freshener in a 1 m³ room after 5 h (Stranger, 2013). Maisey et al. (2013) reported similar maximum concentrations of α-phellandrene in Australian dwellings.

The rate constant of α-phellandrene with ozone has been measured in a number of studies with results spanning an order of magnitude (Grimsrud et al., 1975; Atkinson et al., 1990; Shu and Atkinson, 1994), with a rate constant of 3.0 × 10⁻¹⁵ (± 35 %) cm³ molecule⁻¹ s⁻¹ favoured (Calvert et al., 2000). High chemical reactivity likely makes ozonolysis a dominant loss process for α-phellandrene in the atmosphere; however, experimental information regarding reaction products is limited to OH radical yields, measured by Herrmann et al. (2010) to be 26–31 and 8–11 % for the ozonolysis of the two double bonds, and acetone yields, which were reported by Reissell et al. (1999) to be minor (< 2 %). Recently, the reaction mechanism was investigated theoretically for the first time by Mackenzie-Rae et al. (2016), who mapped the potential energy surface to first-generation products. A basic overview of the reaction pathways is provided in Fig. 1, with a comprehensive discussion of the reaction mechanism of α-phellandrene with ozone based on findings of Mackenzie-Rae et al. (2016) pertinent to this study provided in the Supplement (Sect. S1).
This study aims to experimentally characterise the reaction of α-phellandrene with ozone in detail for the first time by exploring and characterising both the gaseous and particle phases, with the impact of Criegee scavengers and NO\textsubscript{2} on the system addressed. In doing so, the impact of a highly reactive and potentially important monoterpene will be parameterised.

2 Materials and method

2.1 Experimental set-up and procedure

A total of 11 dark α-phellandrene ozonolysis experiments were conducted using the indoor smog chamber facility at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). A complete description of the facility and chamber setup is given in Wang et al. (2014). Briefly, the GIG-CAS smog chamber consists of a 30 m\textsuperscript{3} fluorinated ethylene propylene (FEP) reactor housed inside a temperature-controlled room. The reactor was flushed with purified dry air for at least 48 h prior to each experiment, until no residual hydrocarbons, O\textsubscript{3}, NO\textsubscript{2}, or particles were detected, with the impact of off-gassing of radicals from the reactor walls during experiments under the dark, dry conditions considered negligible (Wang et al., 2014). Two Teflon-coated fans located inside the reactor ensure rapid homogenisation of introduced species. Liquid reactants were vapourised via injection into a heating system similar to that of gas chromatography, before being carried by nitrogen gas through FEP Teflon lines into the reactor. Ozone was generated using a commercial ozone generator (VMUS-4, Azco Industries Ltd.), with pure oxygen feed gas. Initial mixing ratios of the reactants varied between 10 and 175 ppb for α-phellandrene (Aldrich Chemical Company, Inc., USA) and between 56 and 500 ppb for O\textsubscript{3}. α-Phellandrene was injected prior to admission of O\textsubscript{3} into the chamber, with O\textsubscript{3} added through two separate additions in experiments 7 and 10 to facilitate the identification of detected species as either first- or second-generation products. Anhydrous cyclohexane (Sigma-Aldrich, 99.5 %) was added in sufficient quantity in all but two experiments to scavenge > 95 % of OH radicals (Aschmann et al., 1996; Herrmann et al., 2010), with the remaining experiments used to assess the impact of cyclohexane’s inclusion. Formic acid (J&K Scientific Ltd., 98 %) was added to experiments 6 and 7 as a stabilised Criegee intermediate (sCI) scavenger to better understand the impact of sCIs on gas-phase species distribution and, importantly, particle-phase formation and growth, for which it has been identified as a significant precursor (Bonn et al., 2002; Bateman et al., 2009; Sakamoto et al., 2013; Wang et al., 2016). Prior to O\textsubscript{3} addition in experiment 11, 385 ppb of NO\textsubscript{2} was added through a septum installed in one of the injection ports using a gas-tight syringe, with the inclusion providing an alternative representation of tropospheric nocturnal chemistry in a polluted environment. All experiments had 2.5 µL of acetonitrile injected as a dilution tracer, with the top frame of the reactor periodically lowered to maintain a positive pressure differential inside the reactor. Experimental run times ranged from 205 to 305 min, with a final reactor volume typically between 6 and 8 m\textsuperscript{3}. The starting conditions for each experiment are listed in Table 1. The high reactivity of α-phellandrene towards ozone results in reaction half lives that
## 2.2 Characterisation of gas and particle phases

Volatile organic compounds (VOCs) were measured online with a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF 2000, Ionicon Analytik GmbH, Austria) (Jordan et al., 2009; Graus et al., 2010), using H$_3$O$^+$ reagent ions. For data collected in the first seven experiments in Table 1, the PTR-TOF drift tube was operated at 2.2 mbar and 60°C, with a drift tube field of 600 V cm$^{-1}$ ($E/N = 136$ Td). Significant fragmentation was observed under this regime, with a drift tube voltage of 484 V cm$^{-1}$ ($E/N = 112$ Td) found to be optimal (Supplement Sect. S3). The refined operating conditions were then used for experiments 8–11. PTR-TOF spectra were collected at a time resolution of 2 s. Data were processed using the PTR-TOF data analyser (Müller et al., 2013), with 30 spectra averaged to improve counts of trace species. A generic H$_3$O$^+$ rate constant of $2 \times 10^{-9}$ cm$^3$ s$^{-1}$ was used for conversion into ppb, except for those species where experimental or theoretical data exist (Cappellin et al., 2012; Tani, 2013).

Gas-phase O$_3$ and NO$_x$ were measured online using dedicated monitors (EC9810 and 9841T, Ecotech, Australia), which were calibrated regularly using a Thermo Scientific model 146i multi-gas calibrator unit. In all experiments, excluding experiment 11 where it is added, NO$_x$ concentrations were negligible ($< 1$ ppb). The O$_3$ analyser experienced significant interference (had a false bias) from $\alpha$-phellandrene, which was corrected for using PTR-TOF measurements.

Particle number size distributions were measured online with a scanning mobility particle sizer (SMPs; TSI Inc., USA) (Wang and Flagan, 1990), consisting of an electrostatic classifier (TSI 3080) fitted with a TSI 3081 differential mobility analyser (DMA) and condensation particle counter (CPC, TSI 3775). Sheath and aerosol flow rates were 3.0 and 0.3 L min$^{-1}$, respectively, with voltage inside the DMA varied exponentially from $-10$ to $-9950$ V every 240 s to provide a mobility spectrum over particle diameters 14–750 nm. Higher moment size distributions were calculated by assuming spherical particles (Wiedensohler et al., 2012).

A high-resolution time-of-flight aerosol mass spectrometer (AMS; Aerodyne Research Incorporated, USA) was used to measure particle chemical composition in real time (Jayne et al., 2000; DeCarlo et al., 2006). The AMS was operated in the high-sensitivity V mode and high-resolution W mode, switching between modes every 2 min. AMS data were analysed in Igor Pro 6.2 (Wavemetrics) using the ToF-AMS data analysis toolkits Peak Integration by Key Analysis (PIKA) and Sequential Igor Data Retrieval (SQUIRREL). Updates were made to the fragmentation table following a similar method to Chen et al. (2011), with a detailed discussion provided in the Supplement (Sect. S5). Conductive silicon tubes were used as sampling lines for the SMPS and AMS to reduce electrostatic losses of particles, whilst all other instruments had FEP Teflon feed lines. Losses of VOCs and particles in the transfer lines are estimated to be less than 5 % (Liu et al., 2015).

---

Table 1. Starting conditions for $\alpha$-phellandrene chamber ozonolysis experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature (K)</th>
<th>Relative humidity (%)</th>
<th>$\alpha$-phellandrene (ppb)</th>
<th>O$_3$ (ppb)</th>
<th>Additives$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>297.1 ± 0.4</td>
<td>2.5 ± 0.6</td>
<td>19 ± 7</td>
<td>&gt; 259</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>2</td>
<td>297.5 ± 0.5</td>
<td>2.1 ± 0.7</td>
<td>10 ± 4</td>
<td>&gt; 86</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>3</td>
<td>297.2 ± 0.2</td>
<td>2.3 ± 0.6</td>
<td>21 ± 8</td>
<td>&gt; 83</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>4</td>
<td>297.4 ± 0.5</td>
<td>2.2 ± 0.9</td>
<td>32 ± 13</td>
<td>&gt; 193</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>5</td>
<td>297.6 ± 0.7</td>
<td>1.8 ± 0.4</td>
<td>29 ± 11</td>
<td>&gt; 114</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>6</td>
<td>298.0 ± 0.3</td>
<td>1.6 ± 0.1</td>
<td>16 ± 6</td>
<td>&gt; 470</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>7</td>
<td>298.0 ± 0.1</td>
<td>1.9 ± 0.2</td>
<td>19 ± 8</td>
<td>&gt; 499</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>8</td>
<td>298.7 ± 0.6</td>
<td>5.2 ± 0.2</td>
<td>61 ± 24</td>
<td>&gt; 56</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>9</td>
<td>298.5 ± 0.4</td>
<td>4.9 ± 0.4</td>
<td>67 ± 27</td>
<td>&gt; 101</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>10</td>
<td>298.2 ± 0.5</td>
<td>4.8 ± 0.3</td>
<td>175 ± 69</td>
<td>&gt; 174</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>11</td>
<td>298.1 ± 0.4</td>
<td>4.5 ± 0.2</td>
<td>88 ± 35</td>
<td>&gt; 132</td>
<td>NO$_2^c$</td>
</tr>
</tbody>
</table>

$^a$ All experiments had acetonitrile (2.5 µL) added as a dilution tracer.

$^b$ 800 ± 80 ppb added prior to starting experiment.

$^c$ 385 ± 5 ppb added prior to starting experiment.
3 Results and discussion

3.1 Gas-phase analysis

3.1.1 Peak identification and yields

Significant fragmentation was observed in the PTR-TOF upon injection of starting materials into a clean reactor. \( \alpha \)-Phellandrene was detected at \( m/z \) 137 at 32–34% depending on drift tube conditions, consistent with fragmentation observed in the PTR-MS studies of Misztal et al. (2012) and Tani (2013) (Supplement Sect. S2). Acetonitrile was found exclusively at \( m/z \) 42 and remained constant throughout all experiments, indicating that dilution effects in the reactor are negligible. Despite having a lower proton affinity than water, cyclohexane was detected at \( m/z \) 85, although overall sensitivity is greatly reduced. The detection of cyclohexane is likely the result of termolecular reactions in the PTR-TOF (Smith and Španěl, 2005). Meanwhile, in a separate characterisation experiment, formic acid was found at \( m/z \) 47, with minor fragments at \( m/z \) 48, 49 and 65 (< 2%).

Observed interferences are expected to impact detection of \( \alpha \)-phellandrene’s degradation products, biasing signals to lower \( m/z \). Aldehyde, ketone, alcohol, ester and acid-bearing compounds are known to dehydrate following protonation to yield a MH\(^+\) (\(-\mathrm{H}_2\mathrm{O}\)) daughter ion (Smith and Španěl, 2005; Blake et al., 2006). Furthermore, multifunctional carbonyl compounds can eject a second water molecule from nascent MH\(^+\) ions yielding a MH\(^+\) (\(-\mathrm{H}_2\mathrm{O}_2\)) daughter ion, whilst complex acid-bearing molecules have been observed to fragment via the loss of formic acid to produce MH\(^+\) (\(-\mathrm{HCOOH}\)) ions and esters through ejection of –OR groups to yield MH\(^+\) (–ROH) (Španěl et al., 1997; Španěl and Smith, 1998). Uncertainty arising from fragmentation limits quantitative analysis for the majority of species, with standards neither available nor prepared. Nevertheless, Table 2 lists peaks routinely detected by the PTR-TOF across the 11 experiments. Note that \( m/z \) includes the addition of H\(^+\).

Figure 2 shows time profiles of major species detected by the PTR-TOF during the ozonolysis of \( \alpha \)-phellandrene in experiment 5. The peak of \( \alpha \)-phellandrene observed upon its addition was the result of the reactor fans being switched on immediately prior to the introduction of acetonitrile in this experiment.

![Figure 2](image_url)
Table 2. Identified ions detected by the PTR-TOF. Refer to Fig. 3 for product structures.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Formula</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary signals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>H$_3$O$^{18+}$</td>
<td>Hydronium ion</td>
</tr>
<tr>
<td>37</td>
<td>(H$_2$O)$_2$H$^+$</td>
<td>Water cluster</td>
</tr>
<tr>
<td>55</td>
<td>(H$_2$O)$_3$H$^+$</td>
<td>Water cluster</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>CH$_3$CNH$^+$</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28, 39, 40, 41, 42, 43, 44, 45, 54, 55, 56, 57, 58, 67, 68, 69, 70, 82, 83, 84, 85, 86, 81, 99, 100, 116, 117, 83, 101</td>
<td>C$<em>6$H$</em>{12}$H$^+$</td>
<td>Cyclohexane and fragments</td>
</tr>
<tr>
<td>Formic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47, 48, 49, 65</td>
<td>CH$_2$O$_2$H$^+$</td>
<td>Formic acid</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43, 61, 62, 79</td>
<td>C$_2$H$_4$O$_2$H$^+$</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>$\alpha$-phellandrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43, 67, 69, 79, 81, 82, 83, 91, 92, 93, 94, 95, 109, 119, 121, 135, 136, 137, 138, 139, 153</td>
<td>C$<em>{10}$H$</em>{16}$H$^+$</td>
<td>See the Supplement (Sect. S2)</td>
</tr>
<tr>
<td>Ozonolysis products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>CH$_3$OH$^+$</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>45</td>
<td>C$_2$H$_4$OH$^+$</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>47</td>
<td>CH$_2$O$_2$H$^+$</td>
<td>Formic acid</td>
</tr>
<tr>
<td>59</td>
<td>C$_2$H$_2$O$_2$H$^+$</td>
<td>Glyoxal</td>
</tr>
<tr>
<td>61</td>
<td>C$_2$H$_4$O$_2$H$^+$</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>73</td>
<td>C$_3$H$_4$O$_2$H$^+$</td>
<td>Methyl glyoxal</td>
</tr>
<tr>
<td>87</td>
<td>C$_3$H$_2$O$_2$H$^+$</td>
<td>Identified oxidation products$^b$</td>
</tr>
<tr>
<td>115, 97</td>
<td>C$<em>6$H$</em>{10}$O$_2$H$^+$</td>
<td></td>
</tr>
<tr>
<td>129, 111</td>
<td>C$<em>7$H$</em>{12}$O$_2$H$^+$</td>
<td></td>
</tr>
<tr>
<td>143</td>
<td>C$<em>7$H$</em>{16}$O$_3$H$^+$</td>
<td></td>
</tr>
<tr>
<td>85, 99, 109, 125, 139, 155</td>
<td>–</td>
<td>Unidentified oxidation products</td>
</tr>
<tr>
<td>167, 169, 185</td>
<td>–</td>
<td>Gas-phase dimers</td>
</tr>
</tbody>
</table>

$^a$ Winterhalter et al. (2009).
$^b$ Refer to Fig. 3.
$^c$ Detected in experiments 9 and 11.

ing that the observed m/z 169 is not simply a direct product ion of $\alpha$-phellandrene. Other major first-generation product ions expected include m/z 185, which corresponds to a range of isomeric species formed through either excited or thermalised CI rearrangement reactions, whereby three oxygen atoms are added for no loss of carbon or hydrogen (e.g. acids, esters, epoxides, secondary ozonides), and m/z 155, which can be formed through radical transfer and subsequent CHO loss in the hydroperoxide channel (Mackenzie-Rae et al., 2016). Both these ions were detected in the PTR-TOF but again had concentrations which increased throughout the experiments, suggesting that they have large contributions from saturated species. This continual increase remained true in experiments which added a large secondary dose of ozone after commencement of the reaction (Fig. S4.1), confirming the discussed ions as saturated.

A similar phenomenon, whereby a distinct lack of first-generation products was observed by a PTR-MS, occurred when studying the ozonolysis of $\alpha$-terpinene (Lee et al., 2006; Ng et al., 2006), a structurally similar endocyclic-conjugated monoterpen. In the studies of Lee et al. (2006) and Ng et al. (2006), first-generation products were observed using identical methods for other monoterpen species including 3-carene, $\alpha$-pine, $\beta$-pine, terpinolene and myrcene. It is possible then that for highly reactive monoterpenes such as $\alpha$-terpine and $\alpha$-phellandrene, concentrations of first-generation products do not accumulate sufficiently during experiments for gas-phase detection. However, as discussed Sect. 3.1.3 and 3.2.1, a simple rate-study analysis shows that residence lifetimes based on gas-phase reactions are sufficient, whilst analysis of saturation concentrations suggests that the majority of predicted first-generation products likely reside in the gas phase.

Recent literature has shown that functionalised organic species experience considerable losses to Teflon chamber walls through gas–wall partitioning (e.g. Matsunaga and Ziemann, 2010; Zhang et al., 2014; Yeh and Ziemann, 2015; Krechmer et al., 2016; La et al., 2016). Observations indicate that organic compounds are not lost to the reactor walls, but rather partition between the gas-phase and Teflon.
3.5. \(\alpha\)-PHELLANDRENE OZONOLYSIS

Figure 3. Partial mechanism for the ozonolysis of \(\alpha\)-phellandrene starting from CI3, yielding product masses detected by the PTR-TOF. Similar constructs for the remaining CIs are provided in the Supplement (Sect. S1).
Figure 4. Determination of gas-phase product yields in experiment 5.

Table 3. Gas-phase molar yields (%) for major α-phellandrene ozonolysis products.

<table>
<thead>
<tr>
<th>No.</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Formic acid</th>
<th>Glyoxal</th>
<th>Acetic acid</th>
<th>Methyl glyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.9 ± 2</td>
<td>8.3 ± 2</td>
<td>37 ± 9.0</td>
<td>23 ± 5</td>
<td>13 ± 3</td>
<td>3.7 ± 0.9</td>
</tr>
<tr>
<td>2</td>
<td>5.9 ± 1</td>
<td>4.4 ± 1</td>
<td>24 ± 6</td>
<td>9.0 ± 2</td>
<td>9.0 ± 2</td>
<td>3.1 ± 0.7</td>
</tr>
<tr>
<td>3</td>
<td>5.9 ± 1</td>
<td>5.4 ± 1</td>
<td>22 ± 5</td>
<td>6.2 ± 1</td>
<td>12 ± 3</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>4</td>
<td>5.0 ± 1</td>
<td>3.8 ± 0.9</td>
<td>28 ± 6</td>
<td>7.6 ± 2</td>
<td>11 ± 2</td>
<td>5.7 ± 1</td>
</tr>
<tr>
<td>5</td>
<td>3.3 ± 0.8</td>
<td>2.6 ± 0.6</td>
<td>30 ± 7</td>
<td>16 ± 4</td>
<td>12 ± 3</td>
<td>5.1 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>7.0 ± 2</td>
<td>7.6 ± 2</td>
<td>24 ± 6</td>
<td>22 ± 5</td>
<td>8.5 ± 2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8.7 ± 2</td>
<td>0.2 ± 0.04</td>
<td>22 ± 5</td>
<td>3.4 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.4 ± 1</td>
<td>2.3 ± 0.5</td>
<td>28 ± 6</td>
<td>17 ± 4</td>
<td>16 ± 4</td>
<td>5.2 ± 1</td>
</tr>
<tr>
<td>9</td>
<td>7.5 ± 2</td>
<td>2.5 ± 0.6</td>
<td>35 ± 8</td>
<td>21 ± 5</td>
<td>20 ± 5</td>
<td>5.3 ± 1</td>
</tr>
<tr>
<td>10</td>
<td>7.9 ± 2</td>
<td>2.2 ± 0.5</td>
<td>29 ± 7</td>
<td>17 ± 4</td>
<td>13 ± 3</td>
<td>9.2 ± 2</td>
</tr>
<tr>
<td>11</td>
<td>1.2 ± 0.3</td>
<td>0.41 ± 0.09</td>
<td>10 ± 2</td>
<td>7.6 ± 2</td>
<td>5.0 ± 1</td>
<td>2.1 ± 0.5</td>
</tr>
</tbody>
</table>

the reported yield as an average of the entire ozonolysis system.

Formic and acetic acid were both found to be produced with high yields. The fragmentation pattern of acetic acid was determined in a separate calibration experiment, with 88 % residing at m/z 61 and the remaining mass distributed over m/z 43, 62 and 79, corresponding to dehydration to the acylium ion, the $^{13}$C isotope and protonation by a water cluster, respectively. Correcting for fragmentation, yields of formic and acetic acid were found to range from 22 to 37 % and 9 to 22 %, respectively, across the conducted experiments. Yields of formic acid are considerably higher than what has been reported for the ozonolysis of other terpenes, whilst acetic acid yields are consistent with species containing an endocyclic bond (Lee et al., 2006); although a subtle difference in methodology should be noted with Lee et al. (2006) calculating yields with respect to the parent hydrocarbon. The addition of NO$_2$ was found to reduce yields of both formic and acetic acid to 10 ± 2 and 5 ± 1 %, respectively, with O$_3$ losses through reaction with NO$_x$ accounted for. The addition of NO$_2$ therefore acts as an inhibitor to acidic group formation, likely by scavenging acyl peroxy radicals to form peroxyacyl nitrates (PANs). Alternatively, NO$_2$ can impact the chemistry of the system by reacting with stabilised secondary ozonides (SOZs), although no changes in acid product yields were observed in the experiments where sCIs were scavenged, indicating that this channel is negligibly important in forming low-molecular-weight acids.

In characterising the PTR-TOF transmission curve, acetaldehyde and all other oxygenated VOCs in the gas-standard (Ionicon, Analytik GmbH, Austria) showed no evidence of fragmentation. Therefore, assuming no fragmentation for the remaining oxidation products provides yields of formaldehyde, acetaldehyde, glyoxal and methyl glyoxal of 5–9, 0.2–8, 6–23 and 2–9 %. Nevertheless, fragmentation of methyl glyoxal through CO loss in the PTR-TOF has been reported (Müller et al., 2012), which would simultaneously reduce its own yield whilst increasing the
Table 4. Minor gas-phase molar yields (%) for α-phellandrene ozonolysis.

<table>
<thead>
<tr>
<th>No.</th>
<th>m/z 87</th>
<th>m/z 97</th>
<th>m/z 109</th>
<th>m/z 111</th>
<th>m/z 115</th>
<th>m/z 129</th>
<th>m/z 139</th>
<th>m/z 143</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5 ± 0.6</td>
<td>1.1 ± 0.3</td>
<td>0.58 ± 0.1</td>
<td>2.9 ± 0.7</td>
<td>3.3 ± 0.8</td>
<td>3.4 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.5 ± 0.6</td>
<td>0.87 ± 0.2</td>
<td>0.19 ± 0.04</td>
<td>3.6 ± 0.9</td>
<td>3.0 ± 0.7</td>
<td>2.3 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.2 ± 0.8</td>
<td>1.3 ± 0.3</td>
<td>0.61 ± 0.1</td>
<td>3.0 ± 0.7</td>
<td>1.3 ± 0.3</td>
<td>4.4 ± 1</td>
<td>1.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.5 ± 0.6</td>
<td>0.21 ± 0.05</td>
<td>0.74 ± 0.2</td>
<td>3.7 ± 0.9</td>
<td>3.0 ± 0.7</td>
<td>1.4 ± 0.3</td>
<td>3.7 ± 0.9</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>5</td>
<td>3.5 ± 0.8</td>
<td>1.1 ± 0.3</td>
<td>0.78 ± 0.2</td>
<td>3.7 ± 0.9</td>
<td>3.0 ± 0.7</td>
<td>1.4 ± 0.3</td>
<td>3.7 ± 0.9</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>6</td>
<td>0.13 ± 0.03</td>
<td>0.45 ± 0.1</td>
<td>2.4 ± 0.6</td>
<td>1.7 ± 0.4</td>
<td>1.5 ± 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.75 ± 0.2</td>
<td>2.0 ± 0.5</td>
<td>1.1 ± 0.3</td>
<td>4.8 ± 1</td>
<td>3.1 ± 0.7</td>
<td>1.4 ± 0.3</td>
<td>4.2 ± 1</td>
<td>4.4 ± 1</td>
</tr>
<tr>
<td>8</td>
<td>5.4 ± 1</td>
<td>0.76 ± 0.2</td>
<td>0.68 ± 0.2</td>
<td>2.2 ± 0.5</td>
<td>3.0 ± 0.7</td>
<td>1.9 ± 0.5</td>
<td>3.8 ± 0.9</td>
<td>5.1 ± 1</td>
</tr>
<tr>
<td>9</td>
<td>2.3 ± 0.5</td>
<td>2.7 ± 0.6</td>
<td>0.69 ± 0.2</td>
<td>4.0 ± 0.9</td>
<td>2.7 ± 0.6</td>
<td>6.0 ± 1</td>
<td>3.9 ± 0.9</td>
<td>4.4 ± 1</td>
</tr>
<tr>
<td>10</td>
<td>7.4 ± 2</td>
<td>0.12 ± 0.03</td>
<td>0.13 ± 0.03</td>
<td>0.15 ± 0.03</td>
<td>0.09 ± 0.02</td>
<td>0.91 ± 0.2</td>
<td>0.29 ± 0.07</td>
<td>0.40 ± 0.09</td>
</tr>
</tbody>
</table>

yield of acetaldehyde. A similar phenomenon is also expected of glyoxal; nonetheless, acetaldehyde yields remain low and consistent with findings reported for other terpene species. Formaldehyde yields are consistent with other terpene species containing multiple internal double bonds, e.g. α-humulene and α-terpinene (Lee et al., 2006). The addition of a sCI scavenger was found to have little impact on product distribution or yields, suggesting that the sCI-formic acid complexes ultimately decompose to produce similar gas-phase products to SCIs that degrade through conventional channels. Whether decoupling of the sCI-acid complex occurs inside the reactor or upon protonation in the PTR-TOF remains unknown. Similarly, no significant differences in yields were observed between experiment 9 and OH-scavenged experiments, with decomposition into smaller carbon species counterintuitively invariant to action by the OH radical, strengthening the argument that fragmentation inside the PTR-TOF is non-negligible. Meanwhile, in experiment 11, yields of formaldehyde, acetaldehyde, glyoxal and methyl glyoxal were 1.2 ± 0.3, 0.7 ± 0.2 and 2.1 ± 0.5 %, respectively. A comparison of rate constants of O3 with α-phellandrene (3.0 × 10−13 cm3 molecule−1 s−1) and NO2 (3.5 × 10−17 cm3 molecule−1 s−1) suggests that the majority of O3 will be consumed by α-phellandrene with formation of the nitrate radical relatively minor (Calvert et al., 2000; Atkinson et al., 2004). Nevertheless, NO2 is in excess in the system, with a systematic reduction in product yields indicative of a shift towards RO2- and NO2-dominated chemistry, producing peroxy-nitrate-containing products (Draper et al., 2015).

Heavier second-generation products routinely detected across experiments are listed in Table 2, with yields for a number of these products given in Table 4. The absence of a yield indicates that the peak was not detected by the PTR-TOF, which typically occurred for minor peaks in experiments with lower starting α-phellandrene concentrations. Again, no fragmentation was assumed in determining yields, although some ions do differ by common fragment mass amounts, suggesting that fragmentation may be important. For example, m/z 185 and 167, m/z 129 and 111 and m/z 115 and 97 all differ by 18 amu, suggesting that the latter masses could be dehydrated fragments. Whilst strong correlation (R2 > 0.99) between these pairs of peaks is observed, it is not consistent across the entire dataset, suggesting that there exist multiple contributors to the aforementioned signals. Similar instances are also observed for peaks separated by 28 amu (e.g. m/z 143 and 115) and 46 amu (e.g. m/z 185 and 139).

Calculated yields for these larger products were in general <5 %, with detected products sufficiently volatile such that gas–wall partitioning losses are thought to be minor (see Fig. 9). Again, the presence of OH radicals in experiment 9 had little effect on product yields. Addition of NO2 to the system in experiment 11 resulted in significantly reduced yields, with overall distribution remaining similar and no new peaks or evidence of nitrate-containing compounds observed. Nonetheless, alkyl nitrates are known to readily lose HNO3 after protonation in the PTR-TOF, resulting in the formation of bare alkyl ions (D’Anna et al., 2005; Aoki et al., 2007; Duncianu et al., 2017). Proposed structures for some of these larger second-generation products, along with plausible formation mechanisms, are shown in Fig. 3, although it is possible that more than one species contributes to an observed oxidation product mass. A large number of products also remain unidentified, with their m/z unable to be transcribed to plausible, mechanistically derived structures.

Figure 2 shows that product signals at m/z 31, 59, 73 and 87 show a sharp increase upon commencement of the reaction, suggesting that these products are formed directly from α-phellandrene ozonolysis. Nevertheless, a large fraction of the product mass for these ions is generated after α-phellandrene consumption, indicating that yields are largely driven by contributions from second-generation species. Slower initial production of the remaining ions suggests that their formation is linked to consumption of first-generation products. Interestingly, the peaks corresponding to the heaviest ions, m/z 167, 169 and 185, have relatively constant temporal profiles which also lack an accelerated increase upon...
Figure 5. Mechanism of O₃ addition to the proposed m/z 169 structures, yielding pairs of Criegee intermediates and carbonyl-containing products.

a second addition of ozone, a feature that is apparent among lighter product ions. Their unique time profiles imply that they are derived from a source secondary to ozonolysis, such as gas-phase accretion reactions, with modelling support for this provided in the Supplement (Sect. S4).

Formation of prescribed products after the second ozonolysis is in agreement with the proposed degradation mechanism (Fig. 3), which predicts a number of both small and large species to form upon fragmentation of the carbon backbone. A large fraction of the smaller products come from decomposition of the three-carbon system (C₁₋₃, C₇, Fig. 1) bridging the conjugated double bonds in α-phellandrene, which segment from the rest of the molecule after the second ozone addition. For example, plausible mechanisms can be traced to methyl glyoxal formation irrespective of the order of addition of ozone to the two double bonds, with the only prerequisite being that the first addition of ozone adds one carbonyl group to the C₁₋₃-C₇ system. An example showing this from a proposed first-generation product is provided in Fig. 5. Subsequent decomposition of the C₁₋₃-C₇ Criegee biradical fragment can yield products including formaldehyde, formic acid and acetic acid. Meanwhile, functionalisation of the larger seven-carbon system bridging the conjugated bonds in α-phellandrene can give rise to a large number of heavier second-generation products. The m/z 129 is assigned to 2-propan-2-ylbutanedial, which can be formed from a number of pathways (e.g. Fig. 3). The m/z 115 is assigned to 2-propan-2-ylpropanedial, which is formed if a CI from either addition participates in the hydroperoxide channel, resulting in CHO fragmentation. Conversely, if instead of fragmentation, stabilisation occurs after a 1,5-hydrogen shift, then the product detected at m/z 143 shown in Fig. 3 may form. In all instances, detected second-generation products can be formed from a wide variety of predicted first-generation products independent of the order of addition of ozone to the two double bonds (Supplement Sect. S1).

3.1.2 Determination of OH yields

The OH radical scavenger, cyclohexane, reacts with OH to form both cyclohexanone and cyclohexanol (Atkinson et al., 1992; Berndt et al., 2003), with cyclohexanone (m/z 99) used as the OH radical tracer in this study. In a characterisation experiment, 98 and 85 % of cyclohexanone (Sigma Aldrich, 99.8 %) was found to reside at m/z 99 when the PTR-TOF drift tube was operated at 112 and 136 Td, respectively, with the remaining mass distributed over dehydrated and cluster peaks at m/z 81, 116 and 117. A minor ozonolysis product is also detected at m/z 99 (Sect. 3.1.1); however, the two peaks are resolvable in the PTR-TOF.

A major uncertainty in determining OH yields is the yield of cyclohexanone formed from the reaction of cyclohexane with OH radicals. Atkinson et al. (1992) reported the combined yield of cyclohexanone and cyclohexanol to be 0.55 ± 0.09, with cyclohexanone/cyclohexanol ratios typically ranging from 0.8 to 1.4, depending on the terpene investigated. In contrast, Berndt et al. (2003) reported a cyclohexanone yield of 0.53 ± 0.06. In this study, the OH yield is based on the average of these two findings, with a cyclohexanone yield from the reaction of OH and cyclohexane of 0.41 ± 0.14 used. Scavenging is assumed to be 95 % efficient based on the volume of cyclohexane introduced into the reactor, with the error in this assumption thought to be minimal with respect to the inherent uncertainty in cyclohexanone yields. Background interference from cyclohexane, of which a small portion is oxidised by O₃ to cyclohexanone in the drift tube, is corrected for (Winterhalter et al., 2009).

OH yields for the initial reaction of ozone with α-phellandrene were calculated from the slope of OH produced against α-phellandrene reacted. As both m/z 99 and 137 are major signals in the PTR-TOF, spectra were not averaged during analysis, resulting in a 2 s time resolution. A characteristic OH-production time profile is shown in Fig. 6, which can be separated into three regions. The initial part of the experiment is characterised by a linear section, where α-phellandrene is the primary source of OH radicals. The gradient obtained from linear regression in this regime is equivalent to the OH yield from ozonolysis of the first double bond in α-phellandrene (Fig. 7a). The α-phellandrene-dominated regime is short-lived with respect to total OH production time in the reactor, suggesting that first-generation products are also highly reactive and large producers of OH radicals. As the reaction proceeds, fast-reacting first-generation products begin to contribute to the OH budget, whilst α-phellandrene becomes increasingly less
Table 5. Measured and modelled OH radical yields and modelled rate constants for α-phellandrene ozonolysis experiments.

<table>
<thead>
<tr>
<th>α-phellandrene</th>
<th>First-generation products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental OH yield (%)</td>
</tr>
<tr>
<td>k₁ (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>Lit.</td>
<td>3.0 ± 1⁰</td>
</tr>
</tbody>
</table>

a Calvert et al. (2000).
b Herrmann et al. (2010).

![Figure 6](image_url)

Figure 6. OH radical production versus α-phellandrene consumption for the first 18 min of experiment 3.

The average OH yield for the reaction of the first double bond in α-phellandrene across the 10 experiments was found to be 35 ± 12 %, whilst the average OH yield from the ozonolysis of the second reacting double bond was 15 ± 7 %. Both these determined values are slightly higher than the values calculated in Herrmann et al. (2010), although they agree well within uncertainty limits. Whilst experimental methodology is similar, Herrmann et al. (2010) conducted their analysis under the assumption that the two double bonds in α-phellandrene react at significantly different rates, such that

![Figure 7](image_url)

Figure 7. OH production from the (a) first and (b) second addition of ozone to α-phellandrene in experiment 3 against α-phellandrene and ozone consumption, respectively.
95% of α-phellandrene reacts before first-generation products start to be consumed. However, as Fig. 6 shows, first-generation products contribute to the OH radical budget considerably earlier than this. As a result, Herrmann et al. (2010) is likely to have underpredicted OH yields of first-generation products, inadvertently apportioning their contribution to α-phellandrene, whose OH yields would subsequently be overpredicted. The method employed in this study is thought to provide a more accurate distinction between OH radical production from α-phellandrene and its first-generation products. From the determined yields, it can be concluded that the hydroperoxide channel does play an important role in the decomposition of α-phellandrene by ozone, supportive of findings from a recent theoretical study (Mackenzie-Rae et al., 2016).

3.1.3 Modelling rate constants and OH yields

The conjugated system in α-phellandrene provides two reactive sites for ozone addition. Based on analogy with rate constants from simpler alkenes, such as cyclohexene ($k = 8.1 \times 10^{-17} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$) and 1-methyl-1-cyclohexene ($k = 1.66 \times 10^{-16} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$) (Calvert et al., 2000), inductive effects are expected to make the methyl-substituted double bond the more reactive addition site. However, recent theoretical results suggest the contrary (Mackenzie-Rae et al., 2016), with steric effects raising the energy barrier for entry to the more substituted double bond, resulting in addition to the less substituted double bond in α-phellandrene being favoured. This finding is consistent with experimental evidence for isoprene, where methacrolein, not methyl vinyl ketone, is the favoured first-generation product (Paulson et al., 1992; Grosjean et al., 1993; Aschmann and Atkinson, 1994; Rickard et al., 1999). Nevertheless, the average energy difference for addition to the two double bonds is minor, with both entry channels expected to be important.

Given the high chemical reactivity of both double bonds in α-phellandrene, it is interesting to investigate the reactivity of first-generation products. The following reaction parameterisation was therefore constructed to determine the average rate constant of ozone with all first-generation species:

$$\alpha - \text{phellandrene} + \text{O}_3 \stackrel{k_1}{\rightarrow} \text{FG} + x\text{OH} \quad (R1)$$

$$\text{FG} + \text{O}_3 \stackrel{k_2}{\rightarrow} \text{SG} + y\text{OH} \quad (R2)$$

$$\text{O}_3 \stackrel{k_3}{\rightarrow} \text{wO}_3, \quad (R3)$$

where FG represents all first-generation products, SG represents all second-generation products, wO3 is ozone lost to the reactor walls and $x$ and $y$ are stoichiometric coefficients representing OH yields from each reaction step. The rate constant for the reaction of ozone with α-phellandrene ($k_1$) was constrained to the literature value (Calvert et al., 2000), whilst a first-order ozone wall loss rate of $k_3 = 2-8 \times 10^{-6} \text{s}^{-1}$ was used based on a number of calibration experiments. Remaining parameters, namely $x$, $y$ and $k_2$, were varied to optimise model performance. The reaction scheme was solved using the online numerical integrator AtChem (https://atchem.leeds.ac.uk/) for all experiments, barring 9 and 11 due to the unconstrained influence of NO2 and/or OH radicals.

Figure 8 shows the results of the simulation of ozone consumption and OH production for three different experiments, with optimised parameters for each experiment given in Table 5. Considering simplicity, the model performs surprisingly well. Based on all experiments, the average simulated rate constant for the reaction of first-generation products with ozone was $k_2 = 1.0 \pm 0.7 \times 10^{-16} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. Although the ozonolysis of first-generation products is around 30 times slower than that of α-phellandrene, it is still faster than the ozonolysis of numerous monoterpenes including α-pinene, β-pinene, sabine, 3-carene and β-phellandrene (Calvert et al., 2000). Using a typical background tropospheric ozone mixing ratio of 30 ppb, atmospheric lifetimes ($\tau$) of α-phellandrene and its first-generation products can be estimated by

$$\tau \approx \frac{1}{k_i[\text{O}_3]}. \quad (1)$$

The atmospheric lifetime of α-phellandrene is therefore $\tau_1 \sim 7.5 \text{ min}$, whilst the average lifetime of first-generation products is calculated to be $\tau_2 \sim 3.75 \text{ h}$. Both α-phellandrene and its first-generation products therefore have a relatively short atmospheric lifetime with respect to ozone and are unlikely to be involved in long-range transport phenomena. Instead, complete saturation likely occurs in the chemical environment to which α-phellandrene is emitted, thus impacting the local radical, acid and SOA budgets. Interestingly, increasing the ozone concentration to conditions found in chamber experiments results in first-generation product lifetimes of the order of tens of minutes, which is more than sufficient for gas-phase detection. The inability to detect first-generation products is therefore indicative of an underlying sampling or detection issue.

OH production is additionally included in the model to assist in parameterising yields from α-phellandrene and the average of its first-generation products. Experimental assessment of OH yields carries an inherent uncertainty, in that linear regression was used to fit data belonging to a segment of a curve (Fig. 5), with information in the “combination” section notionally discarded. Model parameterisation allows for a more complete description, although mechanistic simplicity renders the results far from quantitative. Instead, its purpose is to both validate experimental findings and allow further constraints to be placed on OH production from the α-phellandrene system.

The average modelled OH yields are $53 \pm 10$ and $13 \pm 5\%$ for α-phellandrene and its average first-generation products, respectively. The model suggests α-phellandrene makes a greater contribution to the OH budget than was cal-
Gas–particle partitioning occurs in competition with gas–wall partitioning, a process that is also dependent on species saturation vapour concentrations (Supplement Sect. S6). In parameterising gas–wall partitioning, the Teflon film is often considered to have an equivalent organic aerosol mass concentration \( C_w \). Values for \( C_w \) vary significantly in the literature, with Ziemann and co-workers reporting values of \( C_w \sim 2–40 \, \text{mg m}^{-3} \) (Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2015), Zhan et al. (2014) reporting \( C_w \) values from 0.0004 to 300 \, \text{mg m}^{-3} \) and Krecmer et al. (2016) showing values of \( C_w \) to vary with \( C^* \), from \( C_w = 0.016 \, \text{mg m}^{-3} \) for \( C^* < 1 \) up to 30 \, \text{mg m}^{-3} \) for \( C^* > 10^4 \). The reasons for the large discrepancies between studies are unknown; however, they are likely due to differing deformation and activities of the Teflon walls (Krecmer et al., 2016). Nonetheless, comparing reported values to SOA loadings generated during the chamber experiments reported in this work, it is evident that gas–wall partitioning is at least competitive, if not dominant, compared to gas–particle partitioning. The impact is shown in Fig. 9 by plotting the fraction of an organic species that remains in the gas phase over different saturation vapour concentrations using \( C_w = 5 \, \text{mg m}^{-3} \) and an SOA loading of 200 \, \text{µg m}^{-3}. Under this scenario, gas–wall partitioning dominates, with compounds having \( C^* < 10^2 \, \text{µg m}^{-3} \) predominantly residing in the walls with a small fraction in the aerosol phase after equilibrium is established, whereas species with \( C^* > 10^6 \, \text{µg m}^{-3} \) remain almost entirely in the gas phase. Compounds with \( 10^2 < C^* < 10^6 \, \text{µg m}^{-3} \) will partition to varying extents depending on their volatility and functional group composition between the wall, gas and particle phases (Krecmer et al., 2016). However, no corrections for gas–particle partitioning are made in the present study, given that no product vapour loss rate measurements were made for the GIG-CAS chamber and the large variability in literature values of \( C_w \). With-
The majority of predicted first-generation and detected second-generation gas-phase products are classified as intermediate volatility compounds (IVOCs) (Donahue et al., 2012). As IVOCs, they are considered to have quite low vapour pressures but nonetheless reside almost exclusively in the gas phase. Of the proposed species, only the first-generation acids (e.g. Fig. 3) are classified as semi-volatile organic compounds (SVOCs), a classification given to those species which are expected to have sizeable mass fractions in the aerosol phase. Nevertheless, rapid aerosol formation is observed upon reaction of α-phellandrene and ozone as shown in Fig. 10, with sharp increases in particle number (dN/dlogDp) and volume (dV/dlogDp) concentrations observed. With no aerosol seed, nucleation must be driven by supersaturation of condensible species formed in the initial stages of the reaction. Donahue et al. (2013) argue that nucleation occurs through compounds that have extremely low volatility (ELVOC, $C^* < 3 \times 10^{-3} \mu g m^{-3}$). For the ozonolysis of other monoterpenes, ELVOC formation has been proposed to occur through gas-phase accretion reactions (Bate-man et al., 2009; Heaton et al., 2009; Camredon et al., 2010) and autoxidation processes (Ehn et al., 2014; Jokinen et al., 2015). Meanwhile, to condense onto fresh aerosol but not homogeneously nucleate, vapours need to have saturation concentrations in the $10^{-3}$–$10^{-2} \mu g m^{-3}$ range (Donahue et al., 2011; Pierce et al., 2011), placing them in the low-volatility organic compound bin. Formation of these compounds can be explained through conventional gas-phase chemistry (Donahue et al., 2011). It is therefore evident from Fig. 9 that the simple mechanistic overview provided to explain formation of gas-phase products in Sect. 3.1.1 and in Mackenzie-Rae et al. (2016) is insufficient to account for aerosol observations, with more complex reactions or reaction processes such as autoxidation, oligomerisation and/or heterogeneous oxidation required to develop species of sufficiently low vapour pressure for both particle nucleation and growth (Hallquist et al., 2009).

The maximum number of particles inside the reactor occur within the first few minutes of the reaction commencing (time resolution of the SMPS), with a small average particle diameter (≈40 nm). Rapid nucleation is consistent with the findings of Jokinen et al. (2015), who, based on limonene and α-pinene, concluded that endocyclic biogenic VOCs are efficient ELVOC producers upon ozonolysis. Coagulation of the newly formed aerosol decreases the number of particles, whilst further partitioning of low-volatility oxidation products increases the volume, with maximum aerosol concentration attained around 30 min into each experiment. After this point, irreversible wall losses supersedes gains from partitioning, with the volume, and hence mass, of aerosol decreasing inside the reactor.

In the early stages of experiments, the number concentration is a useful proxy for measuring the amount of nucleation occurring in the system (Bonn et al., 2002). As Fig. 11 shows, the addition of a Criegee scavenger systematically reduces initial particle number concentrations, concurrent with a shift of SOA to larger diameters. These changes suggest a reduction in the number of SOA-nucleating agents, implying that the reaction of α-phellandrene sCIs is important in forming ELVOC and IVOC compounds, whilst ruling out the reaction of sCIs with formic acid as a nucleating mechanism. This finding is consistent with experimental literature that is now building around sCIs as a source of new particle formation, whether through intramolecular SOZ formation (Bonn et al., 2002), bimolecular reaction with first-generation prod-
Figure 10. (a) Particle number (cm$^{-3}$) and (b) volume ($\mu$m$^3$ cm$^{-3}$) size distributions for experiment 3.

ucts (Bateman et al., 2009) or oligomer formation through reaction with peroxy radicals (Sadezky et al., 2006, 2008) or hydroperoxides (Sakamoto et al., 2013). Processes such as these would all be precluded by the addition of formic acid to the system. Similarly, there is a reduction in the $\alpha$-phellandrene normalised number distribution when NO$_2$ is added (Fig. 11). Like formic acid, NO$_2$ can also react with sCIs (Johnson and Marston, 2008) and therefore potentially inhibit particle formation and growth. If this were the case, then results from this ozonolysis study likely represent an upper limit to SOA formation under ambient conditions, although more experiments are necessary to confirm the impact of NO$_2$ on SOA formation in the $\alpha$-phellandrene system.

Assuming spherical particles, effective aerosol densities were calculated by comparing distributions of vacuum aerodynamic and electric mobility diameters, using the AMS and SMPS, respectively (DeCarlo et al., 2004; Katrib et al., 2005). Results are listed in Table 3. The average density across all experiments was found to be $1.49 \pm 0.2$ g cm$^{-3}$, indicating that the aerosol exists in a solid or waxy state (Kostenidou et al., 2007). This value is consistent with the SOA density found in the ozonolysis of other monoterpenes under similar conditions, which typically ranges from 1.15 to 1.73 g cm$^{-3}$ (Bahreini et al., 2005; Kostenidou et al., 2007; Saathoff et al., 2009; Shilling et al., 2009). Because the particles are potentially non-spherical, the quoted effective density represents a lower bound of the true $\alpha$-phellandrene SOA density, with error from assuming spherical particles expected to be less than 10% (DeCarlo et al., 2004; Bahreini et al., 2005). It is noted that the densest aerosol was produced in experiment 11, which had NO$_2$ added, although one experiment is insufficient for reliable conclusions. The aerosol density was found to be insensitive to a range of other experimental parameters, including starting $\alpha$-phellandrene and ozone concentrations, aerosol loading, aerosol oxidation state and the presence of CI scavengers. These findings are in contrast to studies conducted on $\alpha$-pinene (Shilling et al., 2009) and $\beta$-caryophyllene (Chen et al., 2012), in which particle density was found to decrease as chamber aerosol loadings.
CHAPTER 3. EXPERIMENTAL

F. A. Mackenzie-Rae et al.: Ozonolysis of α-phellandrene

Table 6. Aerosol loadings, effective densities, oxidation states and yields for α-phellandrene ozonolysis experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>Total SOA mass* (µg m⁻³)</th>
<th>Density (g cm⁻³)</th>
<th>ΔΩC</th>
<th>Yield (Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>861.1±9</td>
<td>1.29±0.05</td>
<td>−0.91±0.3</td>
<td>0.81±0.3</td>
</tr>
<tr>
<td>2</td>
<td>21.5±2</td>
<td>1.32±0.06</td>
<td>−0.65±0.2</td>
<td>0.37±0.2</td>
</tr>
<tr>
<td>3</td>
<td>121.3±13</td>
<td>1.37±0.05</td>
<td>−0.93±0.3</td>
<td>1.03±0.4</td>
</tr>
<tr>
<td>4</td>
<td>311.9±33</td>
<td>1.57±0.05</td>
<td>−0.93±0.3</td>
<td>1.74±0.7</td>
</tr>
<tr>
<td>5</td>
<td>178.0±19</td>
<td>1.36±0.05</td>
<td>−1.0±0.3</td>
<td>1.11±0.5</td>
</tr>
<tr>
<td>6</td>
<td>52.0±6</td>
<td>1.38±0.05</td>
<td>−0.77±0.3</td>
<td>0.60±0.2</td>
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<tr>
<td>7</td>
<td>27.6±3</td>
<td>1.34±0.05</td>
<td>−0.63±0.2</td>
<td>0.25±0.1</td>
</tr>
<tr>
<td>8</td>
<td>199.7±21</td>
<td>1.69±0.06</td>
<td>−0.82±0.3</td>
<td>0.72±0.3</td>
</tr>
<tr>
<td>9</td>
<td>341.0±36</td>
<td>1.61±0.05</td>
<td>−0.83±0.3</td>
<td>0.90±0.37</td>
</tr>
<tr>
<td>10</td>
<td>658.1±70</td>
<td>1.60±0.05</td>
<td>−0.99±0.3</td>
<td>0.71±0.3</td>
</tr>
<tr>
<td>11</td>
<td>504.9±53</td>
<td>1.90±0.06</td>
<td>−1.0±0.3</td>
<td>1.02±0.4</td>
</tr>
</tbody>
</table>

* Wall-loss corrected (Pathak et al., 2007).

cause the AMS is known to suffer from transmission losses caused by particles bouncing off the vapouriser and, to a lesser extent, shape-dependent collection losses whilst focusing the particle beam (Matthew et al., 2008; Slowik et al., 2004; Huffman et al., 2005). Whilst it is noted that the SMPS does not measure particles with diameters larger than 750 nm, as shown in Fig. 10, this shortcoming is expected to have minimal impact on reported yields in this work (Wiedensohler et al., 2012).

Wall-loss-corrected mass loadings for each experiment are given in Table 6, along with fractional aerosol yields (Y). The fractional aerosol yield is defined as the amount of organic particulate matter that is produced (ΔM₀, µg m⁻³) for a given amount of precursor VOC reacted (ΔHC, µg m⁻³) (Odum et al., 1996) and provides a convenient way of assessing the bulk aerosol-forming potential of an individual VOC. Utilising the gas–particle partitioning framework, aerosol yield can be described as a function of organic aerosol mass concentration (Pankow, 1994; Odum et al., 1996):

\[ Y = \frac{\Delta M_0}{\Delta HC} = \frac{\Delta M_0}{\sum_i \alpha_i K_{om,i} \Delta M_0}, \]  

where \( \alpha_i \) is the stoichiometric factor and \( K_{om,i} \), the temperature-dependent equilibrium-partitioning constant of product \( i \).

A characteristic yield plot is given in Fig. 12. Whilst a large number of products are expected to contribute to the particle phase, SOA yield is best fit using the parameters \( \alpha_1 = 1.2 \pm 0.2 \) and \( K_{om,1} = 0.022 \pm 0.002 \) m⁻³, with higher-order fits found to be superfluous. The fitted constants offer little physical insight, other than perhaps the average of all \( \alpha \) and \( K_{om} \) values but nonetheless can be used in regional and global modelling (Chung and Seinfeld, 2002; Tsigeridis and Kanakidou, 2003; Henze and Seinfeld, 2006; Jathar et al., 2016).

Increased, in accordance with changes in aerosol oxidation state.

Aerosol densities were used to convert SMPS volume concentrations into mass loadings (µg m⁻³). Wall loss effects were corrected for by assuming a size-independent first-order loss process (Pathak et al., 2007), by modelling data at the end of each experiment, after gas-aerosol partitioning had reached equilibrium. Calculated wall loss rate constants, which ranged from 0.32 to 0.79 h⁻¹, were then applied to correct mass loading data for respective experiments. This way, differences between individual chamber simulations are accounted for. Determined wall loss rates are consistent with those found for α-pinene ozonolysis in the chamber (Wang et al., 2014).

The same method was used to correct V-mode AMS data, with results given in the Supplement (Sect. S7). Clustering of points around the 1 : 1 line in Fig. S7.1 indicates general agreement between mass loadings calculated using the AMS and SMPS (Shilling et al., 2008). Nevertheless, density-corrected SMPS data is preferred in this work, primarily because the AMS is known to suffer from transmission losses caused by particles bouncing off the vapouriser and, to a lesser extent, shape-dependent collection losses whilst focusing the particle beam (Matthew et al., 2008; Slowik et al., 2004; Huffman et al., 2005). Whilst it is noted that the SMPS does not measure particles with diameters larger than 750 nm, as shown in Fig. 10, this shortcoming is expected to have minimal impact on reported yields in this work (Wiedensohler et al., 2012).

Wall-loss-corrected mass loadings for each experiment are given in Table 6, along with fractional aerosol yields (Y). The fractional aerosol yield is defined as the amount of organic particulate matter that is produced (ΔM₀, µg m⁻³) for a given amount of precursor VOC reacted (ΔHC, µg m⁻³) (Odum et al., 1996) and provides a convenient way of assessing the bulk aerosol-forming potential of an individual VOC. Utilising the gas–particle partitioning framework, aerosol yield can be described as a function of organic aerosol mass concentration (Pankow, 1994; Odum et al., 1996):

\[ Y = \frac{\Delta M_0}{\Delta HC} = \frac{\Delta M_0}{\sum_i \alpha_i K_{om,i} \Delta M_0}, \]  

where \( \alpha_i \) is the stoichiometric factor and \( K_{om,i} \), the temperature-dependent equilibrium-partitioning constant of product \( i \).

A characteristic yield plot is given in Fig. 12. Whilst a large number of products are expected to contribute to the particle phase, SOA yield is best fit using the parameters \( \alpha_1 = 1.2 \pm 0.2 \) and \( K_{om,1} = 0.022 \pm 0.002 \) m⁻³, with higher-order fits found to be superfluous. The fitted constants offer little physical insight, other than perhaps the average of all \( \alpha \) and \( K_{om} \) values but nonetheless can be used in regional and global modelling (Chung and Seinfeld, 2002; Tsigeridis and Kanakidou, 2003; Henze and Seinfeld, 2006; Jathar et al., 2016).
Figure 12 shows that α-phellandrene produces a large amount of aerosol upon ozonolysis compared to other monoterpenes (Wang et al., 2014; Saathoff et al., 2009; von Hessberg et al., 2009). Formation of the necessary semi-volatile organic compounds is likely driven by the presence of two highly reactive endocyclic double bonds, with functionalisation rather than fragmentation dominating for the first addition (Lee et al., 2006). Both experiments where a CI scavenger was added lie below the fitted yield curve, strengthening the argument for sCIs as a source of condensible products. Nevertheless, yields from the two experiments differ by almost a factor of 2 despite having similar starting conditions, with further experiments necessary to better quantify the impact of sCIs on yields. Cyclohexane has been shown to reduce SOA yields in ozonolysis experiments (Bonn et al., 2002; Keywood et al., 2004; Saathoff et al., 2009), although no such effects were observed in this study.

The second addition of ozone, in general, fragments the molecule but in doing so increases relative oxygen content. Thus, the relative contribution of first- and second-generation products to SOA is empirically difficult to predict. Figure 13 shows SOA mass as a function of α-phellandrene reacted, producing time-dependent aerosol growth curves. In all experiments where α-phellandrene was completely consumed, dominant vertical growth profiles are traced. This increase in aerosol mass after complete consumption of parent hydrocarbon is characteristic of compounds with more than one double bond (Ng et al., 2006) and suggests that, when formed, second-generation products make an important contribution to the total aerosol mass. It is therefore likely that a large number of second-generation species fall in the IVOC or SVOC category in Fig. 9.

Whilst concentrations of precursors are somewhat elevated in experiments compared to ambient conditions, results nonetheless show α-phellandrene ozonolysis products to be heavily involved in both particle nucleation and growth processes. In polluted environments (e.g. inner-city forests, consumer products), a high SOA yield results in a large fraction of α-phellandrene partitioning into the particle phase irrespective of gas-phase loadings. Meanwhile, a strong nucleation potential makes α-phellandrene ozonolysis a strong candidate to help explain the intense and frequent nocturnal nucleation events observed in Eucalypt forests (Lee et al., 2008; Suni et al., 2008), which are already believed to be caused by monoterpane oxidation products (Ortega et al., 2009, 2012). Indeed, the reaction conditions used in these experiments better reflect this clean environment, where reactions of RO₂ with HO₂ and other RO₂ radicals dominate along with unimolecular rearrangements. Such conditions favour the formation of low-volatility compounds, with the highest SOA yields for monoterpenes found under low-NOₓ conditions (Presto et al., 2005; Ng et al., 2007; Capouet et al., 2008; Eddingsaas et al., 2012). Under these conditions, ozonolysis reactions remain important (Perraud et al., 2012; Zhao et al., 2015), which is conducive to autoxidation processes and therefore nascent SOA formation and growth due to enhanced propensity for intramolecular rearrangements (Ehn et al., 2014; Jokinen et al., 2015). SOA yields measured in experiment 11 are consistent, however, with the other ozonolysis experiments in this study (Fig. 12), suggesting that the impact of NOₓ on SOA yields during the
ozonolysis of α-phellandrene is limited, with sufficient condensible products still able to be produced (Draper et al., 2015). Nonetheless, the reduction in aerosol number concentration in the initial stages of experiment 11 does suggest that formation pathways of ELVOC species (i.e. oligomerisation, autoxidation) are suppressed by the inclusion of NO₂ (Per- raud et al., 2012). Detailed modelling studies are required to establish the relative importance of α-phellandrene in different environments, although evidence suggests that it is likely a contributor to nucleation events and aerosol growth in regions where it is emitted.

3.2.2 SOA composition

Resolution in the W mode of the AMS is sufficient to unambiguously identify chemical formulae of detected ions (De- Carlo et al., 2006; Aiken et al., 2007). Ions are formed, however, using high-energy electron impact ionisation (70 eV), resulting in significant fragmentation. The complexity of aerosol produced, along with an unknown number of fragmenta- tion pathways, including the possibility of charge migration and other internal rearrangements, makes it exceedingly difficult to obtain clear structural information about SOA constituents from the AMS. For this reason, filter samples were collected and analysed to identify SOA constituents, with results to be published in a companion paper. Nevertheless, the AMS remains useful for analysing bulk properties of the aerosol to gain further insight into the system.

Bulk elemental composition can be estimated by averaging ion contributions across the entire mass spectrum (Aiken et al., 2007). Raw measured atomic ratios are converted to estimated ratios using the calibration factors of Aiken et al. (2008), namely 0.91 ± 10% for hydrogen-to-carbon (H/C), 0.75 ± 31% for oxygen-to-carbon (O/C) and 0.96 ± 22% for nitrogen-to-carbon ratios, respectively, thus accounting for chemical biases in fragmentation.

Figure 14 shows the typical temporal profile of aerosol composition observed over an experiment. Initial aerosol formation and growth is driven by highly oxygenated species; however, as the organic aerosol (OA) medium grows and less functionalised species begin to partition, the overall oxidation state rapidly decreases, as seen by a drop in O/C and respective rise in H/C ratios. Once gas–particle partitioning slows and aerosol-loss processes dominate, there is a shift in equilibrium, with the more volatile aerosol constituents evaporating back into the gaseous phase. It can therefore be concluded that many of the SOA products generated during the chamber ozonolysis of α-phellandrene in this study are semi-volatile (Donahue et al., 2012). Nitrogen-containing species were found to make little contribution to the aerosol formed in experiment 11, with an average N/C ≈ 0.002 dur-
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ing the experiment. Nitrate and PAN functionality is believed to significantly reduce the vapour pressure of constituents (Capouet and Müller, 2006; Pankow and Asher, 2008), with the result implying a small gas-phase concentration. Nevertheless, there exists evidence that organic nitrate contribution to SOA may be kinetically driven, rather than volatility driven (Perraud et al., 2012).

The average oxidation state of carbon ($\text{OS}_c$) in aerosol comprising of carbon, hydrogen and oxygen was parameterised by Kroll et al. (2011) as

$$\text{OS}_c \approx 2\text{O}/\text{C} - \text{H}/\text{C}.$$  

Although the definition ignores the effects of peroxides, whose oxygen atoms carry an oxidation state of $-1$, it nonetheless serves as a useful metric for representing the degree of oxidation of organic species in complex aerosol mixtures. Figure 15 shows that $\text{OS}_c$ decreases from $-0.61$ to $-1.00$ as the particle loading increases from 21.5 to 658.1 µg m$^{-3}$, suggesting a strong link between mass loading and degree of functionalisation, consistent with the findings of Shilling et al. (2009) for the ozonolysis of α-pinene.

The fastest change in $\text{OS}_c$ is observed to occur at lower mass loadings. Calculated $\text{OS}_c$ classifies the aerosol formed throughout the campaign as semi-volatile oxygenated organic aerosol (SV-OOA) (Kroll et al., 2011), consistent with numerous monoterpene and O$_3$ chamber experiments (Bateeman et al., 2009; Aiken et al., 2008; Shilling et al., 2009; Chhabra et al., 2010; Chen et al., 2011). SOA density predictions from elemental ratios using the parameterisation of Kuwata et al. (2012) show some agreement with measured values (Supplement Sect. S8).

A van Krevelen plot of the entire dataset is given in Fig. 16. The impact of CI scavengers, cyclohexane and NO$_2$ on OA in van Krevelen space is observed to be minor. The important parameter was found to be aerosol mass loadings, with changes resulting in vertical shifts consistent with a change in oxidation state. Ozonolysis reactions are unique, as oxygen can be added and condensable products formed with no loss (and possibly gain) of hydrogen. Because of this, generic functionalisation lines used to characterise reactions in van Krevelen space (Heald et al., 2010; Chhabra et al., 2011) are not applicable.

It is evident from Fig. 16 that the majority of predicted species have a lower O/C ratio compared to what is measured for the bulk of the aerosol. It is therefore unlikely that any of the detected gas-phase species are substantially contributing to the generated aerosol, which instead is dominated by more functionalised products. Whilst it is likely that species comprising the OA are also present in the gas phase, they exist below the detection threshold of, or are lost in detection by, the PTR-TOF. Indeed, the presence of a filter prior to the PTR-TOF inlet may hinder detection of less volatile species, as elevated levels of OA on the filter may coax species into partitioning (Turpin et al., 2000; Kirchstetter et al., 2001).

The carbon mass balance for each experiment is shown in Fig. 17. It was calculated by summing the gas-phase yields of all product ions, assuming a carbon number of 6 for unidentified products, with SOA yields, whose carbon content was determined from elemental ratios measured in each experiment. The carbon balance ranged from 25 to 131 %. General losses in the system, such as vapour losses to the Teflon walls, affect the ability to close the carbon mass balance for most experiments, with performance worse in those experiments with lower starting α-phellandrene concentrations due to an inability to detect minor gas-phase products. It is evident from Fig. 17 that, despite having lower yields, heavier gas-phase products make a larger contribution to the carbon mass balance than lighter species such as formaldehyde, glyoxal, formic acid and acetic acid, whose nominal yields are higher. Meanwhile, experiment 4 had a carbon mass balance exceeding 100 %, which is thought to be the result of an erroneously high SOA yield (Fig. 12). It is immediately obvious from the carbon mass balances that a large fraction of α-phellandrene partitions into the aerosol phase upon ozonolysis, exemplifying the impact α-phellandrene can have on SOA formation and growth. Currently, the species comprising SOA generated from α-phellandrene ozonolysis remains unidentified; however, a complete analysis of filter samples collected during these experiments is underway, in preparation for a follow-on publication.

4 Conclusions

The reaction of α-phellandrene with ozone was studied in depth for the first time through 11 chamber experiments. In the gas phase, only signals with increasing temporal profiles were detected by the PTR-TOF, indicative of second-generation products. Of these, small species ($\leq C_3$) were found to be produced in the highest yields, namely formaldehyde (5–9 %), acetaldehyde (0.2–8 %), glyoxal (6–23 %),

![Figure 15. Average oxidation state of carbon for increasing SOA loadings generated through α-phellandrene ozonolysis experiments, with the general trend shown.](image-url)
methyl glyoxal (2–9%), formic acid (22–37%) and acetic acid (9–22%), with yields of all products suppressed by the addition of NO₂. Despite having lower yields, heavier second-generation products were found to make a larger contribution to the carbon mass balance. A small number of second-generation products were tentatively identified based on a constructed gas-phase mechanism, including 2-propan-2-ylpropanedial and 2-propan-2-ylbutanediol. Experimental OH-radical yields of 35 ± 12% and 15 ± 7% for α-phellandrene and its first-generation products are in good agreement with those reported in Herrmann et al. (2010) and show the hydroperoxyl channel to be an important pathway, with model output from a simple reaction pa-

rameterisation suggesting experimental yields to be a lower bound. Meanwhile, modelling provides a rate coefficient of 1.0 ± 0.7 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ for the average reaction of first-generation products with ozone at 298 K. This equates to an atmospheric lifetime of around 3.75 h, higher than many other monoterpenes, and suggests that complete saturation of α-phellandrene likely occurs in the environment to which it is emitted.

α-phellandrene was found to form a large amount of aerosol upon reacting with ozone. A homogeneous nucleation burst of fresh aerosol was observed in all experiments within the first few minutes of the reaction, indicating a rapid formation of ELVOC species. Addition of a Cl scavenger inhibited nucleation, suggesting that sClIs are important precursors in forming compounds of low volatility in the system. The mechanism behind this remains unknown, although numerous pathways have been proposed in the literature for ClIs from other alkenes with more experiments required. Addition of NO₂ was found to reduce initial nucleation, although overall yields remained the same. The average effective SOA density was determined to be 1.49 ± 0.2 g cm⁻³ with an oxidation state varying from 0.56 to 1.02 depending on mass loadings. SOA growth curves show both first- and second-generation species contribute to the particulate phase, driving aerosol growth through to completion of the reaction. SOA yield is best fit by a one-product model with σ₁ = 1.2 ± 0.2 and K⁰m,₁ = 0.022 ± 0.02 m³ µg⁻¹, with the SOA-forming potential from α-phellandrene ozonolysis greater than other monoterpenes previously investigated in the literature.
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High radical, acid and SOA yields, coupled with a high reactivity, result in α-phellandrene having an immediate and significant impact on its local environment. Indeed, it appears likely that ozonolysis of α-phellandrene contributes to the significant blue haze and intense and frequent nocturnal nucleation events observed over Eucalypt forests. Characterisation and parameterisation of both the gaseous and particle phases formed from the ozonolysis of α-phellandrene therefore better our understanding of the impact of biogenic emissions and begin to enable the inclusion of this potentially important monoterpenic future atmospheric models.

Data availability. A website dedicated to the smog chamber is currently under construction and will include all chamber data. In the meantime, original data pertaining to this work can be obtained upon request from Xinming Wang (wangxm@gig.ac.cn).

The Supplement related to this article is available online at https://doi.org/10.5194/acp-17-6583-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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3.5. α-PHELLENDRENE OZONOLYSIS


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3.5. α-PHELLANDRENE OZONOLYSIS


Article Supplementary Information

Supplementary information for the published article, ‘Ozonolysis of α-phellandrene – Part 1: Gas- and particle-phase characterisation’, consists of 8 sections, as listed below. The supplementary entries S.2 and S.3, which respectively describe the fragmentation pattern of α-phellandrene in the PTR-TOF and the optimisation of the PTR-TOF drift tube energy, are discussed in detail in Section 3.2.2 and so are not repeated. Similarly, all the information pertaining to supplementary entry S.5, which discusses the changes made to the default AMS fragmentation table, can be found in Section 3.2.5 and has duly been removed to avoid content repetition. The remaining Supplementary sections, S.1, S.4, S.6, S.7 and S.8, are now provided in their published form.

S.1 α-phellandrene Degradation Mechanism

S.2 α-phellandrene PTR-TOF Fragmentation

S.3 PTR-TOF Drift Tube Settings

S.4 Peaks m/z 167, 169, 185 – Dimers?

S.5 AMS Fragmentation Table

S.6 Discussion of Gas-Wall Losses

S.7 Comparison of SMPS and AMS Aerosol Mass Loadings

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Supplement of

Ozonolysis of α-phellandrene – Part 1: Gas- and particle-phase characterisation

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S.1  α-phellandrene Degradation Mechanism

Addition of O₃ to the double bonds in α-phellandrene occurs through the well-established Criegee mechanism (Johnson and Marston, 2008), forming primary ozonides POZ1 and POZ2. These structures can rapidly interconvert (Mackenzie-Rae et al., 2016), and decompose to yield four Criegee intermediates, CI1, CI2, CI3 and CI4, as shown in Figures S.1.1 and S.1.2. The CIs, stabilised or chemically activated, can decompose through unimolecular processes as those described in this supplementary entry, with thermalised CIs additionally able to partake in bimolecular reactions with available atmospheric species (Johnson and Marston, 2008; Vereecken and Francisco, 2012). The following discussion, though not exhaustive, does provide an overview of what are thought to be the most important pathways in the ozonolysis of α-phellandrene, leading to the second-generation product ions detected by the PTR-TOF.

Figure S.1.1. Mechanism of O₃ addition to the more substituted double bond in α-phellandrene up to first-generation products. Species in boxes had ions of their
corresponding mass detected by the PTR-TOF, with arrows showing detected masses correlating to products formed from a second ozonolysis. A more exhaustive description of the mechanism originating from CI3 is provided in Fig. 7 of the main text.

**Figure S.1.2.** Mechanism of O3 addition to the less substituted double bond in α-phellandrene up to first-generation products. Species in boxes had ions of their corresponding mass detected by the PTR-TOF, with arrows showing detected masses correlating to products formed from a second ozonolysis.

### S.1.1 Hydroperoxide Channel

Excited syn-CIs can access the hydroperoxide channel, whereby the CI rearranges via a syn-sigmatropic hydrogen shift into a vinyl hydroperoxide, before dissociating into an OH and alkyl radical (Johnson and Marston, 2008; Vereecken and Francisco, 2012). Further reactions of the alkyl radical lead to a range of multifunctional products. This channel is generally used to explain OH radical formation during alkene ozonolysis, with experimental OH yields suggesting it is
accessed approximately $35 \pm 12\%$ and $15 \pm 7\%$ of the time by α-phellandrene and its first-generation degradation products respectively.

Conventional thought is that the hydroperoxide channel proceeds through a 1,4-hydrogen shift (Johnson and Marston, 2008), with the mechanism shown for CI2 and CI4 in Figures S.1.1 and S.1.2, yielding HP2 and HP4. Subsequent decomposition through OH loss follows, with an oxygen molecule adding to the 2-oxo-alkyl radicals yielding the peroxo radicals RAD2 and RAD4. The peroxo radicals can react with other peroxo radicals or atmospheric species to give alkoxy radicals OX2 and OX4, or react with other peroxo radicals in a disproportionation reaction to form α-hydroxycarbonyls (ROH2, ROH4) and α-dicarbonyls (CARB4). The alkoxy radicals formed from the hydroperoxide channel of CI2 and CI4 have a number of possible fragmentation and rearrangement reactions however, given the presence of α-carbonyl groups, fragmentation into CHO and a dicarbonyl species (CARB3, CARB7) is thought to dominate (Jenkin et al., 1997; Vereecken and Peeters, 2009). The alkoxy radicals can also react with HO2 to form the α-hydroxycarbonyls ROH2 and ROH4, whilst OX2 can also react with O2 to produce CARB4.

Whilst a conventional 1,4-hydrogen shift is available in CI1 by engaging the syn-methyl group, theoretical calculations showed an allyl-resonance stabilised 1,6-hydrogen shift to form HP1 is exceedingly favoured (Mackenzie-Rae et al., 2016). An analogous channel forming HP3 from CI3 also exists, which is important, as conventional 1,4-hydrogen shifts are structurally unavailable in CI3. Upon loss of OH, electron density is spread over 3 carbons, providing multiple quasi-radical sites for oxygen addition. Theoretical calculations suggest all canonical structures contribute, with formation of the more stable tertiary peroxo radicals shown in Figures S.1.1 and S.1.2. After oxygen addition, resonance effects are no longer important, with the reaction mechanism proceeding as described for CI2 and CI4. Decomposition of OX3 yields the dicarbonyl CARB3. The major product expected from the decomposition of OX1 is CARB2. Meanwhile the isopropyl radical can form acetone, acetaldehyde and formaldehyde, all of which are detected in large quantities in the PTR-TOF. Multiple fragmentation and re-
arrangement (e.g. 1,5-H shift) reactions are also possible for all radical species produced in the hydroperoxide channel of α-phellandrene CIs, with a plethora of products expected (Atkinson, 1997; Atkinson and Arey, 2003), the detail of which extends beyond the scope of the present study.

S.1.2  Ester or ‘Hot’ Acid Channel
Excited CIs can additionally re-arrange to form dioxiranes, although theoretical calculations show this to only be competitive for anti-conformers of CI2, CI3 and CI4 to form DIO2, DIO3 and DIO4 respectively (Mackenzie-Rae et al., 2016). Dioxiranes are known to rearrange to acids and esters (Vereecken and Francisco, 2012), with theoretical calculation showing re-arrangement of DIO2 and DIO4 to epoxides EPOX2 and EPOX4 is also possible. This reaction has precedence in the organic literature where dioxiranes are used as strong epoxidising agents (Murray, 1989). Epoxidation saturates the molecule, such that further reaction with ozone is unlikely. Nevertheless m/z 185 was not observed to increase rapidly upon commencement of the reaction indicating that epoxide formation is either of minor importance or lost during sampling and detection by the PTR-TOF like other first-generation products. For DIO1 and DIO3, theoretical calculations show ESTER1a and ESTER3 formation is favoured.

S.1.3  Stabilised CI Reactions
Excited POZs and CIs may be collisionally stabilised, yielding thermalised CIs. Theoretical calculations show the most favourable intramolecular reaction for thermalised α-phellandrene CIs is rearrangement into secondary ozonides (SOZs), forming SOZ1 from CI1 and CI2, and SOZ2 from CI3 and CI4. Rearrangement of SOZ1 and SOZ2 into acids and esters face large reaction barriers (Mackenzie-Rae et al., 2016), with the two SOZs likely to be thermalized and undergo a second reaction with ozone.

Intramolecular rearrangement occurs in competition with bimolecular reactions of CIs with available atmospheric species (e.g. HO, NO, SO, aldehydes, carboxylic acids). Inside the reactor thermalised CIs are most likely going to react with H2O, forming dicarbonyls (CARB1, CARB5) or acids (ACID2, ACID3, ACID4).
(Atkinson, 1997). The acids formed are analogous to pinonic and limononic acids, which are important SOA constituents in the ozonolysis of α-pinene (Ma et al., 2007) and limonene (Leungsakul et al., 2005; Bateman et al., 2009).

![Figure S.1.3. First-generation acids formed from the reaction of water with stabilized Cls.](attachment:image)

**Figure S.1.3.** First-generation acids formed from the reaction of water with stabilized Cls.

### S.1.4 Reactions of First-Generation Products

Ozonolysis of α-phellandrene does not break the molecule as a whole. As a result first-generation products, in general, retain olefin functionality and are susceptible to further ozonolysis. The mechanistic channels available are similar to what has been described for α-phellandrene, although now POZ decomposition segments the molecule, forming pairs of products consisting of a Cl and stable carbonyl species. An example of this is shown in Figure 5.

Figures S.1.1 and S.1.2 reference masses of products that are formed as direct carbonyl product from ozonolysis of first-generation products, which are also detected by the PTR-TOF. These include methyl glyoxal \((m/z\ 73)\), which is formed from first-generation products **CARB1**, **CARB2**, **CARB3**, **CARB5**, **CARB7**, **ROH1**, **ROH2**, **ROH4**, **ACID2** and **ACID4**, 2-propan-2-ylbutanodial \((m/z\ 129)\) which can be formed from **CARB1**, **CARB5**, **ESTER1a**, **ESTER1b**, **ESTER3** and **ACID3** and 2-propan-2-ylpropanedial \((m/z\ 115)\) which is formed from **CARB3**, **CARB7** and **ROH3**. Analogous species can be formed with different functional groups according to parent species structure, although these are not detected by the PTR-TOF and are expected to be respectively minor.

Conversely Cl fragments decompose similarly to the pathways discussed for **CI1**, **CI2**, **CI3** and **CI4** resulting in a much more varied product distribution, although
for second-generation CIs intramolecular SOZ formation (when available) is unlikely to occur due to excessive ring strain (Chuong et al., 2004). Additionally the two novel channels discussed for α-phellandrene CIs, namely a 1,6-hydrogen shift and dioxirane epoxidation are no longer available pathways for the saturated second-generation products. Smaller CI products formed upon scission of the carbon backbone likely lead to the production of the small species (< C₃) that dominate the measured gas-phase product distribution e.g. formaldehyde, acetaldehyde, formic acid and acetic acid. Additionally these smaller species are formed from fragments produced by radical-rearrangement and decomposition reactions that occur during gas-phase degradation e.g. glyoxal, acetone. Meanwhile participation of larger CI fragments formed from each of the first-generation products through the different possible mechanistic channels rapidly yields a large number of potential second-generation products expressing a variety of functionalities (Aumont et al., 2005). Detailing each of these products is out of the scope of the present study.
S.4 Peaks m/z 167, 169, 185 – Dimers?
Signals at m/z 167, 169 and 185 are relatively invariant to a second addition of ozone to the reactor, lacking the characteristic rapid increase in concentration observed for lighter product ions (Figure S.4.1). This suggests that the peaks are formed through a process supplementary to direct ozonolysis. One possible candidate is product-product reactions, such as gas-phase accretion. To test the validity of this proposition, the simple model described in Section 3.1.3 of the main manuscript was extended by including the following code:

\[ FG + FG \xrightarrow{k_4} DIMER \]  \hspace{1cm} (S.4.1)
\[ SG + SG \xrightarrow{k_5} DIMER \] \hspace{1cm} (S.4.2)

Results are plotted for Experiment 10, where the rate constants were set to \( k_4 = k_5 = 3.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) to achieve output on the same scale as the observed peaks. The model shows that a subsidiary process to the main ozonolysis scheme is capable of producing output similar to what is observed for m/z 167, 169 and 185 (Figure S.4.1), suggesting that the peaks may correspond to products of gas-phase accretion reactions. Their high molecular weights are suggestive of parent formulas such as \( \text{C}_9\text{H}_{10}\text{O}_3 \), \( \text{C}_9\text{H}_{12}\text{O}_3 \) and \( \text{C}_9\text{H}_{12}\text{O}_4 \) for m/z 167, 169 and 185 respectively. These formulas are consistent with first-generation products, although the peaks do not show the expected decay, whilst being too rich in carbon for expected second-generation products, whose formation is likely to be coupled with large parent fragmentation. It is therefore likely, although at this stage entirely speculative, that a process such as gas-phase accretion drives formation of the heavier species detected by the PTR-TOF in the ozonolysis of α-phellandrene.
Figure S.4.1. Time profiles for ozone, a typical second-generation product ($m/z$ 115) and peaks $m/z$ 167, 169 and 185 in experiment 10, along with output from a simple dimer formation model.
S.6 Discussion of Gas-Wall Losses

The volatile species propene, acetonitrile and cyclohexane were not observed to experience losses inside the GIG-CAS reactor (this study, Wang et al., 2014). Nevertheless recent studies have shown that low volatility organic gases experience considerable losses onto reactor Teflon wall surfaces (e.g., Matsunaga and Ziemann, 2010; Zhang et al., 2014; Yeh and Ziemann, 2015; Krechmer et al., 2016; La et al., 2016). Studies have observed that organic compounds are not lost to the reactor walls, but rather partition between the gas-phase and Teflon walls in a reversible process that eventually reaches equilibrium. The time required for equilibrium depends on reactor geometry, pressure, turbulence inside the reactor and diffusion coefficients. Sorption of gaseous organic compounds to the wall and corresponding desorption from the wall back to the gas-phase can be parameterised using Raoult’s law, treating the wall as a phase into which the organic compounds can partition (Matsunaga and Ziemann, 2010). The equilibrium state thus depends on compound volatility and can be modelled analogously to gas-particle absorptive partitioning, originally developed by Pankow (1994). Matsunaga and Ziemann (2010) argued that the fraction of an organic compound X that partitions into the walls at equilibrium is represented by:

\[
\frac{[X]_w}{[X]_g} = K_w C_w = \frac{C_w}{C_w^*} = \frac{R T C_w}{M_w Y_w P_L^0}
\]

where \(C_w\) is the equivalent organic aerosol mass concentration associated with the Teflon film, \(K_w\) is the gas-wall partitioning coefficient (with saturation concentration \(C_w^*\) being the inverse) and is equal to \(RT/M_w Y_w P_L^0\), where \(M_w\) is the mean molecular mass of the Teflon film, \(Y_w\) is the activity coefficient for the compound absorbed into the Teflon film, \(P_L^0\) is the liquid vapour pressure of the compound, \(R\) is the ideal gas constant and \(T\) the temperature.

Wall loss of organics occurs in competition with gas-particle partitioning. Assuming all SOA is absorbing so that \(C_{SOA}\) simply becomes \([SOA]\) and using the parameterisation of Pankow (1994).

\[
\frac{[X]_{SOA}}{[X]_g} = K_{SOA} C_w = \frac{C_{SOA}}{C_{SOA}^*} = \frac{R T [SOA]}{M_{SOA} Y_{SOA} P_L^0}
\]
The fraction of an organic compound \( X \) remaining in the gas-phase at equilibrium (\( F_g \)) relative to its total concentration can therefore be given by:

\[
F_g = \frac{[X]_g}{[X]_{total}} = \frac{[X]_g}{[X]_g + [X]_w + [X]_{SOA}} = \frac{1}{1 + \frac{C_w}{C_{SOA}} + \frac{[SOA]}{C_{SOA}}} \tag{S.6.3}
\]

For simplicity aerosol that is lost to the walls continues to be considered as constituting the aerosol phase.

Activity coefficients for ozonolysis products of \( \alpha \)-phellandrene in SOA generated from its decomposition were calculated using the method discussed in the main manuscript, with values ranging from 0.1 – 4. The mean molecular weight of the SOA is assumed to be 200 g mol\(^{-1}\) in this work. With no available constraining information the activity coefficient of compounds absorbed into Teflon walls is assumed as 1 for simplicity (Matsunaga and Ziemann, 2010; Krechmer et al., 2016). The mean molecular mass of the Teflon film is assumed to be 250 g mol\(^{-1}\) based on the masses of \(-[\text{CF}_2\text{CF}_2]_n\)- and \(-[\text{CF}_2\text{CF}([\text{CF}_3])_n\)- subunits. Using these values, and given that \( R, T \), and \( P_L^0 \) are the same irrespective of the medium the vapour is partitioning into, the fraction of an organic compound in the gas-phase at equilibrium can be equated to:

\[
F_g = \frac{1}{1 + \frac{4/5C_w + [SOA]}{C_{SOA}}} \tag{S.6.3}
\]

assuming a value of \( \gamma_{SOA} = 1 \). The value of \( C_w \) is therefore an important parameter in determining the fraction of an organic compound that remains in the gas-phase and thus available for detection.
S.7 Comparison of SMPS and AMS Aerosol Mass Loadings

Wall loss rates calculated for density corrected SMPS and V-mode AMS data using the method of Pathak et al. (2007) are given in Table S.7.1. Minor differences are observed between experiments, however overall loss rates measured by the two instruments correlate well. Determined loss rates were used to correct respective loading data.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wall Loss Rate (h⁻¹) SMPS</th>
<th>Wall Loss Rate (h⁻¹) AMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.51 ± 0.01</td>
<td>0.550 ± 0.005</td>
</tr>
<tr>
<td>2</td>
<td>0.58 ± 0.02</td>
<td>0.51 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.469 ± 0.007</td>
<td>0.482 ± 0.006</td>
</tr>
<tr>
<td>4</td>
<td>0.553 ± 0.004</td>
<td>0.520 ± 0.004</td>
</tr>
<tr>
<td>5</td>
<td>0.46 ± 0.01</td>
<td>0.539 ± 0.007</td>
</tr>
<tr>
<td>6</td>
<td>0.46 ± 0.01</td>
<td>0.55 ± 0.01</td>
</tr>
<tr>
<td>7</td>
<td>0.76 ± 0.02</td>
<td>0.72 ± 0.02</td>
</tr>
<tr>
<td>8</td>
<td>0.69 ± 0.01</td>
<td>0.72 ± 0.02</td>
</tr>
<tr>
<td>9</td>
<td>0.47 ± 0.01</td>
<td>0.525 ± 0.008</td>
</tr>
<tr>
<td>10</td>
<td>0.323 ± 0.007</td>
<td>0.326 ± 0.004</td>
</tr>
<tr>
<td>11</td>
<td>0.429 ± 0.006</td>
<td>0.479 ± 0.008</td>
</tr>
</tbody>
</table>

Table S.7.1. Aerosol wall loss rates measured by the SMPS and AMS for the α-phellandrene chamber ozonolysis experiments.

A scatter plot of total mass loading as measured by the SMPS and AMS, after correcting for wall losses, is shown in Figure S.7.1. The clustering of points around the 1:1 line indicates a general agreement between the two instruments, which is supportive of the assumption of spherical particles. The AMS systematically underrepresents aerosol yields under lower chamber mass loadings (< 100 μg m⁻³) compared to the SMPS, which is indicative of a collection efficiency of less than unity. Under larger chamber loadings (>100 μg m⁻³) data points are scattered either side of the 1:1 line. This is likely due to a cancellation of errors between the instruments, with larger particles that are cut off by the SMPS (dₘ > 750 nm) becoming more influential. Without calibrating collection
losses in the AMS, quantitative assessment remains speculative; nevertheless general agreement with the SMPS is observed.

**Figure S.7.1.** SOA particle mass loading as measured by the AMS compared to those determined by density corrected SMPS volume loading data, with wall-losses corrected for. Dashed line is 1:1.
S.8  SOA Density Parameterisation

This study used the same method for measuring particle density and particle composition as Kuwata et al. (2012); namely comparing AMS and SMPS measurements of vacuum and mobility diameters respectively for the density and using an AMS with Aiken et al. (2008) calibration factors to measure elemental composition. The parameterisation developed by Kuwata et al. (2012) for predicting densities from elemental composition is therefore expected to be applicable. Using the Kuwata et al. (2012) parameterisation densities were predicted using elemental compositions averaged over entire experiments, with results compared to measured values in the Fig. S.8.1. Results are agreeable for most experiments except for those where the densest aerosol was produced ($\rho_{\text{org}} > 1.5$ g cm$^{-3}$). For these, predicted density is under predicted signaling either incorrect compositional measurements or that the parameterisation is not applicable. The majority of training data for the Kuwata et al. (2012) parameterisation is for SOA with $\rho_{\text{org}} < 1.5$ g cm$^{-3}$, with validation experiments also utilising aerosol seed particles – a notable difference compared to experiments conducted in this work. With respect to experimental measurements, the elemental ratio calibration factors of Aiken et al. (2008) do carry significant errors and recently have been superseded by Canagaratna et al. (2015). Further testing of density parameterisations is therefore recommended.
Figure S.8.1. Comparison of predicted to measured organic material density for α-phellandrene measured in this work (crosses, size reflect uncertainty) and α-pinene measured by Kuwata et al. (2012) (black circles). Predictions are made based on elemental composition using the parameterisation of Kuwata et al. (2012). Dashed line represents 1:1, whilst dotted lines show ±12% error representing the prediction accuracy envelope claimed by Kuwata et al. (2012).
References


Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and
3.5.2 Article Presentation: Part 2

Title Ozonolysis of α-phellandrene – Part 2: Compositional analysis of secondary organic aerosol highlights the role of stabilised Criegee intermediates

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Candidate Contribution I have contributed at an overall level of about 70% to the published work. Contributions were made to all aspects of the study, including research design, conducting necessary experiments, analysing output and manuscript preparation and submission.

S. M. Saunders
(On behalf of all other co-authors)
Ozonolysis of α-phellandrene – Part 2: Compositional analysis of secondary organic aerosol highlights the role of stabilised Criegee intermediates

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Abstract.
The molecular composition of secondary organic aerosol (SOA) generated from the ozonolysis of α-phellandrene is investigated for the first time using high pressure liquid chromatography coupled to high-resolution Quadrupole-Orbitrap tandem mass spectrometry. In total, 21 prominent products or isomeric product groups were identified using both positive and negative ionisation modes, with potential formation mechanisms discussed. The aerosol was found to be composed primarily of polyfunctional first- and second-generation species containing one or more carbonyl, acid, alcohol and hydroperoxide functionalities, with the products significantly more complex than those proposed from basic gas-phase chemistry in the companion paper (Mackenzie-Rae et al., 2017a). Mass spectra show a large number of dimeric products are also formed. Both direct scavenging evidence using formic acid, and indirect evidence from double bond equivalency factors, suggests the dominant oligomerisation mechanism is the bimolecular reaction of stabilised Criegee intermediates (SCIs) with non-radical ozonolysis products. Saturation vapour concentration estimates suggest monomeric species cannot explain the rapid nucleation burst of fresh aerosol observed in chamber experiments, hence dimeric species are believed to be responsible for new particle formation, with detected first- and second-generation products driving further particle growth in the system. Ultimately, identification of the major constituents and formation pathways of α-phellandrene SOA leads to a greater understanding of the atmospheric processes and implications of monoterpane emissions and SCIs, especially around Eucalypt forests regions where α-phellandrene is primarily emitted.

1 Introduction

Aerosols are abundant in the atmosphere, playing an important role in the climate system by scattering and absorbing...
A common feature of atmospheric aerosol is the presence of condensed secondary organic material, formed as a result of oxidation of volatile organic compounds (VOCs) into less volatile, condensable, species (Jimenez et al., 2009; Kanakidou et al., 2005). With significant biogenic emissions (Guenther et al., 1995, 2012), high chemical reactivity (Atkinson and Arey, 2003) and large secondary organic aerosol (SOA) formation yields (Griffin et al., 1999; Hoffmann et al., 1997), monoterpenes are important contributors to organic aerosol globally, with their ozonolysis a dominant pathway for SOA formation and growth (Jokinen et al., 2015; Ortega et al., 2012; Zhao et al., 2015a). One monoterpenic acid for which little study has been conducted is α-phellandrene. With an ozonolysis rate constant of \(3.0 \times 10^{-15} \pm 35\% \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), α-phellandrene is one of the most reactive monoterpenes (Atkinson and Arey, 2003). α-Phellandrene has been measured in field studies in Brazil (Kesselmeier et al., 2000) and Japan (Ramasamy et al., 2016), although it has been noted that ambient detection is made difficult by its extremely high reactivity (Geron et al., 2000; Saxton et al., 2007). Believed then to be of particular importance is the abundance of α-phellandrene in extracts of numerous species of Eucalyptus (Brophy and Southwell, 2002; Li et al., 1995; Maghsoodlou et al., 2015; Pavlova et al., 2015), with Maleknia et al. (2009) and He et al. (2000) having identified α-phellandrene in emissions of various Eucalypt species in the laboratory. Native to Australasia, the remarkable adaptability, rapid growth rates and high quality wood of Eucalyptus has led to plantation forestry in more than 100 countries spanning six continents (> 20 million ha), making Eucalyptus the most widely planted hardwood forest trees in the world (Myburg et al., 2014).
This paper extends the current discussion by analysing filter samples collected during the α-phellandrene ozonolysis chamber experiments (as described in Mackenzie-Rae et al., 2017a). Samples were analysed using a combination of liquid chromatography with soft-ionisation electrospray mass spectrometry. This technique is sensitive towards polar organic molecules containing basic or acidic (ionisable) functional groups, with the technique having previous success in identifying compounds within SOA generated from monoterpene ozonolysis (e.g. Bateman et al., 2009; Camredon et al., 2010; Walser et al., 2008; Witkowski and Gierczak, 2017). The objective of this study is therefore to identify SOA constituents from the gas-phase ozonolysis of α-phellandrene, and their associated formation mechanism for the first time.

2 Method

2.1 Chamber experiments

SOA was generated and sampled during eleven dark α-phellandrene ozonolysis experiments using the indoor smog chamber facility at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS, Wang et al., 2014). The complete experimental design and details are provided in the companion paper (Mackenzie-Rae et al., 2017a). Briefly and relevant to the current discussion, α-phellandrene (10 – 175 ppb, Aldrich Chemical Company, Inc., USA) and ozone (56 – 500 ppb) were mixed in a background matrix of purified air. All experiments were conducted under low humidity conditions (RH ≤ 5%), room temperature (~298 K) and ambient pressure (~760 Torr). All but two experiments (9 and 11) had anhydrous cyclohexane (Sigma-Aldrich, 99.5%) added in sufficient quantity as an OH radical scavenger, with one of the non OH-scavenged experiments having 385 ppb of NO₂ added (experiment 11). Two experiments (6 and 7) had 800 ± 80 ppb formic acid (J&K Scientific Ltd., 98%) added as a SCI scavenger (Bonn et al., 2002; Winterhalter et al., 2009). Particle number size distributions were measured by a scanning mobility particle sizer (SMPS; TSI Incorporated, USA) (Wang and Flagan, 1990), with particle mass concentrations calculated to range from 21 – 660 µg m⁻³, whilst particle chemical composition was measured in real-time by a high-resolution time-of-flight aerosol mass spectrometer (AMS; Aerodyne Research Incorporated, USA) (DeCarlo et al., 2006; Jayne et al., 2000). Aerosol samples were collected on pre-fired Whatman quartz microfiber filters (47 mm) by pumping air through the filter at 16 – 25 slpm, for a minimum of two hours after chamber conditions had reached a steady state. Filter samples were then wrapped in foil and stored at 4°C prior to analysis. Specific starting conditions and information pertaining to SOA collection for each of the 11 experiments are presented in the Table 1.

2.2 Sample preparation and analysis

Filter samples were extracted by sonication using LC-MS Optima grade water (Fisher Scientific) as the solvent (Hamilton et al., 2008). The sample solution was then filtered through a 0.45 µm pore syringe (Millex-HA), with a further 1 mL of water added to the dry filter paper residue for a second extraction following the same method. Combined extraction samples were
then evaporated to dryness using a V10 vacuum solvent evaporator (Biotage, 36°C, 8 mbar). Lastly, the residue was re-
suspended in 500 µL of 50:50 methanol:water (Optima LC-MS grade, Fisher Scientific) solution, with dissolution aided by
the Biotage evaporator (4000 rpm). Sample exposure to ambient light was minimised throughout the extraction process. Pre-
conditioned filters, prepared by heating blank filter papers (Whatman Quartz microfiber filters, 47 mm) in a furnace at 550°C
for 5 hours, were analysed as a procedural blank following the same method.

Samples were analysed using reverse-phase high-performance liquid chromatography (HPLC) (Agilent 1100 series,
Berkshire, UK) coupled to a Q-Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Scientific). Samples (30
mL) were injected using an autosampler and separated using a Pinnacle DB C18 column with 5 µm particle size (Thames
Restek, UK). The starting mobile phase consisted of a gradient from 85% water with 0.1% formic acid (Sigma Aldrich), and
15% methanol (LC-MS Optima grade, Fisher Scientific), to 10% of the water/formic acid solution and 90% methanol over
13 minutes, before holding this ratio for a further minute. Electrospray ionisation (ESI, 35 eV) was used in both positive and
negative modes with full mass spectra scans acquired between m/z 50–750 range with a resolution of 70,000 at m/z 200.
Ions were additionally fragmented using high-energy collisional dissociation to yield tandem mass spectrometry (MS/MS)
for structural identification. The MS was frequently mass-calibrated using ESI positive and negative ion calibration solutions
(Pierce, Thermo Scientific). Data analysis were conducted using Xcalibur mass spectrometry software, assuming the only
atoms present were 12C, 13C, 1H and 16O in the negative ionisation mode in addition to 23Na in the positive ionisation mode.
Analysis of the pre-conditioned filters showed only baseline noise, confirming that the peaks in the chromatograms were not
due to artefacts of sample preparation. No evidence of methylation, which has been reported in other works using methanol
as the extracting solvent (Walser et al., 2008), was observed in any of the tandem mass spectra.

3 Results and discussion

3.1 Product identification

Because all first- and second-generation products of α-phellandrene ozonolysis contain at least one functional group that is
capable of ionisation (Mackenzie-Rae et al., 2016, 2017a), it is reasonable to assume that a high proportion of water soluble
SOA components will be observed, with the analyte R being observed as [R–H]− ion in the negative mode and [R+Na]+ ion
in the positive mode. Negative mode analysis leads to formation of deprotonated ions; hence molecules containing functional
groups that readily lose a proton, such as carboxylic acids, are frequently observed in this mode. Meanwhile in positive mode
analysis, ions are produced by protonation or cationisation with sodium ions (Na+), which are present in the glassware used
and, in the case of oxygenated functionalities, can improve detection and sensitivity (Hamilton et al., 2008). Hence groups
that more readily accept a positive charge, such as carbonyls, are often observed in positive mode analysis, which are
expected to be dominated by sodium ion adducts (Camredon et al., 2010). Accurate mass measurements were used to assign
molecular formulae to SOA components with mass accuracy of less than 2 ppm. α-phellandrene has an interesting structure
for understanding SOA formation mechanisms. It has two double bonds within the ring; reaction with ozone at the first bond opens the ring, while the second ozone addition causes fragmentation. Thus the dominant SOA components from the first oxidation will likely have 10 carbons. Those produced from the second will have seven or three carbons, with the latter unlikely to form significant SOA mass. The following sections will focus initially on the composition of SOA formed during standard α-phellandrene ozonolysis experiments. The final section will focus on the impact of adding a SCI scavenger during the experiments.

3.1.1 Negative mode

The chromatograms produced using negative mode ionisation were reasonably consistent across the experimental suite, showing the same characteristic major peaks irrespective of experimental conditions. Two example chromatograms, from experiments with and without formic acid, are shown in Fig. 1 with major peaks detected across all experiments labelled in retention time order. Using high mass accuracy tandem mass spectra, the structure of 12 major compounds have been identified (Table 2), with structural elucidation consistent with postulated degradation mechanisms (Mackenzie-Rae et al., 2016, 2017a). Labelled tandem mass spectra are provided in the Supplement (Sect. S1). All identified species contain carboxylic acid functionality, with a characteristic loss of 44 Da from the parent signal observed in all tandem mass spectra, showing a clear bias in negative mode ESI towards compounds containing acid functionality.

The peak at retention time 7.06 minutes (N8) is the major peak in all negative mode chromatograms, with [M–H] = m/z 159 and a neutral formula of C7H12O4. A molecular formula with 7 carbon atoms indicates a second-generation product. In addition to a loss of 44 Da, the tandem mass spectra is also characterised by a loss of 18 Da, suggesting the presence of further functionalisation, in this case likely an alcohol group. Two plausible isomeric species have been suggested based on this information (Table 2). As shown in Fig. 2 for one isomer, acid formation occurs through stabilisation of the CI from one ozone addition, whilst the CI from the other addition decomposes via the hydroperoxide channel; whereby the excited CI isomerises through a H-shift to form a vinylhydroperoxide which subsequently decomposes into a vinoxy radical and a hydroxyl radical (Johnson and Marston, 2008; Niki et al., 1987). Molecular oxygen then adds to the vinoxy radical which ultimately yields an alcohol group. Both of these are major reaction pathways and can explain the high abundance of compound N8 in α-phellandrene SOA. Theoretical results show the energy barrier for accessing the hydroperoxide channel from the primary CI generated from the more substituted double bond is around 20 kJ mol–1 lower in energy than the respective barrier for accessing the hydroperoxide channel from the relevant CI from the less substituted double bond (Mackenzie-Rae et al., 2016). Based on this information, the secondary-alcohol isomer (formation mechanism shown in Fig. 2) is favoured as compound N8.

Alternatively, if the peroxy radical formed during the hydroperoxide channel were to form a ketone rather than an alcohol, then compound N1 would be formed, as shown in Fig. 2. This product was identified at retention time 3.81 minutes, with a
[M–H] = m/z 157 and a neutral formula of C₇H₁₀O₄. The mechanism yielding adjacent aldehyde and ketone functional groups is only accessible for the Cls formed from ozonolysis of the more substituted double bond in α-phellandrene, with the other Cls unable to form a ketone without fragmenting, due to the α-carbons being tertiary. This comparative lack in mechanistic flexibility, along with a higher vapour pressure, may explain why compound N1 is relatively minor compared to N8.

The prominent peaks at retention times 5.01 (N4) and 5.39 minutes (N5) are due to isomeric molecules with [M–H] = m/z 175 and a neutral formula of C₇H₁₂O₅. These two peaks are observed in all samples analysed, with varying relative intensities. Tandem mass spectra for these two species are similar with a number of common ion peaks, suggesting similar structures containing acid and hydroxyl functionalities, differing only by positioning of these functional groups within the molecule. Nonetheless, a small number of minor differences in MS/MS fragmentation enables structural elucidation. N4 is formed through initial ozonolysis of the least substituted double bond, with the second addition of ozone participating in the hydroperoxide channel on the fragment C₇ backbone, before undergoing a number of isomerisations, as shown in Fig. 3. Meanwhile N5 is formed from ozone addition occurring in the reverse order. In general, the peak area of N4 is around twice as large as that for N5. The exact structures were confirmed by comparison to reference spectra available in the online mzcloud database (https://www.mzcloud.org/), with similarities of 94 and 96 % for N4 and N5 respectively (see Supplement Sect. S1). Given vapour pressures are likely to be very similar (Table 2), this observation suggests that either initial attack at the least substituted double bond in α-phellandrene is favoured, or the CI formed from ozonolysis of the more substituted double bond in α-phellandrene is more likely to participate in the hydroperoxide channel than the CI from ozonolysis of the less substituted double bond, both of which are consistent with recent theoretical findings (Mackenzie-Rae et al., 2016).

Relative to compound N8, peak areas for N4 and N5 are suppressed upon introduction of NO₂ into the system (experiment 11, also no cyclohexane). Similar inhibition is not observed in the other ozonolysis experiment where cyclohexane was not added (experiment 9); thus it is concluded that it is the addition of NO₂ to the system that precludes formation of compounds N4 and N5 by preferentially reacting with the acyl peroxy radical. Therefore it is expected that compounds N4 and N5 become increasingly significant contributors to SOA generated from α-phellandrene under increasingly ‘NOₓ-limited’ conditions.

Peaks at retention times 4.15 (N2) and 4.86 (N3) minutes are found consistently among the chromatograms from all samples, and correspond to products with [M–H] = m/z 145 and 187 and neutral formulas of C₆H₁₀O₄ and C₇H₈O₆ respectively. The high oxygen content of both products indicates that at least one of the ozone additions decomposes through the hydroperoxide channel, with further intramolecular H-transfers and oxygen additions possible throughout radical decomposition (Crounse et al., 2013; Kurtén et al., 2015). Proposed structures for compounds N2 and N3, derived from tandem mass spectra (Supplement Sect. S1), are given in Table 2.
Compound N6 and N7 at retention times 6.01 and 6.23 minutes, have a [M–H]– = m/z 143 and are assigned a neutral formula of C7H12O3. These species are formed through the CIs from both ozone additions being stabilised, resulting in aldehyde and carboxylic acid functionality as shown in Fig. 2 for N6. The impact of a SCI scavenger on the relative abundance of these species is discussed further in section 3.5.

Observed in the majority of chromatograms, compound N11 has [M–H]– = m/z 185 and a neutral formula of C9H14O4, with a diacid functionality proposed. However gas-phase formation of N11 (Supplement Sect. S2) is only possible through a hydroperoxide pathway that has been shown by theoretical calculations to be uncompetitive (Mackenzie-Rae et al., 2016). Furthermore, whilst compound N11 shows consistency with the tandem spectrum, a loss of 88 Da that may be expected for a diacid is not observed. Therefore the proposed structure of compound N11 is only tentative, and potentially involves unconsidered surface or condensed phase chemistry.

Compound N13 is present in all chromatograms as a major peak with a retention time of 9.92 (except for experiment 11 which had NO2 added) and has [M–H]– = m/z 183 and a neutral formula of C10H16O3. The tandem mass spectrum is relatively uninformative, being dominated by a fragment ion at m/z 139, suggesting that loss of the carboxylic acid group results in a stable ion. Given this information, compound N13 is ascribed to the first-generation acids (Table 2), with the exact isomer unable to be determined. First-generation acids are predicted to be major first-generation products in the gas-phase (Mackenzie-Rae et al., 2016), and so their detection in the particle phase is not surprising given their low vapour pressures.

Compound N12, observed in all chromatograms, has a [M–H]– = m/z 199 and is assigned a neutral formula of C10H16O4. As discussed in section 3.5, the peak area of this species is reduced in the presence of a SCI scavenger. Only two main fragment ions are formed (loss of CO2 and CO2+H2O) and further fragmentation using MS3 yielded no additional ions. Two potential structures have been proposed. The first is a compound formed through the hydroperoxide channel undergoing a 1,6-H shift isomerisation, as proposed in Mackenzie-Rae et al. (2016), with a schematic shown in Fig. 4. However this pathway would not be inhibited by the addition of a CI scavenger, as it is predominantly formed through re-arrangement of excited CIs. Alternatively, N12 can be attributed to a diacid. One possibility is that the diacid forms through abstraction of the aldehydic hydrogen by the CI, as shown in Fig. 4. The mechanism however, which was first proposed by Ma et al. (2007) to explain pinonic acid formation from a-pinene, was shown to be uncompetitive with competing pathways by computational calculations (Mackenzie-Rae et al., 2016). An alternative prospect is that aldehyde groups are oxidised to carboxylic acids, increasing the mass by 16 Da, in a process that has been proposed to occur non-negligibly in the aerosol phase (Walser et al., 2008). For example, first-generation acids such as N13 could be oxidised to diacids. Therefore the current proposal of compound N12 remains tentative. Similarly, compound N9, observed at a retention time of 7.51 minutes, can form through oxidation of the carbonyl group in N12 to an acid. N9 is observed as a minor product in the majority of chromatograms, with a [M–H]– = m/z 215 and a neutral formula of C10H16O5. The tandem mass spectrum is supportive of a diacid. Alternatively,
the same product can be formed following the same pathway as N12 with an additional 1,7-H shift between the acyl groups before radical termination, as shown in Fig 4.

3.1.2 Positive mode

Chromatograms produced from positive mode analysis are reasonably consistent across the experimental dataset showing similar major product peaks, with the chromatogram from a representative experiment shown in Fig. 5. Tandem mass spectra from the positive mode however offers little structural insight, with identity of the major product peaks listed in Table 3 tentatively assigned based on mass to charge ratios and mechanistic insight (Mackenzie-Rae et al., 2016, 2017a). Preference is given to structures containing at least one carbonyl group, consistent with positive mode ESI charging mechanics. Where overlap is observed with negative mode spectra, the same species are reassigned. For example, compound N8 is found in the positive mode at a similar retention time of 7.17 minutes, with [M+Na]\(^+\) = 183. Given this, the P3 hydroperoxide containing isomer shown in Table 2 is assigned to the peak at 8.75 minutes. A corollary is that acidic isomers detected in the negative mode are unlikely to be responsible for peaks in the positive mode if corresponding retention times are significantly different.

A dominant feature of all positive mode chromatograms is the large peak at retention time 5.06 minutes, which has [M+Na]\(^+\) = m/z 151, and is assigned a neutral formula of C\(_7\)H\(_{12}\)O\(_2\). This species is assigned to the major second-generation product P1, a dicarbonyl species. Similarly, compound P2 ([M-H]^− = m/z 137, C\(_6\)H\(_{10}\)O\(_2\)) is also a major dicarbonyl second-generation product, with P1 and P2 having both been detected in the gas-phase (Mackenzie-Rae et al., 2017a). Estimated vapour pressures support their primary residence in the gaseous phase (Fig. 6). However, given their expected high gas-phase concentrations, coupled with high aerosol loadings for most experiments inside the reactor, it is not unreasonable to assume enhanced partitioning of these prominent intermediate-volatile gas-phase species (Leungsakul et al., 2005; Walser et al., 2008). In addition, they may be present as a result of decomposition of larger species during the analysis.

The heaviest two products observed in the positive ionisation mode, P7 and P8, are attributed to peroxide containing products from the hydroperoxide channel that have undergone additional intramolecular hydrogen abstractions and molecular oxygen additions. Termed autoxidation, this process has been used to explain aerosol formation from the reaction of monoterpenes with ozone in relatively clean environments, as it can result in the formation of compounds of extremely low volatility (Ehn et al., 2014; Jokinen et al., 2015). As shown in Fig. 6, the saturation vapour concentrations of P7 and P8 are not sufficient for nucleation, however their presence in the filter samples suggests autoxidation is occurring during α-phellandrene oxidation, with it entirely possible that, upon further intramolecular H-transfers, species of the volatilities discussed in Ehn et al. (2014) and Jokinen et al. (2015) may be formed.
3.2 Product vapour pressures

Whilst the SOA analysed consists of a complex mixture of compounds, chromatographic analysis suggests that the SOA is dominated by a small number of major constituents. To assess the validity of identified products of differing functionalities as major aerosol constituents, saturation vapour concentrations (C*, µg m$^{-3}$) for all predicted compounds were estimated (method is described in Supplement Sect. S3) with results given in Tables 2 and 3, and plotted in two-dimensional volatility oxidation space in Fig. 6. Vapour pressures were found to span almost 10 orders of magnitude, indicating considerable variability in volatilities of proposed particle-phase products. At the organic particle mass loadings found during the chamber experiments (20 – 660 µg m$^{-3}$), organic compounds of intermediate volatility (IVOCs) are expected to primarily reside/partition into the gaseous phase, and therefore be minor contributors to the particle phase (Donahue et al., 2012).

Compounds classified as semi-volatile organics (SVOCs) are likely to have sizeable mass fractions in both the gaseous and aerosol phase at mass loadings encountered during chamber experiments, whilst those low volatility organic compounds (LVOCs) are thought to exist predominantly in the particle phase (Donahue et al., 2006, 2012).

Figure 6 shows the most prominent peaks detected in both the positive and negative mode chromatograms (namely m/z 160, 176, 184 and 200) are IVOCs and SVOCs. Three products were determined to be of low volatility, with these all C$_{10}$ species with between 5 and 7 oxygen atoms, whilst both first- and second-generation species are classified as SVOCs. Of the 21 products or product groups identified, 11 are C$_{7}$ or smaller second-generation products, with the increase in volatility associated with losing at least three carbons compensated in part by the decrease in volatility resulting from increased functionalisation, as shown in Figure 6. For both first- and second-generation products there is a clear negative correlation between C* and O/C, with an offset due to the size of the hydrocarbon backbone between generations.

Figure 6 shows that none of the major particle phase species detected are classified as having extremely low volatility (ELVOCs), which has been argued as being a necessary requirement for compounds to homogenously nucleate upon supersaturation (Donahue et al., 2013; Heaton et al., 2007). The detected compounds are therefore unlikely to be responsible for the rapid burst of freshly nucleated aerosol observed upon α-phellandrene reacting with ozone (Mackenzie-Rae et al., 2017a), but rather they progressively condense onto the nucleated core once aerosol clusters have grown past a critical size.

For the ozonolysis of other monoterpenes, ELVOC formation has been proposed to occur through gas-phase accretion reactions (Bateman et al., 2009; Camredon et al., 2010; Heaton et al., 2007, 2009; Lee and Kamens, 2005; Tolocka et al., 2004) and autoxidation processes (Ehn et al., 2014; Jokinen et al., 2015). Higher mass compounds possibly formed as a result of these reaction pathways were detected in both positive and negative mode spectra, and are discussed further in the following section.
3.3 High-resolution mass spectral analysis

In order to investigate the overall composition of the SOA, an average mass spectrum was produced of the section of the chromatogram where SOA components eluted (i.e. not including the dead volume or the final gradient equilibrium period). Figure 7a shows a representative mass spectrum in the m/z range 50 – 400 obtained in the positive mode (experiment 10). The spectrum contains over 280 peaks with intensities exceeding 0.5% of the most abundant peak at m/z 223. An example negative mode spectra is shown in Fig. 7b, and contains over 200 peaks in the m/z range 50 – 450 with intensities exceeding 0.5% of the most abundant peak at m/z 199. In both spectra, peaks are predominantly clustered into wide groups separated by 14 amu (CH$_2$). The two spectra are explicitly compared in Fig. 7c by subtracting $^{23}$Na from the positive mode spectrum and adding $^1$H to the negative mode spectrum, making the plot pertinent to the neutral analytes. Depending on the experiment, either the peak at m/z 160, 176 or 200 is the most intense. The compounds at MW = 200 Da correspond to the dominant first generation SOA products at C$_{10}$H$_{16}$O$_4$ (N12, P6 isomers), whereas the compounds at MW = 160 and 176 Da correspond to the dominant second generation SOA products at C$_7$H$_{12}$O$_4$ (N8, P3 isomers) and C$_7$H$_{12}$O$_5$ (N4 and N5) respectively. Therefore the ratio of these is a reflection of the degree of oxidation that had occurred when the filter samples were collected. Other abundant peaks routinely found in both the positive and negative ion mode spectra include m/z 144, 186 and 216, corresponding to products N6/N7, N11 and N9 respectively. There are some differences in the two spectra as a result of different ionisation efficiencies of SOA components. In addition, the larger downward peaks in the negative mode at m/z 156 and m/z 140 in Fig. 7c, are actually the result of a loss of CO$_2$ due to in-source fragmentation from SOA components at MW = 184 Da and MW = 200 Da. This highlights that caution is needed if a direct ESI with no prior separation approach is used. The assigned chemical formulas were also used to generate Kendrick plots, shown in the Supplement (Sect. S4), to investigate homologous families of molecules based on either CH$_2$ (KM$_{CH2}$) or O (KM$_O$) units. Although the spectral distribution is similar in both modes, there are sufficient differences that analysis of both ionisation modes is necessary for complete characterisation of SOA composition.

3.4 Analysis of dimer products

A recognisable feature of the mass spectra in both modes in Figure 7 is the presence of monomers up to about m/z 250, followed by dimers from m/z 250 – 500, corresponding to two oxygenated α-phellandrene product units. Similar clustering of peaks in mass spectra from SOA generated by monoterpene ozonolysis has been extensively reported (Bateman et al., 2009; Camredon et al., 2010; Heaton et al., 2007; Reinhardt et al., 2007; Tolocka et al., 2004; Walser et al., 2008). The intensity of the oligomeric signals are lower than the major monomeric peaks, and remain fairly consistent across the dimer domain. Proposed formulas range from C$_{12}$H$_{22}$O$_{13}$ to C$_{14}$H$_{20}$O$_{13}$. Whilst relative intensities are lower than monomeric species, dimers by nature contribute more mass and so are likely to have an important impact on the aerosol phase, especially in nucleation and early growth processes. Metrics such as O/C and H/C ratios, Kendrick mass defects and the double bond equivalency index (DBE) can be used to identify structural similarities and functionalities of SOA samples.
Species identified in the positive and negative modes, using the average mass spectra in Figure 7, are plotted in Van Krevelen space in Fig. 8. The majority of products have O/C ratios between 0.3 and 0.7, and H/C ratios between 1.5 and 1.7. The species detected show significant variation in elemental composition, although no significant differences in the distribution between products detected in positive and negative modes was observed. Furthermore, the distribution of monomer and oligomer species is similar, with oligomers having a similar average O/C but a narrower O/C range.

Using assigned chemical formulas, DBEs were calculated for all major spectral peaks (RI > 5%). Peaks containing an odd mass were taken as corresponding to molecules with one $^{13}$C atom and were subsequently excluded. Calculated DBE values are plotted against carbon number in Fig. 9, with markers scaled by peak intensity (from SOA collected in experiment 10). The DBE values for major spectral components in the positive and negative modes were found to range from 2 – 5, with the largest peaks being monomers with a DBE of 2 or 3. The results suggest that most first-generation C$_{10}$ products likely contain one C=C double bond and two C=O groups, whilst saturated second-generation C$_{7}$ species contain two to three C=O bonds.

Heavier oligomeric species have a DBE ranging from 3 to 5. A clear split can be seen in the SOA composition between monomers containing 10 or less carbons and oligomers. The smallest dimers at C$_{12}$ are likely the result of reaction between two C$_{6}$ monomers, whilst the group at C$_{13}$ is likely the result of reaction between either a C$_{6}$ and C$_{7}$ monomer, or a C$_{10}$ and a C$_{3}$ product, formed from reaction at the second double bond. A further, more numerous group at C$_{15}$–C$_{20}$ is also seen and is likely a combination of a wider variety of C$_{7}$-C$_{10}$ species. Considering the DBEs of the base monomeric species, dimeric DBEs are consistent with oligomer formation through SCIs, peroxyhemiacetal and hemiacetal mechanisms. This is because the cumulative DBE of two monomers decreases by one upon accretion through these mechanisms. In contrast, for oligomerisation pathways involving dehydration, such as aldol condensation and esterification, the DBE is additive when going from monomers to a dimer. Given the prominence of monomeric species with a DBE of 3, one would expect to see dimeric products with a DBE of 6 if condensation pathways were significant. Of the remaining considered accretion pathways, hemiacetal formation has previously been found to be thermodynamically unfavourable (Barsanti and Pankow, 2004), whilst peroxyhemiacetals are likely to be thermally labile and thus potentially unstable when subject to high temperatures during ESI ionisation (Camredon et al., 2010; Suratt et al., 2006). It is therefore concluded that oligomerisation through bimolecular reaction of SCIs is likely to be the major accretion process from α-phellandrene ozonolysis under chamber simulation conditions.

Table 4 lists the mass of potential dimers that could be formed from the reaction of select SCIs with first- and second-generation products. The majority of the proposed masses from these bimolecular addition reactions were detected in the positive and negative ionisation mode mass spectra. In the literature, Bateman et al. (2009) proposed that the dominant
oligomerisation mechanism in the ozonolysis of limonene is the reaction between SCIs and stable first-generation products, whilst Lee and Kamens (2005), Hall and Johnston (2012) and Kristensen et al. (2016) showed that reactions of SCIs with first-generation carboxylic acids are sources of dimers in the ozonolysis of α-pinene. For isoprene ozonolysis, Sakamoto et al. (2017) argued that oligomerisation occurs through an initial reaction of an SCI with an organic acid, followed by sequential insertion of SCIs. This mechanism has support from their prior study into the ozonolysis of ethylene (Sakamoto et al., 2013). Meanwhile, for linear alkenes and enol ethers, Sadezky et al. (2006, 2008) and Zhao et al. (2015b) proposed that oligoperoxides, formed from the addition of SCIs to organic peroxy radicals, are responsible for SOA formation and growth.

In addition to formation from SCIs, numerous other accretion processes have been proposed in the literature to account for particle-phase oligomers including peroxyhemiacetal formation, hemiacetal formation, aldol condensation and acid anhydride and ester formation, which are summarised in reviews by Hallquist et al. (2009), Kroll and Seinfeld (2008) and Ziemann and Atkinson (2012). These processes have been proposed to occur in the gas-phase, heterogeneously through reactive uptake on the surface of aerosols and/or via two condensed monomers. SOA products were detected at the m/z values of dimers predicted to be formed via these pathways, with different monomer combinations, and accretion pathways, resulting in multiple dimeric products of the same mass. So whilst it is likely that the reaction of SCIs is important in forming dimers, significant contributions from other accretion channels cannot be readily discounted, with further investigation necessary to determine the relative importance of discussed dimerisation/oligomerisation channels.

3.5 Impact of SCI scavenging on SOA composition

Over the last decade, many studies have shown that SCI are important precursors to SOA formation, using a range of SCI scavengers to investigate effects on yields, masses, number and composition of the particles formed. Recent results from Sakamoto et al. (2017) showed that SOA formation from isoprene ozonolysis was suppressed at high RH due to scavenging of the CH₂OO SCI through rapid reaction with water. However, a portion of the SCIs formed had lower reactivity towards water, mostly likely one or more of the corresponding C₄ SCI formed upon ozonolysis (Newland et al., 2015). In contrast, Kristensen et al. (2014) found that new particle formation and the amount of dimer-type molecules formed during α-pinene ozonolysis increased at higher RH values. Bonn et al. (2002) reported a significant decrease in new particle formation and aerosol yields at higher RH values for the ozonolysis of exocyclic monoterpenes, with number concentration only moderately affected and no significant change in yield observed for the ozonolysis of endocyclic alkenes. Recent work from Newland et al. (2017) has shown that the reaction of certain C₁₀/C₉ monoterpene SCIs with water are slower than that for CH₂OO. Therefore, the reactivity of SCI with water is structurally dependent and may determine the effect of relative humidity on reducing SOA formed via SCI oligomerisation.

Zhao et al. (2016) found that particle number and higher molecular weight products formed from the ozonolysis of α-cedrene, a C₁₅ sesquiterpene, were significantly reduced upon addition of formic acid, HC(O)OH, as a SCI scavenger.
Ahmad et al., (2017) have recently shown that adding acetic acid or acetone to limonene ozonolysis experiments significantly delayed the formation of particles leading to reduced SOA masses and a reduction in particle numbers, with acetic acid showing the strongest effect. These findings are consistent with the study of Bonn et al. (2002), who showed the addition of formic acid to have a significant inhibiting effect on nucleation and on total aerosol volume for the ozonolysis of β-pinene, with similar but less drastic changes reported for α-pinene. Similar observations were also reported in the companion paper using formic acid as an SCI scavenger in the α-phellandrene ozonolysis experiments, with SCI scavenged experiments showing a large reduction in initial particle number concentrations, suggesting a reduction in the number of SOA-nucleating agents, and lower total SOA yields (Part 1, Mackenzie-Rae et al., 2017a).

In order to investigate the impact of the SCI on the formation of dimers and SOA composition more generally, a series of experiments were carried out with high concentrations of formic acid (Table 1, experiments 6 and 7). Figure 1 shows the main differences in the chromatograms from SCI scavenged experiments were an increase in the relative amount of compounds N10 and N7, and a decrease in the amount of compounds N12 and N13. Compound N10 has [M-H] = m/z 173 and is assigned a neutral formula of C9H14O3. It is a relatively minor species in the majority of filter samples, however is observed as a major peak at retention time 7.96 minutes in the chromatograms of SOA produced with formic acid added as a SCI radical scavenger (experiments 6 and 7). Tandem mass spectra offer some insight, with losses of 44 Da and 62 Da (carboxylic acid and another oxygenated functional group). A small fragment ion at m/z 83 (C5H10O) indicates a carbonyl or acid functionality in the α-position to the branched side chain. The structure contains 8 carbons, suggesting it is formed via reaction of a C7 second-generation product and formic acid. The scavenging mechanism of SCI by formic acid is known to form a hydroperoxy methyl formate (HPMF) for the CH2OO SCI (Neeb et al., 1995; Hasson et al., 2001; Sakamoto et al., 2013). Horie et al. (1997) have detected 1-hydroperoxyethyl formate (HPEF) using FTIR spectrometry in cis/trans-but-2-ene ozonolysis experiments in the presence of formic acid, which decomposes to acetic formic acid anhydride. Liu et al. (2015) have also looked at the reaction of a range of alkyl substituted SCI with deuterated formic acid and acetic acid using photoelectron spectroscopy, directly detecting a range of partially deuterated alkyl substituted vinylhydroperoxide species formed through an acid-catalysed tautomerisation reaction. Complementary theoretical calculations predict several reaction pathways, including a barrierless insertion reaction to yield a hydroperoxyalkyl formate (Liu et al., 2015, Kumar et al., 2014). An equivalent functionalised hydroperoxyalkyl formate is shown in Fig. 10 for a major second generation SCI (Mackenzie-Rae et al., 2017a). However, the established mechanism cannot explain the formation of the observed product, as dehydration to an acid anhydride species (Neeb et al., 1995; Horie et al., 1997) forms a product with a mass 2 Da too low.

An alternative decomposition process is therefore required to explain formation of N10 from the major second-generation CIs. It is therefore proposed that formic acid can additionally participate in accretion reactions with products, driven by the high concentrations of formic acid inside the reactor. An example is given in Fig. 10, yielding the predicted product through a hemiacetal-type reaction (c.f. Hallquist et al., 2009). Whilst the proposed product could potentially match the MS/MS spectrum, the thermodynamics of its formation remain uncertain. Because aerosol yields were observed to decrease upon the
addition of formic acid (Mackenzie-Rae et al., 2017a), the net effect of the increased product contribution of N10 to the condensed phase is less than that which originates from SCIs in non-scavenged experiments.

There is also a more pronounced peak at R.T. 6.23 minutes (N7) in the formic acid experiments. The two peaks at R.T. = 6.01 min and R.T. = 6.23 min are structural isomers of C\textsubscript{7}H\textsubscript{12}O\textsubscript{3} with the acid and carbonyl functionalities on different sides of the molecule. The MS\textsuperscript{2} spectra are almost identical (loss of 44 and 46 Da, see Supplement Figs. S1.6 and S1.7), with the peak at 6.23 having a small additional peak from loss of CO (28 Da), suggesting the carbonyl is in the \(\alpha\)-position to the branched chain. The structural similarity and enhanced formation of both N7 and N10 upon addition of formic acid suggests that there may be an intrinsic relationship between the two species. One possibility is that N7 is a decomposition product of N10 or other dimeric species formed through SCI scavenging.

The two major peaks that have significantly reduced peak intensities are both C\textsubscript{10} species, containing carbonyl and acidic functionalities (N12 = C\textsubscript{10}H\textsubscript{16}O\textsubscript{4} and N13 = C\textsubscript{10}H\textsubscript{16}O\textsubscript{3}). This result further suggests that these structurally similar species are related, with N12 being formed from further oxidation of N13. The absence of a N13 peak when NO\textsubscript{2} is present suggests that formation is inhibited by NO\textsubscript{2}, which would also scavenge SCIs to form carbonyls. Interestingly, N13 is only moderately impacted when using formic acid as the SCI scavenger, implying that scavenging by formic acid may ultimately result in evolution of acid functionality, either through further degradation or catalysing CI tautomerisation (Kumar et al., 2014; Liu et al., 2015).

The experiments with formic acid were both carried out at low initial a-phellandrene mixing ratios (<20 ppb). The average mass spectra for scavenged and non-scavenged experiments carried out at very low concentrations do not show the obvious dimer region seen in Figure 7, most likely as a result of increased background interferences. In order to assess the change in the oligomer composition, the extracted ion chromatograms were compared for two experiments with and without formic acid but with similar levels of initial VOC (experiments 3 and 7). The change in the relative m/z peak areas associated with the products of reactions of the main SCIs with a range of stable carbonyl and acids for scavenged and unscavenged experiments were estimated and are shown in Table 4. A direct comparison of peak areas is complicated due to a) a large difference in the amount of SOA mass produced (121 versus 28 mg m\textsuperscript{-3}), which will change the volatility distribution of SOA, b) differences in ozone levels in the chamber, and c) the fact that dimers from different reaction pathways can result in dimers of the same mass. However, there are clear differences in the distribution of dimers between the two experiments.

Seven dimer mass peaks [MW = 288, 304 (C\textsubscript{14}), 312, 328, 344, 352, 368 Da, bold numbers in Table 4] showed a reduced peak area when the scavenger was used. Four dimer masses [MW = 256, 270, 302, 304 (C\textsubscript{13}) Da, italicised in Table 4] were more abundant when the scavenger was used. The remainder of masses in Table 4 show either similar peak areas or have inconsistencies, for example the extracted ion chromatogram of m/z 341 [M = 342 Da] has two peaks, one that is similar in both samples and one that is reduced in the presence of formic acid. The number of high mass oligomers was also
The observed change in oligomeric species distributions upon the addition of a SCI scavenger may help to explain macroscopic observations, where the number of aerosol particles observed during the initial stages of experiments were found to decrease upon addition of formic acid (Mackenzie-Rae et al., 2017a). The measured reaction rates of C₁ and C₂ SCI with formic acid have been measured to be very fast, in excess of 1x10¹⁰ cm⁻³ s⁻¹, several orders of magnitude faster than reaction with water (Welz et al., 2014). Given that the concentrations of water inside the reactor was three orders of magnitude larger than the concentration of formic acid (Table 1), the results presented here for α-phellandrene suggest that scavenging of the SCI by small carboxylic acids is much faster than the sink reaction with water, and can lead to a significant drop in the amount of dimers and hence SOA that is formed, with potentially important atmospheric implications (Sipilä et al., 2014). Further work is needed to gain a holistic understanding of SCI chemistry, principally in identifying the chemical pathways that lead to dimer formation from SCIs and characterising the chemical impact of SCI scavengers such as water, NOₓ, SO₂ and oxygenated volatile organic compounds (i.e. acids, carbonyls, alcohols) on atmospheric aerosol composition.

### 4 Conclusion

The compositional components of the organic aerosol formed from the gas-phase ozonolysis of α-phellandrene were identified and characterised for the first time, using a high-resolution Quadrupole-Orbitrap mass spectrometer. In total 21 products or product groups were identified from chromatograms, aided by tandem mass spectrometry, with electrospray ionisation used in both positive and negative modes to gain complementary compositional information. Both polyfunctional first- and second-generation products were found to be prominent in the aerosol, with products significantly more complex than those proposed from basic gas-phase chemistry in the companion paper (Mackenzie-Rae et al., 2017a). The results therefore suggest that a number of first-generation unsaturated products are sufficiently volatile to remain in the gas-phase and further react with ozone, with many of the resultant second-generation products able to partition into the particle-phase despite saturation vapour concentration estimates classifying a large number of products as semi-volatile. Oligomeric species are observed in both positive and negative mode spectra, with evidence supporting dimerisation through bimolecular reactions of stabilised Criegee intermediates. Suppression of oligomer spectral peaks upon the addition of a stabilised Criegee intermediate scavenger coincided with reduced experimental SOA growth and formation, with stabilised Criegee intermediate dimers, and/or higher order oligomers, believed to be a significant source of the highly condensable products required for the rapid nucleation and growth of new particles observed in the system (Mackenzie-Rae et al., 2017a). Further investigation is required however to better characterise the role of stabilised Criegee intermediates in the system, and to parameterise the specific accretion mechanisms occurring. Nonetheless this study has provided the first understanding of the nature of SOA formed from the ozonolysis of α-phellandrene, and more generally contributes to an enhanced knowledge of...
the atmospheric effects and implications of monoterpene emissions.

Data availability

Labelled tandem mass spectra for all identified products are provided in the Supplementary Information. Data files containing positive and negative stick spectra with prescribed OC, HC, DBE and KMD values have been archived, with the files publicly available at: www.pure.york.ac.uk (doi will be assigned when paper is accepted).

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Competing interests. The authors declare that they have no conflict of interest

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3.5. α-PHELLANDRENE OXONOLYSIS


Figure 1: Negative ionisation mode chromatogram of SOA generated from the ozonolysis of α-phellandrene in (a) a standard experiment and (b) an experiment that had formic acid added as a stabilised CI scavenger. Red line represents sample whilst black line is a preconditioned blank filter. Major negative mode ionisation peaks detected across all experiments (Table 2) are labelled.
Figure 2: Simplified ozonolysis pathway outlining the formation of some major species detected in negative mode ESI. Analogous structures can additionally be traced by varying the order of addition to the two double bonds and/or which CIs participate in the hydroperoxide (HP) and stabilisation channels respectively.

Figure 3: Proposed formation mechanism of compound N4. N5 is formed through an analogous mechanism starting with initial attack of ozone at the more substituted double bond.
Figure 4: Formation mechanisms of compounds N9 and N12.

Figure 5: Positive ionisation mode chromatogram of SOA generated from the ozonolysis of α-phellandrene. Major positive mode ionisation peaks detected across all experiments (Table 3) are labelled.
3.5. α-PHELLANDRENE OZONOLYSIS

Figure 6: α-phellandrene and detected particle phase ozonolysis products from both positive and negative ESI modes plotted in two dimensional volatility-oxidation space, constrained by saturation concentration on the x-axis and O/C elemental ratios on the y-axis. Molecular structures of products are shown. Filled and open circles denote first- and second-generation products respectively, with coloured regions indicating broad volatility classes. Volatility distribution can be compared with gas-phase species through Fig. 9 in Mackenzie-Rae et al. (2017a).
Figure 7: Representative ESI mass spectra from experiment 10 showing peaks with ≥ 0.5% abundance relative to the largest peak in the spectrum for stick spectra in the (a) positive and (b) negative modes. Comparison plot (c) shows mass spectra after subtracting $^{23}$Na from the positive $m/z$ scale (up) and adding $^1$H to the negative $m/z$ scale (down).
3.5. α-PHELLANDRENE OZONOLYSIS

Figure 8: Van Krevelen plot comparing online experimental measurements by an AMS (blue shading) (Fig. 18 in Mackenzie-Rae et al., 2017a) with assigned formulas from the ESI mass spectra (RI > 5%) in the negative mode (blue ≤ C_{16}, yellow > C_{16}) and positive mode (green ≤ C_{16}, red > C_{16}). Circle size is proportional to relative signal intensity in either mode.

Figure 9: DBE values plotted against carbon number for ions (RI > 5%) detected in the positive (open circle) and negative (closed circle) ionisation mode spectra from experiment 10. The size of data points is proportional to signal intensity.
**Figure 10:** Reaction of (a) prominent second-generation CI with formic acid and (b) accretion of major second-generation carbonyl with formic acid to yield proposed structure for compound N10. An unknown channel is required to join pathway (a) with product N10.

<table>
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<tr>
<th>Exp No.</th>
<th>Temp. (K)</th>
<th>RH (%)</th>
<th>VOC(^b) (ppb)</th>
<th>(\text{O}_3) (ppb)</th>
<th>Additives</th>
<th>Total SOA Mass ((\mu\text{g} \text{ m}^{-3}))^c</th>
<th>SOA Mass Collected (±0.01, mg)</th>
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<td>1</td>
<td>297.1 ± 0.4</td>
<td>2.5 ± 0.6</td>
<td>19 ± 7</td>
<td>&gt; 259</td>
<td>Cyclohexane</td>
<td>86 ± 9</td>
<td>0.16</td>
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<tr>
<td>2</td>
<td>297.5 ± 0.5</td>
<td>2.1 ± 0.7</td>
<td>10 ± 4</td>
<td>&gt; 86</td>
<td>Cyclohexane</td>
<td>21 ± 2</td>
<td>0.05</td>
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<td>297.2 ± 0.2</td>
<td>2.3 ± 0.6</td>
<td>21 ± 8</td>
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<td>Cyclohexane</td>
<td>121 ± 13</td>
<td>0.21</td>
</tr>
<tr>
<td>4</td>
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<td>2.2 ± 0.9</td>
<td>32 ± 13</td>
<td>&gt; 193</td>
<td>Cyclohexane</td>
<td>312 ± 33</td>
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</tr>
<tr>
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<td>297.6 ± 0.7</td>
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<td>1.6 ± 0.1</td>
<td>16 ± 6</td>
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<td>7</td>
<td>298.0 ± 0.1</td>
<td>1.9 ± 0.2</td>
<td>19 ± 8</td>
<td>&gt; 499</td>
<td>Cyclohexane</td>
<td>28 ± 3</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>298.7 ± 0.6</td>
<td>5.2 ± 0.2</td>
<td>61 ± 24</td>
<td>&gt; 56</td>
<td>Cyclohexane</td>
<td>200 ± 21</td>
<td>0.50</td>
</tr>
<tr>
<td>9</td>
<td>298.5 ± 0.4</td>
<td>4.9 ± 0.4</td>
<td>67 ± 27</td>
<td>&gt; 101</td>
<td>-</td>
<td>341 ± 36</td>
<td>2.50</td>
</tr>
<tr>
<td>10</td>
<td>298.2 ± 0.5</td>
<td>4.8 ± 0.3</td>
<td>175 ± 69</td>
<td>&gt; 174</td>
<td>Cyclohexane</td>
<td>658 ± 70</td>
<td>0.70</td>
</tr>
<tr>
<td>11</td>
<td>298.1 ± 0.4</td>
<td>4.5 ± 0.2</td>
<td>88 ± 35</td>
<td>&gt; 132</td>
<td>NO(_2) (385 ppb)</td>
<td>505 ± 53</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\)Refer to Mackenzie-Rae et al. (2017a).

\(^b\)α-phellandrene.

\(^c\)Wall loss corrected.

**Table 1:** Experimental conditions and SOA collection information for chamber experiments.
<table>
<thead>
<tr>
<th>Product ID</th>
<th>Retention Time (min)</th>
<th>Measured m/z</th>
<th>Neutral Formula</th>
<th>Possible Structures</th>
<th>$P_{vap}$ (atm)</th>
<th>$C^*$ (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>3.81</td>
<td>157.05</td>
<td>C$<em>7$H$</em>{10}$O$_4$</td>
<td></td>
<td>6 × 10$^{-7}$</td>
<td>4 × 10$^3$</td>
</tr>
<tr>
<td>N2</td>
<td>4.15</td>
<td>145.06</td>
<td>C$<em>6$H$</em>{10}$O$_4$</td>
<td></td>
<td>4 × 10$^6$</td>
<td>4 × 10$^7$</td>
</tr>
<tr>
<td>N3</td>
<td>4.86</td>
<td>187.06</td>
<td>C$<em>6$H$</em>{10}$O$_4$</td>
<td></td>
<td>4 × 10$^{11}$</td>
<td>4 × 10$^5$</td>
</tr>
<tr>
<td>N4</td>
<td>5.01</td>
<td>175.06</td>
<td>C$<em>7$H$</em>{12}$O$_5$</td>
<td></td>
<td>6 × 10$^{11}$</td>
<td>6 × 10$^5$</td>
</tr>
<tr>
<td>N5</td>
<td>5.39</td>
<td>175.06</td>
<td>C$<em>7$H$</em>{12}$O$_5$</td>
<td></td>
<td>1 × 10$^{10}$</td>
<td>1 × 10$^6$</td>
</tr>
<tr>
<td>N6</td>
<td>6.01</td>
<td>143.07</td>
<td>C$<em>7$H$</em>{12}$O$_5$</td>
<td></td>
<td>6 × 10$^6$</td>
<td>4 × 10$^4$</td>
</tr>
<tr>
<td>N7</td>
<td>6.23</td>
<td>143.07</td>
<td>C$<em>7$H$</em>{12}$O$_5$</td>
<td></td>
<td>6 × 10$^6$</td>
<td>4 × 10$^4$</td>
</tr>
<tr>
<td>N8</td>
<td>7.06</td>
<td>159.06</td>
<td>C$<em>7$H$</em>{12}$O$_4$</td>
<td></td>
<td>5 × 10$^{14}$</td>
<td>5 × 10$^7$</td>
</tr>
<tr>
<td>N9</td>
<td>7.51</td>
<td>215.09</td>
<td>C$<em>{10}$H$</em>{16}$O$_5$</td>
<td></td>
<td>3 × 10$^{12}$</td>
<td>2 × 10$^7$</td>
</tr>
<tr>
<td>N10</td>
<td>7.96</td>
<td>173.08</td>
<td>C$<em>8$H$</em>{14}$O$_4$</td>
<td></td>
<td>8 × 10$^{6}$</td>
<td>3 × 10$^6$</td>
</tr>
<tr>
<td>N11</td>
<td>8.62</td>
<td>185.08</td>
<td>C$<em>8$H$</em>{12}$O$_4$</td>
<td></td>
<td>3 × 10$^{10}$</td>
<td>1 × 10$^7$</td>
</tr>
</tbody>
</table>
Table 2: Major species detected in negative mode ESI with postulated structures consistent with composition, the mechanism proposed by Mackenzie-Rae et al. (2017a) and tandem mass spectra. Estimated saturation vapour pressures ($P_{vap}$) and saturation vapour concentrations ($C^*$) for each product are also listed. Proposed structure list is not exhaustive, with other isomers existing.
<table>
<thead>
<tr>
<th>Product ID</th>
<th>Retention Time (min)</th>
<th>Measured m/z</th>
<th>Neutral Formula</th>
<th>Possible Structures</th>
<th>P(_{\text{vap}}) (atm)</th>
<th>C* (µg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>5.06</td>
<td>151.10</td>
<td>C(<em>7)H(</em>{12})O(_2)</td>
<td>![Structure P1]</td>
<td>2 \times 10(^4)</td>
<td>2 \times 10(^6)</td>
</tr>
<tr>
<td>P2</td>
<td>6.04</td>
<td>137.10</td>
<td>C(<em>6)H(</em>{10})O(_2)</td>
<td>![Structure P2]</td>
<td>6 - 45 \times 10(^4)</td>
<td>4 - 35 \times 10(^8)</td>
</tr>
<tr>
<td>P3</td>
<td>7.17, 8.75</td>
<td>183.10</td>
<td>C(<em>7)H(</em>{12})O(_4)</td>
<td>![Structure P3]</td>
<td>4 - 64 \times 10(^4)</td>
<td>3 - 48 \times 10(^6)</td>
</tr>
<tr>
<td>P4</td>
<td>6.22</td>
<td>205.08</td>
<td>C(<em>{10})H(</em>{14})O(_3)</td>
<td>![Structure P4]</td>
<td>4 - 12 \times 10(^5)</td>
<td>4 - 11 \times 10(^6)</td>
</tr>
<tr>
<td>P5</td>
<td>6.88, 9.03, 9.36, 9.60</td>
<td>207.10</td>
<td>C(<em>{10})H(</em>{16})O(_3)</td>
<td>![Structure P5]</td>
<td>0.3 - 700 \times 10(^6)</td>
<td>0.2 - 2930 \times 10(^4)</td>
</tr>
<tr>
<td>P6</td>
<td>5.54, 6.67, 7.93, 9.80</td>
<td>223.11</td>
<td>C(<em>{10})H(</em>{16})O(_4)</td>
<td>![Structure P6]</td>
<td>2 - 65 \times 10(^9)</td>
<td>1 - 40 \times 10(^6)</td>
</tr>
<tr>
<td>P7</td>
<td>8.28</td>
<td>253.10</td>
<td>C(<em>{10})H(</em>{14})O(_6)</td>
<td>![Structure P7]</td>
<td>2 \times 10(^{11})</td>
<td>2 \times 10(^3)</td>
</tr>
</tbody>
</table>
Table 3: Major species detected in positive mode ESI with postulated structures consistent with composition and the mechanism proposed by Mackenzie-Rae et al. (2017a), along with estimated saturation vapour pressures ($P_{vap}$) and saturation vapour concentrations ($C^\ast$). Proposed structure list is not exhaustive, with other isomers existing.

<table>
<thead>
<tr>
<th>Stable Species</th>
<th>M.W</th>
<th>72</th>
<th>128</th>
<th>144</th>
<th>160</th>
<th>168</th>
<th>182</th>
<th>184</th>
<th>200</th>
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<tr>
<td></td>
<td>88</td>
<td>ND</td>
<td>216</td>
<td>232</td>
<td>248</td>
<td>256</td>
<td>270</td>
<td>ND</td>
<td>288</td>
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<td></td>
<td>104</td>
<td>ND</td>
<td>232</td>
<td>ND</td>
<td>264</td>
<td>ND</td>
<td>286</td>
<td>ND</td>
<td>304</td>
</tr>
<tr>
<td></td>
<td>144</td>
<td>216</td>
<td>ND</td>
<td>288</td>
<td>304</td>
<td>312</td>
<td>326</td>
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<td>344</td>
</tr>
<tr>
<td>SCIs</td>
<td>158</td>
<td>230</td>
<td>286</td>
<td>302</td>
<td>318</td>
<td>326</td>
<td>ND</td>
<td>342</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>232</td>
<td>288</td>
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<td>320</td>
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<td>360</td>
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<td></td>
<td>184</td>
<td>256</td>
<td>312</td>
<td>328</td>
<td>344</td>
<td>352</td>
<td>ND</td>
<td>368</td>
<td>384</td>
</tr>
</tbody>
</table>

Table 4: m/z of possible dimer products from α-phellandrene ozonolysis formed from the reaction of SCIs with non-radical ozonolysis products. Reaction of SCIs with carbonyl forms secondary ozonides whilst reaction with acids yields acyloxyalkyl hydroperoxides dimers. Masses in bold were reduced upon introduction of a SCI scavenger, masses in italics had increased abundance upon addition of a SCI scavenger and masses in normal font remained similar or were inconsistent upon introduction of a SCI scavenger. ND denotes that the proposed mass was not detected in the ESI mass spectra.
Article Supplementary Information

Supplementary information for the discussion article, ‘Ozonolysis of α-phellandrene – Part 2: Compositional analysis of secondary organic aerosol highlights the role of stabilised Criegee intermediates’, consists of 4 sections, as listed below. The supplementary entries are now provided in their published form.

S.1 Tandem Mass Spectra

S.2 Formation Mechanism of Compound N11

S.3 Saturation Vapour Concentration Estimation

S.4 Kendrick Mass Analysis
Electronic Supplementary Information

Ozonolysis of α-phellandrene – Part 2: Compositional analysis of the secondary organic aerosol highlights the role of stabilised Criegee intermediates

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S.1 Tandem Mass Spectra

Tandem mass spectra for products identified using negative mode ESI, with fragment location sites shown by red lines.

Figure S1.1: Tandem mass spectrum of compound N1.
Figure S1.2: Tandem mass spectrum of compound N2.

Figure S1.3: Tandem mass spectrum of compound N3.
Figure S1.4: Tandem mass spectrum of compound N4 with mzcloud comparison.

Figure S1.5: Tandem mass spectrum of compound N5 with mzcloud comparison.
Figure S1.6: Tandem mass spectrum of compound N6.

Figure S1.7: Tandem mass spectrum of compound N7.

Figure S1.8: Tandem mass spectrum of compound N8.
Figure S1.9: Tandem mass spectrum of compound N9.

Figure S1.10: Tandem mass spectrum of compound N10.

Figure S1.11: Tandem mass spectrum of compound N11.
3.5. α-PHELLENDRENE OZONOLYSIS

Figure S1.12: Tandem mass spectrum of compound N12.

Figure S1.13: Tandem mass spectrum of compound N13.
S.2 Formation Mechanism of Compound N11

The proposed formation mechanism of compound N11 is shown in Figure S.2 below.

![Proposed pathway for formation of compound N11.]

**Figure S2: Proposed pathway for formation of compound N11.**

The pathway involves a vinyl hydroperoxide re-arrangement which has been shown by theoretical calculations to be uncompetitive with other pathways (Mackenzie-Rae et al., 2016). Additionally the mechanism utilises unconventional 1,8-acyl H-shifts, which occur through large, thermodynamically unfavourable cyclic intermediates. As a result the proposed structure and its formation mechanism remains tentative.

S.3 Saturation Vapour Concentration Estimation

The online molecular property predictor UManSysProp (Topping et al., 2016) was used to estimate both pure component vapour pressures and activities. Vapour pressures (P_l, Pa) were estimated using the structure based estimator of Nannoolal et al. (2004) for boiling points coupled with Nannoolal et al. (2008) for vapour pressures. This method has been extensively compared with other structural estimation techniques available in the literature with favourable results (Barley and McFiggans, 2010; O’Meara et al., 2014), although it is noted that it has performed poorly when representing multi-functional organic molecules that contain a high number of hydrogen bonding groups (≥ 4). Activity coefficients (γ) were calculated for a mixed organic system using Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC, Zuend et al., 2008, 2011), and ranged from 0.46 < γ < 1.43. Saturation vapour concentrations (C*, μg m⁻³) were then calculated using these estimated parameters from the following formula (Donahue et al., 2006; Pankow, 1994):

\[
C^* = \frac{10^6 MW_{om} \gamma P_L}{RT f_{om}}
\]

where MW_{om} is the mean molecular weight of the condensed organic material (g mol⁻¹), R is the ideal gas constant (8.314 J K⁻¹ mol⁻¹), T is the temperature (K) and f_{om} is the weight fraction of the particle phase that is absorbing organic material, which is taken as unity in this work.

S.4 Kendrick Mass Analysis

Using assigned chemical formulas for major spectral peaks (RI > 5%), a Kendrick mass analysis was performed by examining CH₂ and O mass defects. Essentially Kendrick plots aid in recognition of homologous families of molecules built by repeated addition of structural units, by re-normalising the IUPAC scale to a Kendrick scale (Kendrick, 1963). In this study, the Kendrick masses KM_{CH₂} and KM₀ are calculated by normalising the exact masses of^{12}CH₂ to 14 amu and^{16}O to 16 amu respectively. Kendrick mass defects (KMD) are then calculated as the difference between the nominal Kendrick mass
(rounded up to the nearest integer) and the actual Kendrick masses. Plotting the Kendrick mass defect against the Kendrick mass creates a Kendrick plot, as shown below.

Figure S4: (a) CH$_2$ Kendrick plot and (b) O Kendrick plot for ions (RI > 5%) detected in the positive (open circles) and negative (closed circles) ionisation mode spectra. The size of the data point is proportional to relative signal intensity.

Figure S4a shows the CH$_2$ Kendrick mass plot constructed using data from both the positive and negative ionisation modes. Here species separated by CH$_2$ units fall on horizontal lines corresponding to families of the form C$_x$H$_y$O$_z$(CH$_2$)$_n$, where x, y and z are fixed and n is variable within a group. Overall, family groups contain on average 3 – 4 members with the largest containing 7, and show CH$_2$ is a common denomination between SOA constituents from α-phellandrene ozonolysis. Going towards heavier compounds there is a gradual increase in $KMD_{CH_2}$, which in general implies a higher degree of oxidation (Reinhardt et al., 2007; Walser et al., 2008), although there is a noticeable decrease in slope when transitioning from monomers to dimers.

Figure S4b shows the O Kendrick mass plot, in which horizontal lines now correspond to families of the form C$_x$H$_y$O$_z$, where x and y are fixed and z variable, that is families of species separated only by number of oxygen atoms. This time family groups averaged one member, indicating that CH$_2$ is a more common denominator than oxygen atoms between product species. This implies that fragmentation and/or accretion is more prominent in the system than functionalisation, although peaks resulting from fragmentation may skew results along with any biases in chemical formula assignment. Nonetheless numerous product families containing up to 5 species, e.g. C$_{10}$H$_{16}$O$_{3-7}$ or C$_7$H$_{12}$O$_{2-6}$, were observed, showing that radical re-arrangement and oxygen addition processes remain important.
References


3.6 Discussion of Canister Sampling

The NO$_2$ and photooxidation $\alpha$-phellandrene chamber experiments provided the only opportunity to monitor the oxidation of $\alpha$-phellandrene using the canister based methodology, given the majority of earlier ozonolysis experiments were inhibited by high cyclohexane concentrations. $\alpha$-phellandrene was detected in the GC-MS at an RT of 28.90 minutes and 28.44 minutes using the 2015 and 2016 analysis procedures and equipment respectively. Peak assignment was confirmed by positive spectral identification, shown in Figure 3.32.

Contaminant peaks, attributable to the injection of $\alpha$-phellandrene into the reactor, were also identified. The majority of these peaks have spectra consistent with monoterpenes, with $\alpha$-pinene and $\beta$-pinene positively identified using the standard calibration mixture. Concomitant monoterpenes likely exist as minor contaminants of the $\alpha$-phellandrene solution supplied by Aldrich Chemical Company, which had no accompanying purity. The most prominent contaminant peak however, eluting at an RT of 29.5 minutes in 2015 and 28.80 minutes in 2016, was assigned to $p$-cymene. Peak assignment was confirmed by positive spectral identification, shown in Figure 3.33, and did not change in area throughout the experiments, consistent with the respectively low reactivity of $p$-cymene compared to $\alpha$-phellandrene. The related signal at $m/z$ 135 was observed in the PTR-TOF, initially being assigned as an $\alpha$-phellandrene fragment. However, signal intensity was found to increase as the drift tube energy was lowered, which is characteristic of a parent species. Furthermore, the PTR-TOF signal varied very little during the conducted experiments, consistent with canister sampling, suggesting $m/z$ 135 in the PTR-TOF is solely at-

![Figure 3.32](image_url)

Figure 3.32: Positive identification of $\alpha$-phellandrene at RT 28.92 minutes in 2015. Top pane (black) shows measured spectra. Bottom pane (green) is $\alpha$-phellandrene’s mass spectra in the NIST database.
Figure 3.33: Positive identification of $p$-cymene at RT 29.48 minutes in 2015. Top pane (black) shows measured spectra. Bottom pane (green) is $p$-cymene’s mass spectra in the NIST database.

tributable to $p$-cymene. It is thought that $p$-cymene is either another contaminant in the $\alpha$-phellandrene solution, or is formed by decomposition of $\alpha$-phellandrene in the heated injection system. Unfortunately time and resources were limited when visiting the GIG-CAS chamber facility and so a thorough characterisation of the supplied $\alpha$-phellandrene solution could not be undertaken. Only $\alpha$- and $\beta$-pinene were accurately quantified in each experiment with the available standard calibration mixture, existing at concentrations less than 1 ppb. Nonetheless chromatograms, an example of which is shown in Figure 3.34 for experiment 15, indicate that $p$-cymene and at least four other monoterpenes are present. Assuming that instrument response is similar for the different monoterpenes, it is estimated that $\alpha$-phellandrene contributes to at least 90% of the $m/z$ 137 signal in the PTR-TOF.

Foreshadowed by the propene–NO$_x$ system (Section 3.4.3), there was a distinct lack of products observed using the canister based methodology for monitoring the degradation of $\alpha$-phellandrene. No product peaks were observed using either the FID or GC-MS in the dark reaction of NO$_2$ with $\alpha$-phellandrene conducted in 2015 or in the photooxidation of $\alpha$-phellandrene in 2016. This is evident in Figure 3.34, where $\alpha$-phellandrene signal decay is visible, yet no new product peaks are formed. Potential reasons for this are discussed in Section 3.4.3. It is worth noting that similar challenges were encountered by Berndt et al. (1996), who in the reaction of $\alpha$-phellandrene with NO$_3$ could not detect organonitrate products using GC-FID/MS. The authors hypothesised that losses in transfer columns, or in other parts of the detection units, were responsible for product loss.

The primary use of canisters in this work is therefore reduced to evaluating the background matrix, that is the cleanliness of the reactor prior to each experiment.
3.7. α-PHELLANDRENE + NO₂

Figure 3.34: Overlaid chromatograms from all canisters collected during experiment 15. Major peaks have been labelled. The absence of new product peaks should be noted.

The canister based methodology has a clear advantage over the PTR-TOF in this domain, as a reliable standard is available, enabling both positive structural identification and quantification. Samples of the reactor air were taken prior to the introduction of any species in order to assess the starting experimental matrix. The average chamber background for 2013, 2015 and 2016 are given in Appendix D. Canisters were taken in 2014, although could not be analysed due to a high instrument demand at the GIG-CAS that year. In all instances, the background was found to contain more than the 5 ppb of NMHCs quoted by the clean air purification system (Wang et al., 2014), with small hydrocarbons (≤ C₄) dominating the mixture. Nonetheless, the background VOCs are expected to have little impact on the results of the discussed chamber experiments, due to their relatively low reactivity and high α-phellandrene concentrations used.

3.7 α-phellandrene + NO₂

NO₂ is a free radical, containing one unpaired electron. At low temperatures NO₂ dimerises to dinitrogen tetroxide (N₂O₄), however under ambient conditions entropic effects drive the reaction generating the free radical form. Despite being a radical, it is commonly assumed that reaction with NO₂ is a negligible removal process for VOCs because reaction rate coefficients under atmospheric conditions are extremely slow (< 10⁻¹⁹ cm³ molecule⁻¹ s⁻¹) (Atkinson et al., 1984; Ohta et al., 1986; Calvert et al., 2000; Stabel et al., 2005; Bernard et al., 2013). However, this removal process is potentially important for dienes and polyconjugated alkenes under high NOₓ conditions (Bernard et al., 2013).
For α-phellandrene, a reaction rate coefficient with NO₂ of $1.1 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ was reported by Reissell et al. (1999), which is in agreement with the earlier rate of $1.3 \pm 0.43 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ reported by Atkinson et al. (1984). Despite being considerably higher than other reported NO₂ rate coefficients in the literature (Calvert et al., 2000), consumption of α-phellandrene by NO₂ remains slow when compared with other major atmospheric oxidants (see Table 1.3). Assuming the following concentrations of atmospheric oxidants: $[\text{OH}] = 2 \times 10^6$ molecules cm⁻³ (12 hour daytime average), $[\text{O}_3] = 7 \times 10^{11}$ molecules cm⁻³ (24 hour average) and $[\text{NO}_3] = 2.5 \times 10^8$ molecules cm⁻³ (12 hour night time average), then NO₂ would have to achieve a concentration greater than $\sim 500$ ppb to be of some, albeit minor, importance. High levels of NO₂ have been measured in different locations around the world using satellites, especially in mega-cities in regions of rapid economic development such as India and China (Richter et al., 2005; Ghude et al., 2008; Sheel et al., 2010; Ma et al., 2013). Meanwhile London, which has the highest NO₂ concentrations in Europe, regularly exceeds its regulatory hourly level of 200 µg m⁻³ (106 ppb) of NO₂ at its busiest and most congested roads and intersections, with historical values greater than 400 ppb having been reported (Bower et al., 1994). In more rural areas, plumes from fossil fuel burning power plants are known to be rich in NO₂. If these plumes were to transgress into forested regions then removal of α-phellandrene by NO₂ may become non-negligible. NO₂ concentrations are often higher in the indoor environment than outdoor ones, due to internal combustion processes such as cooking, cigarettes, unvented heaters and fireplaces, which can lead to concentrations up to the ppm level (World Health Organisation, 2010). Again, if α-phellandrene were introduced under these conditions, e.g. through fragrant household items, then removal by NO₂ may be important. Under these extreme circumstances, the reaction is expected to be a non-negligible source of nitrous acid and nitrogen-containing oxygenated VOCs, such as RNO₂ and ROONO₂, which are known to be toxic to humans (Finlayson-Pitts and Pitts, 2000). One final scenario where the reaction of α-phellandrene and NO₂ may be important is in chamber experiments, where artificially high levels of NO₂ are commonly encountered. This effect has been reported in the experiments of Reissell et al. (1999) who, in their study of the reaction of OH with α-phellandrene in the presence of NO, concluded that 40 – 50% of the observed α-phellandrene decay was due to NO₂, rather than the desired OH initiated reaction.

In the ozonolysis and photooxidation chamber experiments discussed in this thesis, the consumption of α-phellandrene by NO₂ is expected to be minor due to the high concentrations of other more reactive oxidants. Nonetheless, in order to provide a complete assessment of α-phellandrene, and provide information to others who might encounter scenarios where α-phellandrene is consumed by NO₂, three
### 3.7. α-PHELLANDRENE + NO₂

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Temp. (±0.5 K)</th>
<th>RH (±0.2%)</th>
<th>α-phellandrene (ppb)</th>
<th>[NO] (ppb)</th>
<th>[NO₂] (ppb)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>03/09/15</td>
<td>298.3</td>
<td>1.8</td>
<td>122 ± 46</td>
<td>11 ± 4</td>
<td>210 ± 2</td>
<td>325</td>
</tr>
<tr>
<td>13</td>
<td>05/09/15</td>
<td>297.5</td>
<td>4.4</td>
<td>315 ± 120</td>
<td>37 ± 5</td>
<td>1128 ± 6²</td>
<td>304</td>
</tr>
<tr>
<td>14</td>
<td>14/09/15</td>
<td>297.4</td>
<td>2.7</td>
<td>190 ± 74</td>
<td>8 ± 1</td>
<td>612 ± 3</td>
<td>150</td>
</tr>
</tbody>
</table>

²Added through three separate additions.

Table 3.12: Starting conditions for α-phellandrene + NO₂ chamber experiments.

Chamber experiments were conducted investigating the reaction of α-phellandrene with NO₂. All experiments were conducted in the dark, following the same general methodology described for ozonolysis experiments in Section 3.3, substituting O₃ for NO₂. Starting conditions for each of the three experiments are provided in Table 3.12.

#### 3.7.1 Gas-Phase Analysis

**Reaction Mechanism**

The reaction of NO₂ with α-phellandrene proceeds via electrophilic addition to either of the double bonds to form a nitroalkyl radical (Calvert et al., 2000), as shown in Figure 3.35. NO₂ addition to the carbon in the second position is thought to be unfavoured due to steric hindrance (Mackenzie-Rae et al., 2016) and low electron delocalisation. Meanwhile addition to carbons 3 and 6 result in products with high electron delocalisation and so enhanced stability. So, whilst six unique products can form in the reaction of α-phellandrene with NO₂, three from addition to each of the double bonds, NO₂ addition to carbons 3 and 6 is thought to dominate. The proposed mechanism for these two addition sites is shown in Figure 3.35. The abstraction of hydrogen by NO₂ has been proposed to be a minor channel (~1.5%) in the reaction of NO₂ with cyclohexa-1,3-diene (Jenkin et al., 2005) and so is ignored in this work.

The nascent nitroalkyl radical then adds O₂ to form a nitroalkyl peroxy radical, which can react with NO, NO₂ organic peroxy radicals and/or HO₂ radicals. Due to the slow decomposition and hence overall radical concentration, and high concentrations of NO₂ inside the reactor, the reaction of peroxy radicals with NO₂ to form a dinitroperoxy nitrate may also contribute. The nature of α-phellandrene + NO₂ oxidation products and their yields therefore depends on the mix of RO₂ radicals and [RO₂]/[HO₂] ratios, which differ in chamber experiments from the ambient.

Under the experimental conditions, the alkoxy radicals would be expected to react mainly with O₂, although the reaction with NO₂ to form an organo-nitrate
Figure 3.35: Proposed mechanism for the reaction of NO\textsubscript{2} with \(\alpha\)-phellandrene in the dark. Major predicted pathways are shown. Species in boxes have evidence of formation in the PTR-TOF.

... product may also contribute, considering the high NO\textsubscript{2} concentrations. Alkoxy radicals can also decompose, rupturing the 6-membered ring. Reaction with O\textsubscript{2} generates HO\textsubscript{2} radicals and hence, in the presence of NO, leads to formation of the OH radical. This mechanism has been used to explain literature observations of OH radicals in the dark reaction of alkenes with NO\textsubscript{2} (Atkinson et al., 1984; Reissell et al., 1999; Bernard et al., 2013). Nevertheless, NO concentrations are relatively low in all experiments, with HO\textsubscript{2} radicals instead sequestered by NO\textsubscript{2} in the form of HO\textsubscript{2}NO\textsubscript{2} in these experiments, reducing the impact of OH.

\[
\text{HO}_2 + \text{NO}_2 \xrightleftharpoons[M]{} \text{HO}_2\text{NO}_2
\]  

(3.29)

The first-generation products are functionalised monoalkenes for which reaction with NO\textsubscript{2} is thought to be too slow to be of any importance (Calvert et al., 2000), both in these chamber experiments and the ambient.
PTR-TOF Product Identification and Yields

Figure 3.36 shows the time profiles of major species detected during the reaction of NO$_2$ with $\alpha$-phellandrene in experiment 13. In this experiment, NO$_2$ was added in three separate additions. Furthermore, 1060 ppb of ozone was introduced 332 minutes into the experiment to assist in product identification. Signals which increase upon addition of ozone are products of both NO$_2$ and ozone addition, those which show no change are saturated reaction products of NO$_2$, and those peaks which decrease are unsaturated species. The general profiles up to 332 minutes however are characteristic of the three experiments.

Figure 3.36: Time profiles of the major species detected during the reaction of NO$_2$ with $\alpha$-phellandrene in experiment 13. Ozone (1060 ppb) was introduced at 332 minutes.
The most intense product signals in all three experiments were \( m/z \) 43, 47, 59 and 61. Based on the study of short-chain alkyl nitrates by Aoki et al. (2007) and Duncianu et al. (2017), these peaks are assigned to the compounds \( \text{C}_2\text{H}_3\text{O}^+/\text{C}_3\text{H}_7^+ \), \( \text{C}_2\text{H}_7\text{O}^+ \), \( \text{C}_3\text{H}_7\text{O}^+ \) and \( \text{C}_3\text{H}_9\text{O}^+ \) respectively, which are formed through decomposition of nitro-/nitrate-products inside the drift tube. The nitro- and alkyl nitrate products expected to dominate the product distribution are thought to adopt an ion-dipole complex conformation (\( \text{RH}.\text{NO}_2^+ \) and \( \text{ROH}.\text{NO}_2^+ \)), in contrast to the respective covalently bound configurations \( \text{RNO}_2\text{H}^+ \) and \( \text{RONO}_2\text{H}^+ \) upon protonation (Cacace and de Petris, 2000).

\[
\text{H}_3\text{O}^+ + \text{RNO}_2 \rightarrow \text{RH}.\text{NO}_2^+ + \text{H}_2\text{O} \quad (3.30)
\]
\[
\text{H}_3\text{O}^+ + \text{RONO}_2 \rightarrow \text{ROH}.\text{NO}_2^+ + \text{H}_2\text{O} \quad (3.31)
\]

The low binding energy of the formed complexes (Lee and Rice, 1992; Aoki et al., 2007) enables decomposition into \( \text{NO}_2^+ \) and either \( \text{RH} \) or \( \text{ROH} \) for nitro and nitrate containing compounds respectively. Detection of \( \text{NO}_2^+ \) (\( m/z \) 46, shown in Figure 3.36) confirms this.

\[
\text{RH}.\text{NO}_2^+ \rightarrow \text{RH} + \text{NO}_2^+ \quad (3.32)
\]
\[
\text{RH}.\text{NO}_2^+ \rightarrow \text{R}^+ + \text{HONO} \quad (3.33)
\]
\[
\text{ROH}.\text{NO}_2^+ \rightarrow \text{ROH} + \text{NO}_2^+ \quad (3.34)
\]
\[
\text{ROH}.\text{NO}_2^+ \rightarrow \text{RO}^+ + \text{HONO} \quad (3.35)
\]

Alternatively alkyl radicals can be formed directly through collision-induced dissociation of protonated alkyl nitrates formed in Reaction 3.31, through ejection of nitric acid (Aoki et al., 2007; Duncianu et al., 2017).

\[
\text{ROH}.\text{NO}_2^+ \rightarrow \text{R}^+ + \text{HNO}_3 \quad (3.36)
\]

Further collisions of alkyl or alkoxy fragments can generate the small fragment ions detected. For example, \( m/z \) 59 has been assigned to \( \text{C}_3\text{H}_7\text{O}^+ \), although using GC-MS/FID, Reissell et al. (1999) showed that no acetone was formed in the reaction of \( \text{NO}_2 \) with \( \alpha \)-phellandrene. Acetone is therefore not expected to be a reaction product in this work, with \( \text{C}_3\text{H}_7\text{O}^+ \) instead a fragment peak.

All four of these fragment peaks increased significantly in concentration upon the introduction of ozone at the end of experiment 13. This increase however is attributable to isobaric products of \( \alpha \)-phellandrene ozonolysis: formic acid (\( m/z \) 47), glyoxal (\( m/z \) 59) and acetic acid (\( m/z \) 61, 43). Yields are listed in Table 3.13 for each of these ions in the different experiments. These were calculated by comparing
product formation to the loss of $\alpha$-phellandrene, as shown in Figure 3.37, starting with data 20 minutes after the introduction of NO$_2$ to avoid interference from OH radicals. As evidenced by the faster decay rate of $\alpha$-phellandrene in the initial 10 minutes of the experiment, OH radicals are likely introduced along with NO$_2$ through either the presence of NO or via surface chemistry in the Teflon tubing (Reissell et al., 1999). Despite yields being calculated, the applicability to the assigned fragments is uncertain, as they offer little insight into the formation of specific products and are likely variable under different drift tube conditions. Furthermore, it is worth noting that in experiments 12 and 13 the concentration of $\alpha$-phellandrene showed a larger decrease than NO$_2$ over the considered reaction times, suggesting some alternative loss process for $\alpha$-phellandrene inside the reactor (e.g. vapour loss to the walls). Reported yields in this study therefore represent a lower bound.

Detected ions from first-generation products include $m/z$ 109, 133, 153 and 169. These ions all decreased upon addition of O$_3$ at the end of experiment 13. Two of these ions, $m/z$ 169 and 109, were detected in the ozonolysis experiments of $\alpha$-phellandrene and so are assigned to ions containing only carbon, hydrogen and oxygen. $m/z$ 169 is thought to be the first-generation product C$_{10}$H$_{16}$O$_2$, which can be formed through decomposition and ejection of the NO$_2$ group in the gas-phase (Figure 3.35). $m/z$ 109 is assigned to C$_7$H$_8$O$^+$, a fragment of $m/z$ 169 that is formed in the PTR-TOF drift tube, with the two peaks showing excellent correlation in the conducted experiments. The ion detected at $m/z$ 153 is assigned to C$_{10}$H$_{17}$O$^+$, which is formed from isomeric first-generation hydroxynitro-organics that eject NO$_2$ (as HONO) upon protonation (Reaction 3.33). The yield of $m/z$ 153 is given in Table 3.13, and ranges from 0.5 – 6.2%. Interestingly the carbonyl analogue, which is predicted to be a major first-generation product, was detected at $m/z$ 197. However, despite being unsaturated, its concentration did not decrease upon O$_3$ addition,
with its assignment remaining tentative. Lastly, the signal at \( m/z \) 133 is assigned to \( \text{C}_{10}\text{H}_{13}^+ \), which is thought to be a fragment of a nitro-alkylnitrate that loses both nitrogen containing functional groups, along with four hydrogen atoms. Two of the hydrogen atoms are likely lost concurrently with the ejection of the nitro and nitrate groups, with the other two hydrogens speculatively lost as \( \text{H}_2 \).

The remaining product ions are unassigned, although they are thought to be further fragments of nitro-containing products. Given the minor impact of NO\(_2\) initiation in most atmospheric situations, a more detailed analysis, retro-synthetically linking fragment products back to parent compounds, was not conducted. Overall, findings support the conclusion of Duncianu et al. (2017), that is, \( \text{H}_3\text{O}^+ \) ionisation is not appropriate for detection of alkyl nitrates due to the resulting high fragmentation, which generates intense signals of common organic analytes that are unsuitable for reliable identification of parent compounds.

### 3.7.2 Particle-Phase Analysis

#### Aerosol Formation and Yield

Due to the slow reaction of NO\(_2\) with \( \alpha \)-phellandrene, first-generation products are not expected to react. Fragmentation is therefore expected to be minor in the gas-phase, with functionalisation of the hydrocarbon backbone dominating (Kroll et al., 2009). Nonetheless, the aerosol forming characteristic of VOCs with NO\(_2\) is uncertain, with previous literature having focussed exclusively on the gas-phase (Bernard et al., 2013; Atkinson et al., 1984; Reissell et al., 1999; Jenkin et al., 2005). Nitro, nitrate and PAN functionality are all believed to significantly reduce vapour pressure of constituents (Capouet and Müller, 2006; Pankow and Asher, 2008; Compernolle et al., 2011), however similar studies investigating the reaction of monoterpenes with nitrate radicals have shown SOA yields to be variable, with anomalously low SOA yields for some monoterpenes and/or conditions, and high SOA yields for others (Fry et al., 2014; Draper et al., 2015; Nah et al., 2016b; Ng et al., 2017). Invariably SOA was formed in the reaction of \( \alpha \)-phellandrene with NO\(_2\), with analysis undertaken using the methodologies discussed in Section 3.5.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>( m/z ) 43</th>
<th>( m/z ) 47</th>
<th>( m/z ) 59</th>
<th>( m/z ) 61</th>
<th>( m/z ) 73</th>
<th>( m/z ) 87</th>
<th>( m/z ) 141</th>
<th>( m/z ) 153</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>3.4 ± 0.8</td>
<td>2.3 ± 0.5</td>
<td>10 ± 2</td>
<td>3.7 ± 0.9</td>
<td>1.2 ± 0.3</td>
<td>0.6 ± 0.1</td>
<td>0.7 ± 0.2</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>13</td>
<td>8.3 ± 2</td>
<td>4.5 ± 1</td>
<td>14 ± 3</td>
<td>6.0 ± 1</td>
<td>2.2 ± 0.5</td>
<td>1.3 ± 0.3</td>
<td>2.0 ± 0.5</td>
<td>6.2 ± 1</td>
</tr>
<tr>
<td>14</td>
<td>3.7 ± 0.9</td>
<td>5.7 ± 1</td>
<td>8.2 ± 2</td>
<td>5.2 ± 1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>

Table 3.13: Product yields (%) for ions detected in the gas-phase across the three \( \alpha \)-phellandrene + NO\(_2\) chamber experiments.
Corresponding SOA wall loss rates, effective densities, mass loadings and yields are tabulated for the three experiments in Table 3.14.

Despite the reaction of α-phellandrene and NO₂ occurring relatively slowly, appreciable SOA was still generated upon injection of NO₂ into the reactor. This phenomenon is evident in Figure 3.38, which shows the number of particles inside the reactor to increase upon reaction of α-phellandrene with NO₂. The maximum number concentration occurs over an hour after commencement of the reaction in each of the three experiments, considerably longer than the minutes required for the peak number concentration to be reached in the ozonolysis of α-phellandrene. The initial small burst of aerosol is likely the result of α-phellandrene reacting with concomitant OH radicals, with the reaction of α-phellandrene with NO₂ dominating after this. The growth in particle number after the first 10 minutes suggests that the reaction of α-phellandrene with NO₂ forms ELVOCs in sufficient quantity for homogeneous nucleation to occur, the process is just much slower than in the reaction of α-phellandrene with ozone. Furthermore, significantly less particles are formed in the reaction of α-phellandrene with NO₂ compared to ozone for the same amount of α-phellandrene consumed, suggesting that reaction with NO₂ is much less efficient at forming ELVOC vapours. Whether these differences are entirely due to the slower consumption of α-phellandrene by NO₂, or if differences in product distribution also has a role is unknown, although it is noted that SCIs are no longer formed and so an alternative ELVOC producing pathway is required. Peroxy radicals are expected to have much longer lifetimes in the α-phellandrene + NO₂ system compared to ozonolysis, due to the slower rate of precursor consumption and hence RO₂ production. This creates conditions conducive to isomerisation processes like autoxidation (Crounse et al., 2013; Ehn et al., 2014), whilst disfavouring RO₂+RO₂ oligomerisation as a source of ELVOCs. Further partitioning of vapours increases the volume of particles until eventually wall losses supersede gains, with both the number and volume concentrations slowly decreasing at the end of each of the experiments.

Assuming spherical particles, an average effective aerosol density of 1.67 ± 0.08 g cm⁻³ is obtained across the three experiments (DeCarlo et al., 2004). This density is in the range of values reported for SOA generated in the ozonolysis experiments.

<table>
<thead>
<tr>
<th>Wall Loss Rate (h⁻¹)</th>
<th>Density (g cm⁻³)</th>
<th>M_{org} (µg m⁻³)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.15 ± 0.02</td>
<td>1.66 ± 0.09</td>
<td>15 ± 3</td>
</tr>
<tr>
<td>13</td>
<td>0.20 ± 0.006</td>
<td>1.60 ± 0.09</td>
<td>194 ± 23</td>
</tr>
<tr>
<td>14</td>
<td>0.47 ± 0.01</td>
<td>1.76 ± 0.1</td>
<td>48 ± 6</td>
</tr>
</tbody>
</table>

Table 3.14: Wall loss rates, effective densities, corrected mass loadings and fractional yields for SOA generated in the α-phellandrene + NO₂ experiments.
Wall loss corrected (Pathak et al., 2007b) SOA mass loadings were found to range from 15 – 194 µg m$^{-3}$. Fractional aerosol yields are plotted in Figure 3.39. The three experiments are supportive of partitioning theory (Pankow, 1994; Odum et al., 1996), with SOA yield dependent on the amount of precursor mass consumed. Gas-wall partitioning of condensible vapours is not accounted for in yield calculations (Matsunaga and Ziemann, 2010; Zhang et al., 2014b; La et al., 2016), which is expected to be especially problematic for these experiments (more so than ozonolysis) due to the slow formation of aerosol, resulting in similar timescales for particle- and wall-partitioning. Quoted yields therefore represent a lower bound of the SOA forming potential of α-phellandrene with NO$_2$.

A two-product model fit was found to provide an excellent description of SOA yields, with $\alpha_1 = 0.21$, $\alpha_2 = 0.029$, $K_{om,1} = 0.0072$ m$^3$ µg$^{-1}$ and $K_{om,2} = 0.478$ m$^3$ µg$^{-1}$. However, four parameters were used to fit three data points, so the uncertainty in the fitted yield curve remains high. This is why no uncertainties were ascribed to the various parameters. Nonetheless, the fitted coefficients appear to suggest that a large fraction of the SOA is comprised of higher-volatility species, that is, products with lower $K_{om}$.

The fitted yield-curve is compared with the best empirical fit describing SOA yield from the ozonolysis of α-phellandrene in Figure 3.39. It is evident that the ozonolysis of α-phellandrene yields considerably more SOA than reaction with NO$_2$, especially at low mass loadings ($< 50$ µg m$^{-3}$). This evidence supports the narrative that reaction with NO$_2$ is less efficient at forming highly condensible vapours compared to ozone. SOA suppression under high NO$_2$ conditions has been observed in the literature (e.g. Presto et al., 2005b; Ng et al., 2007a; Eddingsaas et al., 2012a;
Figure 3.39: Secondary organic aerosol yield (data and empirical fit) for the reaction of \( \alpha \)-phellandrene with \( \text{NO}_2 \). Yield is compared with the best one-product model fit from the ozonolysis of \( \alpha \)-phellandrene.

Draper et al., 2015), with the kinetic dominance of the \( \text{RO}_2 + \text{NO}_2 \) channel producing metastable peroxy nitrate products. Furthermore, results are testament to the ability of the Criegee intermediate to generate highly-condensible vapours. Nonetheless, SOA generated from the addition of \( \text{NO}_2 \) to \( \alpha \)-phellandrene suggests semi-volatile nitro and nitrate products are formed, with a mass-loading dependence observed.

**Aerosol Composition**

Elemental N/C ratios measured by the AMS show aerosol nitrogen content to be low, ranging from 0.02 to 0.03. This implies one nitrogen for every 30 or more carbon atoms, in contrast to the gas-phase mechanism, where \( \alpha \)-phellandrene is consumed by \( \text{NO}_2 \) yielding a minimum N/C ratio of 0.1. Furthermore, given the high concentrations of \( \text{NO}_2 \) in the reactor, \( \text{RO}_2 + \text{NO}_2 \) reactions are likely to be important, if not the dominant fate of peroxy radicals. Farmer et al. (2010) reported that due to fast thermal dissociation, the AMS quantifies organic nitrates almost exclusively as \( \text{NO}^+ \) and \( \text{NO}_2^+ \) ions. Meanwhile, Rollins et al. (2010) report that 30% of hydroxynitrates (\( \text{R(OH)R}'\text{ONO}_2 \)) nitrogen mass is contained in \( \text{NO}^+ \) and \( \text{NO}_2^+ \) fragments, 12% at \( \text{NH}_x^+ \) fragments, 5% at \( \text{C}_x\text{H}_y\text{O}_z\text{N}^+ \) fragments and 53% at various \( \text{C}_x\text{H}_y\text{N}^+ \) fragments. Similar distributions resulting in a large \( \text{NO}_x^+ \) signal are expected from the measurement of nitro-organics (\( \text{R–NO}_2 \)) in the AMS. The default analysis algorithm used in analysing AMS data assumes that CHO, CHN and CHON ions are organic, with \( \text{NO}_x^+ \) ions assigned to the inorganic nitrate signal. The presence of organonitrates in the SOA therefore has implications on the H/C, O/C and N/C ratios that the AMS reports, with the latter two potentially being significantly underestimated (Farmer et al., 2010; Rollins et al., 2010; Docherty et al., 2011; Fry et al., 2013). Nonetheless, in the absence of inorganic sources of nitrates
inside the reactor during these experiments, the particulate nitrate signal can be apportioned entirely to the organic signal (Chhabra et al., 2011).

Making this change increases the average N/C elemental ratio across the three experiments to 0.06, with the average elemental composition of the SOA across the three experiments becoming C_{10}H_{16}O_{3}N_{0.6} (assuming 10 carbons per SOA constituent, first-generation products). It is therefore approximated that the upper bound for the molar fraction of organic nitrates in the SOA is 60%. In addition to a gain in nitrogen, composition shows a high oxygen content in the SOA with negligible change in hydrogen compared to α-phellandrene. An average addition of three oxygen atoms seems reasonable, at least for the nitro-compounds, with two oxygens prescribed to the nitro group and a further oxygen assigned to a secondary functionality.

An alternative method for estimating the fraction of nitro-organics in SOA is to compare the nitrate to organic aerosol mass ratios (Boyd et al., 2015). The average nitrate/organic mass ratio measured by the AMS across the three experiments is around 0.07. If the nitro-organics are assumed to have an average molecular weight between 200 – 250 g mol\(^{-1}\), based on first-generation products (Figure 3.35), where 46 g mol\(^{-1}\) is attributed to the nitro group and the remaining mass to the organics, then the fraction of aerosol mass composed of organic nitrates is estimated to be 30 – 40%. This value is smaller than the estimated contribution obtained through using elemental ratios, due to the neglect of nitrogen containing organic signals (e.g. C\(_x\)H\(_y\)N and C\(_x\)H\(_y\)ON family groups) in the calculation. Overall, determined values compare well with the fraction of organic mass composed of organic nitrates in the reaction of monoterpenes with NO\(_3\), which have been reported to range from 30 – 40% (Fry et al., 2009), 56 – 82% (Fry et al., 2014) and 45 – 68% (Boyd et al., 2015), suggesting that SOA composition is not too different between NO\(_2\) and NO\(_3\) initiated oxidation reactions.

A typical high-resolution mass spectrum for the aerosol formed is shown in Figure 3.40. A key feature is the high intensity of the NO\(^+\) signal, which contributes to around 5% of the SOA. The majority of nitrogen atoms are detected at NO\(^+\), with the remaining nitrogen atoms detected at NO\(_2^+\), C\(_x\)H\(_y\)N\(^+\) and C\(_x\)H\(_y\)O\(_2\)N\(^+\) ions. The ratio of NO\(^+\) to NO\(_2^+\) ranged from 17 – 30 in the three experiments. Inorganic nitrate (e.g. NH\(_4\)NO\(_3\)) is detected as NO\(^+\) and NO\(_2^+\) with a typical ratio of NO\(^+\):NO\(_2^+\) of 2 – 3 (Alfarra et al., 2006; Cottrell et al., 2008; Fry et al., 2009). The ratio observed for the reaction of α-phellandrene is clearly distinct from the inorganic fragmentation pattern, supporting assignment of the nitrate aerosol as organic. Indeed the NO\(^+\):NO\(_2^+\) ratio is similar to that observed for SOA generated from the oxidation of monoterpenes by the nitrate radical (Fry et al., 2009; Farmer et al., 2010; Boyd et al., 2015). The most abundant peak in the spectra of all three
3.7. α-PHELLANDRENE + NO₂

Figure 3.40: High-resolution aerosol mass spectrum of the SOA formed from the reaction of α-phellandrene with NO₂ in experiment 12. Only ions up to m/z 160 are shown, with signals beyond this minimal. The mass spectrum is coloured to show the contribution of each ion type, with important ions labelled. Inset is the mass concentration time series of the most prominent ion families.

experiments is the C₂H₅O⁺ ion at m/z 43, which is a common marker of fresh aerosol (Kroll et al., 2009; Ng et al., 2010). Its presence suggests the high abundance of carbonyl groups in the SOA, supporting reaction with O₂ as a dominant radical terminating channel.

Species heavier than m/z 160 are not shown in the mass spectrum due to their small contribution. Nonetheless ions heavier than m/z 160 are detected including C₁₀H₁₆O₂⁺, C₁₀H₁₅O₂N⁺ and C₁₀H₁₆O₃N⁺, all of which show good correlation with the aerosol nitrate signal. For organic nitrates, Farmer et al. (2010) proposed that a large fraction of RONO₂ decomposes to RO + NO₂ in the AMS, whilst Rollins et al. (2010) argued that there is also a high degree of molecular rearrangement in addition to simple fragmentation, forming RN⁺ ions. Assuming similar processes are relevant to nitro-organics, many of the heavy ions detected can be assigned to gas-phase species shown in Figure 3.35. For example, detected ions C₁₀H₁₅O⁺ and C₁₀H₁₇O⁺ could be formed from loss of NO₂ from the m/z 197 and 199 species respectively. Similarly C₁₀H₁₆O₂N₂⁺ and C₁₀H₁₆O₃N⁺ ions detected at m/z 196 and 198 could be the result of decomposition of the predicted m/z 244 species through loss of either three oxygen atoms, or NO₂ from the nitrate functional group respectively. Detected at m/z 168, C₁₀H₁₆O₂ is formed through the gas-phase mechanism shown in Figure 3.35, although its high vapour pressure makes it an unlikely contributor to the SOA 3.5.1. However, at this stage, assignment of all condensed phase parent structures is entirely speculative. High mass peaks merely provide evidence that large products exist in the SOA, with offline analysis required for structural elucidation.
The inset in Figure 3.40 shows time series for the major ion family groups detected by the AMS. The NO$_x$ group is observed to increase upon commencement of the reaction, showing nitro- and nitrate-containing products to contribute to early particle formation and growth processes. After peak SOA concentration is reached, non-oxidised fragments (C$_x$) are observed to decrease more rapidly compared to oxidised fragments. Therefore once particle loss processes dominate, the more volatile products, which in general are the least functionalised, begin to partition back into the gaseous phase increasing the relative contribution of the oxidised families.

### 3.7.3 Summary of NO$_2$ Oxidation

Section 3.7 of this thesis presents the first comprehensive investigation into the reaction of NO$_2$ with α-phellandrene, through three chamber experiments. The most intense gas-phase signals detected by the PTR-TOF were small species (≤ C$_3$), attributable to fragments of larger nitro-/nitrate-products. Extensive fragmentation inside the drift tube was confirmed by the detection of a large organic NO$_2^+$ signal. Four ions corresponding to first-generation products were identified in low-yields through the addition of ozone at the end of experiment 13. All other detected product ions remain unassigned, although are thought to predominantly be fragments of nitro-containing products.

The reaction of α-phellandrene with NO$_2$ generates aerosol, showing the oxidant NO$_2$ to form products of sufficiently low volatility for nucleation and aerosol growth processes. This finding is expected to extend to other highly reactive monoterpenes such as α-terpinene. An average effective SOA density of 1.67 ± 0.08 g cm$^{-3}$ was determined, with aerosol yield significantly reduced compared to the ozonolysis experiments. Using a two-product fit, the yield curve best fit by the parameters $\alpha_1 = 0.21$, $\alpha_2 = 0.029$, $K_{om,1} = 0.0072$ m$^3$ µg$^{-1}$ and $K_{om,2} = 0.478$ m$^3$ µg$^{-1}$. Organic nitrates were found to comprise 30 – 40% of this aerosol mass, similar to the nitrate fraction of aerosol formed in monoterpene + NO$_3$ experiments.

This work therefore adds to the growing body of monoterpene aerosol literature which previously spanned photooxidation, ozone and nitrate radical oxidants (Griffin et al., 1999; Lee et al., 2006a,b; Fry et al., 2014; Hallquist et al., 2009). For most monoterpenes however, the reaction with NO$_2$ is thought to occur too slowly to allow sufficient build up of low- and semi-volatile organics. Even for highly reactive compounds, reaction with NO$_2$ is only likely to be non-negligible under the most extreme high NO$_x$ conditions. So, whilst results from this study provide the first insight into SOA produced from reaction with NO$_2$, the information is expected to have minimal real-world application.
3.8 \( \alpha \)-phellandrene Photooxidation

Photooxidation chamber studies provide the best daytime representation of \( \alpha \)-phellandrene in a polluted atmosphere (e.g. photochemical smog). In these experiments gas-phase chemistry is likely to be dominated by the OH radical, with O\(_3\) and the NO\(_3\) radicals also playing an important role. The system is kept intentionally simple by focusing on single VOC (\( \alpha \)-phellandrene)–NO\(_x\)–air irradiations, so that experimental results can be used for mechanism testing and development. Ozone production is most sensitive to mechanism parameters at low VOC/NO\(_x\) ratios, that is, when the system is VOC limited (Dodge, 2000; Wagner et al., 2003). This makes low VOC/NO\(_x\) experiments ideally suited to identify shortcomings of chemical mechanisms. The atmosphere however typically resides in the NO\(_x\) limited scenario (Seinfeld and Pandis, 1998; Monks et al., 2009). Chamber simulations were therefore conducted under a variety of VOC/NO\(_x\) ratios, ranging from 0.16 to 4.6, with initial conditions for the 10 photooxidation experiments listed in Table 3.15.

All experiments were conducted under dry conditions and at around 298 K, except for experiment 19, in which the chamber was cooled to 288 K, and experiment 21, which was conducted at an RH of 52%. The VOC/NO\(_x\) ratio was around unity for most experiments, with an increasingly VOC limited scenario probed in experiments 15 and 22 and a NO\(_x\) limited scenario in experiment 16. The initial ratio of NO to NO\(_2\) was varied in the remaining experiments, through injection of either NO, NO\(_2\) or a combination of the two at the start of the experiment. Changing these physical and chemical starting variables provides a wider examination of the system and allows for a more rigorous examination of the robustness of the constructed chemical mechanism in Chapter 4.

3.8.1 Gas-Phase Analysis

Reaction Mechanism of OH with \( \alpha \)-phellandrene

The major daytime loss processes for \( \alpha \)-phellandrene in the atmosphere are reaction with the hydroxyl radical and ozone, which is expected to be reflected in these photooxidation chamber simulations. The mechanism for the reaction of ozone with \( \alpha \)-phellandrene is discussed in detail in Chapter 2 and Section 3.5. The mechanism for the reaction of OH with \( \alpha \)-phellandrene will now be discussed briefly prior to analysing photooxidation chamber results.

The reaction of OH and \( \alpha \)-phellandrene occurs at a rate of \((3.2 \pm 0.6) \times 10^{-10}\) cm\(^3\) molecules\(^{-1}\) s\(^{-1}\) at 298 K (Atkinson et al., 1986; Peeters et al., 1999). The reaction is primarily expected to occur through addition of the OH radicals to the olefin bonds, with electrophilic addition of OH to \( \alpha \)-phellandrene proceeding similarly to
addition of NO\textsubscript{2} to yield six unique products, three each from addition at either double bond. The six different radical products are shown in Figure 3.41. Addition at carbons 3 and 6 are again thought to be favoured, due to resulting radical stabilisation through allyl resonance.

Hydrogen abstraction from the various C–H bonds in \(\alpha\)-phellandrene is also possible. By directly measuring water as a reaction product, Peeters et al. (1999) reported a significant hydrogen abstraction contribution of 27 ± 10 %. H-atom abstraction is predominantly expected to occur from the non-vinylic C–H bonds in the ring system, with abstraction from these positions facilitated by stabilisation of the formed radical by super-allyl-resonance, which delocalises the unpaired electron over three carbon atoms (see Figure 3.41). Computationally derived C–H bond strengths support this theory, with Vereecken and Peeters (2001) computing strengths of the \(\text{CH}\) and \(\text{CH}_2\) groups inside the ring to be 50 to 170 kJ mol\(^{-1}\) weaker than other C–H bonds in \(\alpha\)-phellandrene. Studies have shown that H-atom abstraction from non-allylic groups in 1,3- and 1,4-cyclohexadiene lead to the formation of benzene (Ohta, 1984; Tuazon et al., 2003; Jenkin et al., 2005), with Aschmann et al. (2011) finding the monoterpane homolog \(\gamma\)-terpinene to form \(p\)-cymene. From this, Aschmann et al. (2011) proposed that reaction of the analogous \(\alpha\)-phellandrene with OH would also yield \(p\)-cymene, but noted feasibility issues in conducting the experiment due to the rapid reaction of \(\alpha\)-phellandrene with both O\textsubscript{3} and NO\textsubscript{2}, which precludes the use of conventional OH radical sources. Evidence from Berndt et al. (1996) suggests that mechanistically the notion is feasible, with \(p\)-cymene detected with a 22% yield in the reaction of NO\textsubscript{3} with \(\alpha\)-phellandrene at 250 mbar under

Table 3.15: Starting conditions for \(\alpha\)-phellandrene photooxidation chamber experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Temp. (±0.5 K)</th>
<th>RH (±0.2%)</th>
<th>VOC\textsuperscript{a} (ppb)</th>
<th>[NO] (ppb)</th>
<th>[NO\textsubscript{2}] (ppb)</th>
<th>VOC (\text{NO}_x)</th>
<th>Run Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>20/08/13</td>
<td>297.7</td>
<td>1.7</td>
<td>48 ± 14</td>
<td>31 ± 1</td>
<td>52 ± 0.5</td>
<td>0.58</td>
<td>271</td>
</tr>
<tr>
<td>16</td>
<td>22/08/13</td>
<td>297.8</td>
<td>1.8</td>
<td>58 ± 16</td>
<td>3.9 ± 0.2</td>
<td>8.8 ± 0.3</td>
<td>4.6</td>
<td>331</td>
</tr>
<tr>
<td>17</td>
<td>25/08/13</td>
<td>298.0</td>
<td>2.4</td>
<td>71 ± 20</td>
<td>22 ± 1</td>
<td>36 ± 1</td>
<td>1.2</td>
<td>292</td>
</tr>
<tr>
<td>18</td>
<td>27/08/13</td>
<td>298.0</td>
<td>2.0</td>
<td>61 ± 18</td>
<td>49 ± 1</td>
<td>9 ± 1</td>
<td>1.1</td>
<td>325</td>
</tr>
<tr>
<td>19</td>
<td>29/08/13</td>
<td>287.7</td>
<td>6.2</td>
<td>60 ± 17</td>
<td>19 ± 1</td>
<td>39 ± 1</td>
<td>1.0</td>
<td>307</td>
</tr>
<tr>
<td>20</td>
<td>03/09/13</td>
<td>297.1</td>
<td>2.1</td>
<td>53 ± 15</td>
<td>2 ± 1</td>
<td>54 ± 2</td>
<td>0.95</td>
<td>244</td>
</tr>
<tr>
<td>21</td>
<td>18/09/13</td>
<td>298.3</td>
<td>52</td>
<td>55 ± 16</td>
<td>22 ± 1</td>
<td>42 ± 2</td>
<td>0.86</td>
<td>300</td>
</tr>
<tr>
<td>22</td>
<td>26/08/16</td>
<td>297.8</td>
<td>9.5</td>
<td>57 ± 16</td>
<td>254 ± 6</td>
<td>100 ± 3</td>
<td>0.16</td>
<td>230</td>
</tr>
<tr>
<td>23</td>
<td>31/08/16</td>
<td>297.5</td>
<td>11</td>
<td>52 ± 15</td>
<td>40 ± 3</td>
<td>8 ± 2</td>
<td>1.1</td>
<td>180</td>
</tr>
<tr>
<td>24</td>
<td>04/09/16</td>
<td>297.7</td>
<td>4.3</td>
<td>66 ± 18</td>
<td>16 ± 2</td>
<td>35 ± 2</td>
<td>1.3</td>
<td>204</td>
</tr>
</tbody>
</table>

\textsuperscript{a}\(\alpha\)-phellandrene.
Figure 3.41: Major reaction pathways for the OH radical with α-phellandrene. Addition and abstraction fractions are taken from Peeters et al. (1999). Note the allyl resonance resulting from OH addition to carbons 3 and 6 and the super allyl resonance formed from H-atom abstraction at carbons 4 and 5.

an atmosphere of nitrogen. A plausible formation mechanism leading to p-cymene formation is shown in Figure 3.42.

Peroxy radical chemistry is fundamentally dictated by the VOC/NO\textsubscript{x} ratio, as this changes the competitive dynamics of the reaction of RO\textsubscript{2} with NO and other peroxy radicals, including HO\textsubscript{2} and RO\textsubscript{2} (refer to Section 1.3.1). This affects the ability of a VOC to recycle NO\textsubscript{x}, as different channels are either radical-propagating or radical-terminating, which impacts total ozone production. The relative prominence of the different peroxy radical channels also changes the final product distribution, impacting SOA yields. For monoterpenes, the highest SOA yields are generally observed under low-NO\textsubscript{x} conditions (Presto et al., 2005b; Ng et al., 2007a; Eddingsaas et al., 2012a; Han et al., 2016; Sarrafzadeh et al., 2016; Zhao et al., 2017). It has been argued that this is due to the products of RO\textsubscript{2}+HO\textsubscript{2} chemistry being inherently less volatile than the products of RO\textsubscript{2}+NO chemistry, however, recently it has been proposed that SOA suppression may largely be due to NO\textsubscript{x} inhibiting new particle formation, leading to a reduction in surfaces for organics.
to condense onto (Wildt et al., 2014; Sarrafzadeh et al., 2016; Zhao et al., 2017). Although decreasing SOA yield with increasing NO\textsubscript{x} is relatively well established, the ability of α-phellandrene to produce SOA through NO\textsubscript{2} initiated experiments suggests that nitro/nitrate products are sufficiently condensible. The behaviour of α-phellandrene may therefore mimic larger more reactive species like sesquiterpenes, where higher SOA yields are observed under high-NOx conditions (Ng et al., 2007a; Tasoglou and Pandis, 2015).

Whilst a range of VOC/NO\textsubscript{x} ratios are examined in this study, for the most part reaction conditions are NO\textsubscript{x} limited. By definition, it is the competition between VOCs and NO\textsubscript{x} for OH radicals that determines the experimental regime. At high VOC/NO\textsubscript{x} ratios, OH will primarily react with VOCs, whilst at a low ratio, reaction with NO\textsubscript{x} dominates (Seinfeld and Pandis, 1998). The second-order rate coefficient for the reaction of OH with NO\textsubscript{2} is $9.89 \times 10^{-12}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} (Atkinson et al., 2004).

\[
\text{OH} + \text{NO}_2 \xrightarrow{M} \text{HNO}_3
\]  

(3.37)

This value is around 32 times smaller than the rate coefficient for α-phellandrene with OH radicals. Thus, when the VOC/NO\textsubscript{x} ratio is approximately 0.03, the reaction rates of α-phellandrene and NO\textsubscript{2} with OH are equal. All experiments start off residing at a higher VOC/NO\textsubscript{x} ratio than this, meaning OH preferentially reacts with α-phellandrene. Therefore the experiments start in the NO\textsubscript{x} limited regime. As the reaction proceeds and α-phellandrene is consumed, generating less reactive products, the system will transition towards being VOC limited\textsuperscript{3}. Experiments are therefore performed under NO\textsubscript{x}-limited ozone formation conditions, such as those often experienced in southern Europe (Nopmongcol et al., 2012) and suburban China (Zou et al., 2015).

Given the relative abundance of NO\textsubscript{x} throughout most experiments, all major peroxy radical reaction pathways are expected to be important under the considered experimental conditions, and so are expressed in Figure 3.42, which traces the reaction of α-phellandrene with OH to first-generation products. The proposed photooxidation degradation scheme is further extended in Chapter 4. The final product distribution is expected to consist of a range of multi-functional compounds generated from OH initiation including alcohols, carbonyls, nitrates, PANs, hydroperoxides, acids and peracids, in addition to those products formed through ozonolysis. Strong irradiation during the experiments precludes the nitrate radical from having a large impact.

\textsuperscript{3}Given NO\textsubscript{x} are not removed sufficiently rapidly.
Photooxidation Gas-Phase Products

Figure 3.44 shows time profiles for experiment 17, which has a VOC/NO\textsubscript{x} ratio of 1.2 and is representative of most of the experiments conducted, and experiment 22, which has a high amount of starting NO\textsubscript{x} and so provides a contrasting scenario. Upon commencement of the reaction, by switching on the lights, α-phellandrene and NO are consumed and NO\textsubscript{2} and O\textsubscript{3} produced. This process occurs much more rapidly in experiment 17 (and indeed all experiments) than experiment 22, due to the high NO concentration inhibiting O\textsubscript{3} and hence OH radical production in experiment 22. Over the course of an experiment O\textsubscript{3}, a product of photochemistry, increases whilst NO\textsubscript{2} decreases through loss and consumption processes. Acetonitrile (m/z 42) was constant throughout all experiments, indicating that dilution effects are negligible. After switching off the lights in the 2016 experiments, Figure 3.44 shows that NO and O\textsubscript{3} rapidly consume one another to produce NO\textsubscript{2}, whose concentration now
increases as it is no longer lost through photolysis. The signal at \( m/z \) 137 does not go to zero, but rather remains around 2 – 3 ppb in the different experiments. This small residual signal is attributed to the slower reacting contaminant monoterpenes present in the \( \alpha \)-phellandrene sample, that were detected in canister sampled air masses by GC-MS (Section 3.6).

Ozone production for the different experiments is shown in Figure 3.43. In general, a large quantity of ozone is produced in each photooxidation experiment, with \( \alpha \)-phellandrene, and its degradation products, therefore able to efficiently cycle NO to NO\(_2\) under the considered experimental conditions. Strong support of this is provided by experiment 16, which had 12.7 ppb of NO\(_x\) added, yet yielded 90 ppb of ozone. The term ‘reactivity’ has been coined to discuss the ability of different VOCs to impact ozone production, with different scales having been developed to quantify VOC ozone formation potential (e.g. Carter, 1994; Derwent et al., 1998). Significant variation in VOC reactivities has been reported, influenced by the following mechanistic factors: how fast the VOC reacts, how many molecules of NO are oxidised when the VOC reacts, effects of the VOC’s reactions on radical concentrations, effects on rate of NO\(_x\) removal, and the reactivities of the VOC’s major oxidation products. Given the high reaction rate of \( \alpha \)-phellandrene, its size (\( \text{C}_{10} \)), the high concentration of ozone produced in these chamber experiments, and that ozone production continued after complete consumption of \( \alpha \)-phellandrene, it is expected that \( \alpha \)-phellandrene would have a high reactivity. Whilst reactivity can be measured in chamber experiments, the gathered dataset is not sufficient. However due to impracticalities in examining all relevant conditions, chamber auxiliary effects and inherent complexities of the atmosphere, atmospheric reactivities are typically determined using relevant airshed models (Carter, 1994; Derwent et al., 1998, 2007; Cheng et al., 2010).

In all experiments, except for numbers 16 and 20, a slight delay in ozone production is observed, with production commencing once the majority of NO was consumed (from reaction with peroxy radicals). Initial consumption of \( \alpha \)-phellandrene is therefore dominated by reaction with OH radicals. Nonetheless, in most experiments, ozone is generated sufficiently fast, and \( \alpha \)-phellandrene is suitably reactive, that consumption by ozone is expected to have an impact. It is only in experiments 18 and 22 that the majority of \( \alpha \)-phellandrene is consumed before O\(_3\) production commences, due to these experiments having the highest starting NO concentrations. The lowest ozone production was found in experiment 22, which had the largest amount of NO\(_x\) added. Changing the humidity was found to have no impact on ozone production.

The gas-phase distribution of organic ions detected by the PTR-TOF was highly consistent across the suite of photooxidation experiments. Those ions which were
Figure 3.43: Time profiles showing large ozone production in the conducted photooxidation experiments. Note the delayed response in experiments with high starting NO concentrations. Wall loss effects have not been corrected for.

detected in all photooxidation experiments are listed in Table 3.16, along with tentative assignments. Product assignment, and indeed the following discussion, is made with consideration of inherent fragmentation occurring inside the PTR-TOF drift tube, with this effect and impact on product detection having already been discussed in Sections 3.5.1 and 3.7.1. In addition to consistent detection, the listed ions were, in general, the most prominent ions in each of the experiments. The average total number of oxidation products observed in these photooxidation experiments was 55 ± 12, which is significantly larger than the number observed in the ozonolysis (29 ± 16) and NO2 (30 ± 17) chamber experiments discussed in Sections 3.5.1 and 3.7.1 respectively. The PTR-TOF was operated under essentially the same conditions for all sets of oxidation experiments, suggesting that the increase in ions is not a result of fragmentation. Given the greater versatility of OH attack on α-phellandrene, and that saturated products can further react (OH radicals, NO3 radicals, photolysis), a greater number of different products are expected from photooxidation compared to ozonolysis or reaction with NO2.

Like the ozonolysis and NO2 experiments, the most prominent ions were low molecular weight species (≤ C3); m/z 31, 43, 45, 46, 59, 61 and 73. As in the ozonolysis study, m/z 31, 45, 47, 61 and 73 were assigned to formaldehyde, acetaldehyde, formic acid, acetic acid and methyl glyoxal respectively. Using GC-FID, Reissell et al. (1999) reported acetone as a product from the reaction of OH radicals (generated from methylnitrate irradiation) with α-phellandrene, with a yield of 8 ± 4 %, although the authors could not ascribe a reaction pathway leading to its formation. Nonetheless, Figure 3.42 shows one plausible reaction mechanism
<table>
<thead>
<tr>
<th>m/z</th>
<th>Formula</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>H₃O¹⁸⁺</td>
<td>Hydronium ion</td>
</tr>
<tr>
<td>37</td>
<td>(H₂O)₂H⁺</td>
<td>Water cluster</td>
</tr>
<tr>
<td>55</td>
<td>(H₂O)₃H⁺</td>
<td>Water cluster</td>
</tr>
</tbody>
</table>

### Acetonitrile

<table>
<thead>
<tr>
<th>m/z</th>
<th>Formula</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>CH₃CNH⁺</td>
<td>Acetonitrile</td>
</tr>
</tbody>
</table>

### α-phellandrene Products

<table>
<thead>
<tr>
<th>m/z</th>
<th>Formula</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>CH₂OH⁺</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>45</td>
<td>C₂H₄OH⁺</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>46</td>
<td>NO₂⁺</td>
<td>Organonitrate frag.</td>
</tr>
<tr>
<td>47</td>
<td>CH₂O₂H⁺</td>
<td>Formic acid</td>
</tr>
<tr>
<td>59</td>
<td>C₂H₂O₂H⁺</td>
<td>Acetone, glyoxal</td>
</tr>
<tr>
<td>61, 43</td>
<td>C₅H₁₀O²⁺</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>73</td>
<td>C₃H₆O₂H⁺</td>
<td>Methyl glyoxal</td>
</tr>
<tr>
<td>87</td>
<td>C₄H₇O⁺</td>
<td>Second gen.</td>
</tr>
<tr>
<td>103</td>
<td>C₅H₁₁O₂⁺</td>
<td>Second gen.</td>
</tr>
<tr>
<td>109</td>
<td>C₇H₉O⁺</td>
<td>Unassigned frag.</td>
</tr>
<tr>
<td>115, 97</td>
<td>C₆H₁₁O₂⁺</td>
<td>Second gen.</td>
</tr>
<tr>
<td>125, 83</td>
<td>C₈H₁₉O⁺</td>
<td>Unassigned frag.</td>
</tr>
<tr>
<td>129, 111</td>
<td>C₇H₁₃O⁺</td>
<td>Second gen.</td>
</tr>
<tr>
<td>139</td>
<td>C₉H₁₅O⁺</td>
<td>First gen. frag.</td>
</tr>
<tr>
<td>141, 101, 89</td>
<td>C₇H₈O₃⁺</td>
<td>Unassigned frags.</td>
</tr>
<tr>
<td>143</td>
<td>C₇H₁₁O₃⁺</td>
<td>Second gen.</td>
</tr>
<tr>
<td>151, 123</td>
<td>C₁₀H₁₅O⁺</td>
<td>First gen.</td>
</tr>
<tr>
<td>155</td>
<td>C₉H₁₅O₂⁺</td>
<td>First gen.</td>
</tr>
<tr>
<td>167</td>
<td>C₁₀H₁₅O₂⁺</td>
<td>First gen.</td>
</tr>
<tr>
<td>169</td>
<td>C₁₀H₁₇O₂⁺</td>
<td>First gen.</td>
</tr>
<tr>
<td>171</td>
<td>C₁₀H₁₉O₂⁺</td>
<td>First gen.</td>
</tr>
<tr>
<td>185</td>
<td>C₁₀H₁₇O₃⁺</td>
<td>First gen.</td>
</tr>
</tbody>
</table>

Table 3.16: Assignment of product ions detected by the PTR-TOF during α-phellandrene photooxidation experiments. Where multiple ions are listed the smaller ion/s are assigned fragment peaks. First generation products refer to those produced from addition at one double bond, whilst second generation are products from two additions.
through the hydrogen abstraction channel, which forms acetone by fragmenting the isopropyl radical. Both acetone and glyoxal are therefore thought to contribute to the $m/z$ 59 signal. The signal at $m/z$ 43 is assigned to the ion $C_2H_3O^+$, which is a common PTR fragment of organic compounds (Duncianu et al., 2017). Its presence shows that fragmentation is occurring inside the PTR-TOF drift tube, making current operation unsuitable for quantitative analysis of larger species. As shown in Table 3.17, which reports the gas-phase yields for the major low-weight products, the $m/z$ 43 signal intensity was reduced relative to other ions in 2016 compared to 2013, due to the reduction in PTR-TOF drift tube energy. The signal at $m/z$ 46 was not observed during the ozonolysis experiments, suggesting that it is a nitrogen containing species. The signal is therefore assigned to $NO_2^+$, which is formed as a fragment of nitrate containing species in the PTR-TOF (Aoki et al., 2007; Duncianu et al., 2017). Thus $m/z$ 46 serves as a useful proxy for monitoring the amount of nitrate formation occurring in the system.

Gas-phase yields were calculated as the slope of the linear least-squares fit between each identified product and $\alpha$-phellandrene. Only the time-period after irradiation in which $\alpha$-phellandrene decreased in concentration was used, with high correlation generally observed ($R^2 > 0.98$). Reported yields therefore pertain exclusively to $\alpha$-phellandrene, and not to the system as a whole. The products discussed all increased in concentration well after $\alpha$-phellandrene was consumed, signalling sizeable contribution from product species. To accurately attribute stoichiometric second-generation yields, first-generation time profiles would be required, however these remain generally unidentifiable in the PTR-TOF.

In general, yields were found to be higher in the 2016 experiments than in the 2013 experiments, with this difference attributed to the improved PTR-TOF drift tube operating conditions used in 2016. Acetone/glyoxal was found to have the highest yield in all experiments. The reported yields, ranging from 9.5 – 18%, are slightly higher than the acetone yield of 8 ± 4% reported by Reissell et al. (1999), however this is likely due to contribution from glyoxal to the signal. Focussing exclusively on the 2013 dataset, experiment 21, which was conducted under the most humid conditions, yielded significantly more formic acid, followed by experiment 16, which had the least amount of $NO_x$ added. These two experiments also had the highest acetic acid yields. Conversely, these two experiments reported the lowest yields of formaldehyde, methyl glyoxal and $NO_2^+$, along with experiment 20, which started off with low NO. Therefore, increasing the humidity or reducing the amount of NO increases the relative prominence of acid forming channels compared to nitrate and carbonyl forming channels from nascent radicals, through increasing the impact of the HO$_2$ radical compared to NO$_x$. These smaller species are thought to be proxies of the system as a whole, with enhanced acid formation occurring throughout the
### Table 3.17: Gas-phase molar yields (%) for major α-phellandrene photooxidation products.

<table>
<thead>
<tr>
<th>No.</th>
<th>Formaldehyde</th>
<th>C₂H₃O⁺</th>
<th>Acetaldehyde</th>
<th>NO₂⁺</th>
<th>Formic acid</th>
<th>Acetone/glyoxal</th>
<th>Acetic acid</th>
<th>Methyl glyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4.9 ± 1</td>
<td>6.4 ± 1</td>
<td>2.9 ± 0.7</td>
<td>9.3 ± 2</td>
<td>4.8 ± 1</td>
<td>14 ± 3</td>
<td>3.5 ± 0.8</td>
<td>4.9 ± 1</td>
</tr>
<tr>
<td>16</td>
<td>2.9 ± 0.7</td>
<td>5.6 ± 1</td>
<td>2.4 ± 0.6</td>
<td>1.9 ± 0.4</td>
<td>5.4 ± 1</td>
<td>9.5 ± 2</td>
<td>4.6 ± 1</td>
<td>3.3 ± 0.8</td>
</tr>
<tr>
<td>17</td>
<td>3.7 ± 0.9</td>
<td>6.0 ± 1</td>
<td>2.1 ± 0.5</td>
<td>4.9 ± 1</td>
<td>4.1 ± 0.9</td>
<td>12 ± 3</td>
<td>3.4 ± 0.8</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>18</td>
<td>4.9 ± 1</td>
<td>5.7 ± 1</td>
<td>2.5 ± 0.6</td>
<td>9.6 ± 2</td>
<td>4.5 ± 1</td>
<td>13 ± 3</td>
<td>2.8 ± 0.6</td>
<td>4.4 ± 1</td>
</tr>
<tr>
<td>19</td>
<td>4.5 ± 1</td>
<td>5.7 ± 1</td>
<td>2.6 ± 0.6</td>
<td>6.1 ± 1</td>
<td>4.1 ± 0.9</td>
<td>11 ± 3</td>
<td>3.1 ± 0.7</td>
<td>4.2 ± 1</td>
</tr>
<tr>
<td>20</td>
<td>4.7 ± 1</td>
<td>6.6 ± 2</td>
<td>2.7 ± 0.6</td>
<td>2.3 ± 0.6</td>
<td>4.0 ± 0.9</td>
<td>12 ± 3</td>
<td>3.4 ± 0.8</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>21</td>
<td>1.2 ± 0.3</td>
<td>7.0 ± 2</td>
<td>2.3 ± 0.5</td>
<td>2.9 ± 0.7</td>
<td>7.1 ± 2</td>
<td>11 ± 3</td>
<td>4.4 ± 1</td>
<td>3.0 ± 0.7</td>
</tr>
<tr>
<td>22</td>
<td>14 ± 3</td>
<td>7.0 ± 2</td>
<td>9.3 ± 2</td>
<td>10.9 ± 3</td>
<td>7.8 ± 2</td>
<td>18 ± 4</td>
<td>5.3 ± 1</td>
<td>8.2 ± 2</td>
</tr>
<tr>
<td>23</td>
<td>9.4 ± 2</td>
<td>7.6 ± 2</td>
<td>2.9 ± 0.7</td>
<td>8.7 ± 2</td>
<td>7.0 ± 2</td>
<td>15 ± 3</td>
<td>6.1 ± 1</td>
<td>7.0 ± 2</td>
</tr>
<tr>
<td>24</td>
<td>10 ± 2</td>
<td>7.7 ± 2</td>
<td>1.7 ± 0.4</td>
<td>7.9 ± 2</td>
<td>6.9 ± 2</td>
<td>13 ± 3</td>
<td>6.9 ± 2</td>
<td>6.4 ± 1</td>
</tr>
</tbody>
</table>

product distribution in experiments 16 and 21. Comparatively, the highest yield of NO₂⁺ was found in experiments 15 and 18, with these experiments having the largest initial concentration of NOₓ and NO respectively. Qualitatively, the effect of temperature made no significant difference to gas-phase yields, although slower decomposition of α-phellandrene was recorded.

A similar, albeit reverse, trend is evident by independently looking at the 2016 results. Here, experiment 22, which has the largest concentration of NOₓ added, shows significantly higher yields of NO₂⁺, formaldehyde and acetaldehyde, along with having the highest yields of acetone/glyoxal and methyl glyoxal. The relative abundance of nitrate and carbonyl species is caused by the preferential reaction of RO₂ with NO, which can either directly form a nitrate, or cycle RO₂ into RO radicals, which can decompose into carbonyl products. After switching off the lights at the end of the 2016 experiments, Figure 3.44 shows that the concentration of major ions remains relatively stable, except for NO₂⁺, which increases now that the nitrate radical is dominating chemistry inside the reactor. Given that photochemistry has ceased, stalling product production, ion stability indicates that detected ions are not heavily impacted by wall loss processes. Reported gas-phase product yields for formaldehyde, acetaldehyde, formic acid, acetone and acetic acid from α-phellandrene photooxidation are compared with results from a range of other monoterpenes in Appendix F, with some consistency observed (Lee et al., 2006b).

Of the heavier detected ions (> C₃), only m/z 123 and 151 show time profiles consistent with first-generation products, that is, one characterised by an increase in concentration whilst α-phellandrene is consumed, reaching a maximum, before decreasing in concentration as the second double bond reacts. m/z 139 shows a similar first-generation time profile in all but experiment 22. m/z 151 is assigned to the fragment C₁₀H₁₅O⁺, with m/z 123 a further fragment of this formed by loss of 260
Figure 3.44: Time profiles for major species detected during photooxidation experiments 17 (left panels) and 22 (right panels). Grey shading denotes time periods where chamber lighting was switched off.

a CO group. Fragmentation was confirmed by a high degree of correlation between the two signals across the experimental dataset. The C$_{16}$H$_{15}$O$^+$ fragment can be attributed to a range of first-generation products, including the first-generation dicarbonyls, with a possible structure shown in Figure 3.45. This is consistent with other monoterpenes, which often record a signal at m/z 151 corresponding to their major first-generation carbonyl products, e.g. pinonaldehyde from $\alpha$-pinene or limonaldehyde from limonene (Lee et al., 2006b). m/z 139 is assigned to C$_9$H$_{15}$O$^+$. Although composition is similar to the peak at m/z 151, differing by only by one carbon atom, the signals are uncorrelated, suggesting different precursor structures. Consequently, C$_9$H$_{15}$O$^+$ is assigned to C$_9$ first-generation products, rather than a fragment of a C$_{10}$ product. Nonetheless, as shown in Figure 3.42, many more first-generation products of $\alpha$-phellandrene are expected upon reaction with OH. As with the ozonolysis study, there appears to be a distinct lack of larger, functionalised products identified by
Figure 3.45: Proposed parent structures formed in the photooxidation of α-phellandrene. Dashed lines show labile bonds whose breakage results in the fragment ions detected by the PTR-TOF.

The PTR-TOF. Whilst heavier ions were routinely detected, including \( m/z \) 167, 169, 171, 185, with these masses attributable to proposed first-generation products, they often have low signal intensity and time-profiles that are not always consistent with that expected of an unsaturated product. Possible reasons for this are discussed in Section 3.5.1.

The remaining detected ions are assigned to saturated higher-generation products and their fragments. Potential structures for many of these are shown in Figure 3.45, although it is noted that isomeric products do exist. Of the proposed products, \( m/z \) 115 and 129 are again assigned to the di-carbonyls 2-propan-2-ylpropanedial and 2-propan-2-ylbutanedial respectively, as in the ozonolysis of α-phellandrene. The peak at \( m/z \) 129 (and its dehydrated fragment \( m/z \) 111) was observed to slowly decrease in some experiments (e.g. see Figure 3.44), indicating that function- alised saturated products remain susceptible to reaction throughout the duration of the experiment. Similarly, \( m/z \) 143 is again assigned to isomeric tri-carbonyl C\(_7\) species, with a possible structure provided in Figure 3.45. The ion at \( m/z \) 87 was assigned to C\(_3\)H\(_3\)O\(_3\)\(^+\) in the ozonolysis of α-phellandrene, due to the propensity of sequential ozonolysis to form a 3-carbon fragment in α-phellandrene. However during photooxidation, with OH addition not directly resulting in fragmentation, \( m/z \) 87 is assigned to C\(_4\)H\(_7\)O\(_2\)\(^+\), although the contribution of the C\(_3\)H\(_3\)O\(_3\)\(^+\) ion cannot be discounted. The product at \( m/z \) 103 was assigned to an alcohol. \( m/z \) 127, assigned to C\(_7\)H\(_{11}\)O\(_2\)\(^+\), was found to have fragments at \( m/z \) 113, 99 and 85. The low hydrogen-to-carbon content of the neutral analyte, C\(_7\)H\(_{10}\)O\(_2\), implies that the it is either unsaturated or cyclic. Given that the ion time profile shows no evidence of unsaturation, and molecules are unlikely to retain the ring structure after sequential addition, the largest fragment at \( m/z \) 127 is itself thought to be a fragment. The
peaks are thus attributed to second generation C$_7$ acids, with various fragmentation pathways around the acid moiety able to explain the observed fragment ions. Apart from $m/z$ 46, no prominent even mass-to-charge ratio oxidation products are detected, suggesting that none of the detected ions contain nitrogen.

Yields for many of these heavier ions are provided in Table 3.18. Again, it is important to point out that yields are calculated with reference to α-phellandrene, which is rapidly consumed at the beginning of each experiment. They therefore do not provide a complete representation of production of the various ions over the course of a chamber experiment, but nonetheless are provided for completeness. One notable drawback is that the reported yields are quite low, a result of the high reactivity of α-phellandrene. The yields provide some support for product assignment shown in Figure 3.45. For example $m/z$ 127, which was attributed to an acid, records its lowest yields in the different campaigns in the experiment featuring the largest amount of NO$_x$. However in general, unlike for the smaller ions, no discernible trends were evident for the different products under the different experimental conditions/regimes.

Of the numerous oxidation products produced, many have been reported in the ambient air, in particular in forested regions, including $m/z$ 111, 113, 123, 141, 151, 155 and 169 (Holzinger et al., 2005; Taipale et al., 2008; Vlasenko et al., 2009; Kim et al., 2010; Park et al., 2013). In the current work, these peaks are assigned either to α-phellandrene oxidation products or their fragments, but are also commonly observed in the oxidation of other monoterpenes (Lee et al., 2006b; Ng et al., 2006). Indeed through various statistical techniques, Wyche et al. (2015) utilised these common product ions to chemometrically classify different terpenes. Such a rigorous analysis is not performed here although, yields of these major ions are compared with photoxidation chamber results for other monoterpenes in Appendix F.

<table>
<thead>
<tr>
<th>No.</th>
<th>$m/z$ 87</th>
<th>$m/z$ 103</th>
<th>$m/z$ 115</th>
<th>$m/z$ 123</th>
<th>$m/z$ 127</th>
<th>$m/z$ 129</th>
<th>$m/z$ 139</th>
<th>$m/z$ 143</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.2 ± 0.4</td>
<td>0.34 ± 0.1</td>
<td>0.72 ± 0.2</td>
<td>0.21 ± 0.06</td>
<td>0.09 ± 0.03</td>
<td>0.27 ± 0.08</td>
<td>0.57 ± 0.2</td>
<td>0.32 ± 0.1</td>
</tr>
<tr>
<td>16</td>
<td>1.4 ± 0.4</td>
<td>0.13 ± 0.1</td>
<td>0.72 ± 0.2</td>
<td>0.39 ± 0.1</td>
<td>0.15 ± 0.05</td>
<td>0.25 ± 0.08</td>
<td>0.67 ± 0.2</td>
<td>0.37 ± 0.1</td>
</tr>
<tr>
<td>17</td>
<td>0.97 ± 0.3</td>
<td>0.14 ± 0.05</td>
<td>0.58 ± 0.2</td>
<td>0.14 ± 0.05</td>
<td>0.15 ± 0.05</td>
<td>0.27 ± 0.09</td>
<td>0.53 ± 0.2</td>
<td>0.28 ± 0.1</td>
</tr>
<tr>
<td>18</td>
<td>1.1 ± 0.3</td>
<td>0.10 ± 0.03</td>
<td>0.58 ± 0.2</td>
<td>0.60 ± 0.2</td>
<td>0.18 ± 0.06</td>
<td>0.43 ± 0.01</td>
<td>1.1 ± 0.4</td>
<td>0.47 ± 0.1</td>
</tr>
<tr>
<td>19</td>
<td>1.2 ± 0.4</td>
<td>0.08 ± 0.03</td>
<td>0.55 ± 0.2</td>
<td>0.25 ± 0.08</td>
<td>0.13 ± 0.04</td>
<td>0.35 ± 0.1</td>
<td>0.66 ± 0.2</td>
<td>0.32 ± 0.1</td>
</tr>
<tr>
<td>20</td>
<td>1.0 ± 0.3</td>
<td>0.57 ± 0.2</td>
<td>0.17 ± 0.05</td>
<td>0.14 ± 0.04</td>
<td>0.22 ± 0.07</td>
<td>0.36 ± 0.1</td>
<td>0.21 ± 0.07</td>
<td>0.40 ± 1.0</td>
</tr>
<tr>
<td>21</td>
<td>1.3 ± 0.4</td>
<td>0.37 ± 0.03</td>
<td>0.37 ± 0.1</td>
<td>0.58 ± 0.2</td>
<td>0.11 ± 0.03</td>
<td>1.2 ± 0.4</td>
<td>0.66 ± 0.2</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td>22</td>
<td>2.6 ± 0.8</td>
<td>0.16 ± 0.05</td>
<td>2.1 ± 0.7</td>
<td>0.29 ± 0.1</td>
<td>0.25 ± 0.08</td>
<td>0.61 ± 0.2</td>
<td>0.72 ± 0.2</td>
<td>0.62 ± 0.2</td>
</tr>
<tr>
<td>23</td>
<td>2.3 ± 0.7</td>
<td>0.13 ± 0.04</td>
<td>1.3 ± 0.4</td>
<td>0.20 ± 0.07</td>
<td>0.52 ± 0.2</td>
<td>0.36 ± 0.1</td>
<td>0.44 ± 0.1</td>
<td>0.36 ± 0.1</td>
</tr>
<tr>
<td>24</td>
<td>2.7 ± 0.9</td>
<td>0.14 ± 0.05</td>
<td>1.2 ± 0.4</td>
<td>0.24 ± 0.08</td>
<td>0.57 ± 0.2</td>
<td>0.39 ± 0.1</td>
<td>0.49 ± 0.1</td>
<td>0.41 ± 0.1</td>
</tr>
</tbody>
</table>

Table 3.18: Gas-phase molar yields (%) for minor α-phellandrene photooxidation products. Where no yield is reported, not enough product was generated in the initial part of the experiment for accurate quantification.
3.8.2 Particle Phase Analysis

Aerosol Formation and Yield

Figures 3.46 and 3.47 show that changes in the gas-phase are accompanied by the formation and growth of new particles. The peak particle number concentration occurs rapidly upon commencement of the reaction, and is followed by growth of the existing particles, driven by coagulation and further condensation of semi-volatile vapours. Similar growth patterns are observed in all experiments, irrespective of initial conditions (e.g. NO$_x$, temperature, humidity), although significant differences in magnitudes do exist.

The sudden increase in particle number concentration upon irradiation indicates homogeneous nucleation of α-phellandrene photooxidation products is responsible, suggesting ELVOCs are rapidly formed. It has been proposed that onlyppt concentrations of ELVOCs are required to drive new particle formation and subsequent growth (Donahue et al., 2013). Figure 3.47 shows nucleation is more prominent under low-NO$_x$ conditions, whilst contrasting experiments 18 and 20 in Figure 3.51, which plots normalised initial particle formation for each experiment, shows NO specifically to be the ELVOC inhibitor. New particle formation therefore increases upon shifting away from a RO$_2$+NO dominated regime towards a RO$_2$ + HO$_2$ or RO$_2$ regime, consistent with other monoterpene chamber studies (Yu et al., 2008; Wildt et al., 2014; Sarrafzadeh et al., 2016; Zhao et al., 2017). This observation supports new particle formation occurring via an autoxidation mechanism involving peroxy radicals (Crounse et al., 2013; Ehn et al., 2014; Kirkby et al., 2016), with the probability of peroxy radical re-arrangements increasing as less RO$_2$ radicals are removed by NO. Respectively, new particle formation also increases at lower-temperatures (experiment 19, Figure 3.51), with intramolecular rearrangements becoming more favourable compared to thermally driven bimolecular reactions. Furthermore, the saturation vapour pressure of a product decreases at lower temperatures, increasing the number of supersaturated products and nucleation rates (Jonsson et al., 2008). Increased new particle formation was also observed when at a higher humidity (experiment 21). Numerous studies have shown a strong dependence between new particle formation and OH radical concentration (Kiendler-Scharr et al., 2009a; Wildt et al., 2014; Sarrafzadeh et al., 2016). For example, Kiendler-Scharr et al. (2009a) showed new particle formation had a power law dependence on OH concentration with an exponent of $\sim$4, indicating that around four OH radicals are consumed to produce vapours that are able to grow to nanometre particles from the oxidation of monoterpens. Increasing the water content in the reactor increases the formation of OH radicals (Reaction 1.6). So, whereas new particle formation is driven by the Criegee radical in the ozonolysis of α-phellandrene, during photooxidation OH
3.8. **α-PHELLANDRENE PHOTOOXIDATION**

(a) Particle number size distribution (cm$^{-3}$) for experiment 15.

(b) Particle volume size distribution (µm$^3$ cm$^{-3}$) for experiment 15.

(c) Particle number size distribution (cm$^{-3}$) for experiment 16.

(d) Particle volume size distribution (µm$^3$ cm$^{-3}$) for experiment 16.

Figure 3.46: Banana plots showing SOA growth under high-NO$_x$ (experiment 15) and low-NO$_x$ conditions (experiment 16). Qualitatively, aerosol formation is the same in each.

Nucleation creates small organic particles, providing an absorptive phase into which additional semi-volatile compounds may preferentially partition. The aerosol phase thus grows simultaneously with gas-phase oxidation. Driven by the high reactivity of α-phellandrene, chemistry inside the reactor evolves quickly, with maximum particle mass loadings in these experiments observed 30 to 60 minutes after irradiation. After this point, gas-phase oxidation has slowed and further gains from partitioning are superseded by wall losses, resulting in the particle mass concentration decreasing. This creation and loss behaviour is shown as banana plots in Figure 3.46, which are characteristic of aerosol formation events (Suni et al., 2008; Ortega et al., 2012; Pierce et al., 2012).

Using the method of DeCarlo et al. (2004), effective aerosol densities were calculated to range from 1.28 – 1.62 g cm$^{-3}$ across the photooxidation experiments, which are listed for each experiment in Table 3.19. Where no density was determined$^4$, the average reported density across the experiments was used (1.42 ± 0.1 g cm$^{-3}$). Error

$^4$Vacuum aerodynamic diameters were not obtained in experiment 18, due to an ill-defined particle mass-size spectrum; and experiment 22, in which the PTOF mode was mistakenly not operated.
from assuming spherical particles is accounted for in the quoted uncertainties (DeCarlo et al., 2004; Bahreini et al., 2005). Density showed no significant correlation with particle mass loading or composition, contrary to the expectation that the most oxygenated, and hence most dense SOA, occurs at lower particle loadings (Shilling et al., 2009; Kuwata et al., 2012). Similar invariance to other experimental parameters, including NO$_x$ concentration, experimental time, humidity and temperature was also observed (Clark et al., 2016). The measured densities are consistent with SOA generated from the ozonolysis of α-phellandrene, suggesting that the generated aerosol exists in a solid or waxy state (Kanakidou et al., 2005), although the SOA is less dense than what was formed during the three NO$_2$ oxidation experiments. Meanwhile, measured densities are slightly higher than what has been reported for SOA generated from the photooxidation of α-pinene, with Alfarra et al. (2006) reporting values ranging from 1.29 – 1.32 g cm$^{-3}$, Ng et al. (2007a) values from 1.32 – 1.33 g cm$^{-3}$, and Yu et al. (2008) a value of 1.21 ± 0.02 g cm$^{-3}$. Nonetheless, higher density values ~1.4 g cm$^{-3}$ have been reported for SOA from the photooxidation of isoprene (Dommen et al., 2006; Ng et al., 2008; Xu et al., 2014; Clark et al., 2016). Values above unity therefore appear typical for biogenic photooxidation, and can thus confidently be used to convert volume concentrations into mass loadings (Wiedensohler et al., 2012). Indeed, results from this study support the use of 1.4 g cm$^{-3}$ as a density for unknown systems, as recommended by Hallquist et al. (2009). Studies which utilise an organic density of 1.0 g cm$^{-3}$, either in measuring SOA (Griffin et al., 1999; Leungsakul et al., 2005a; Song et al., 2005; Pathak et al., 2007a; Zhao et al., 2015a) or in model parameterisations for predicting particle mass yields (Chung and Seinfeld, 2002), are thus likely to underestimate organic particle mass loadings.

Wall loss rates were calculated to range from 0.33 to 0.74 h$^{-1}$ (Pathak et al., 2007b), as listed in Table 3.19. Reported values are consistent with loss rates mea-
### Table 3.19: Wall loss rates, effective densities, corrected mass loadings and fractional yields for SOA generated in the photooxidation of α-phellandrene.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Wall Loss Rate (h(^{-1}))</th>
<th>Density (g cm(^{-3}))</th>
<th>M(_{org}) (µg m(^{-3}))</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.56 ± 0.02</td>
<td>1.29 ± 0.08</td>
<td>16 ± 2</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>16</td>
<td>0.55 ± 0.01</td>
<td>1.42 ± 0.1</td>
<td>84 ± 10</td>
<td>0.26 ± 0.08</td>
</tr>
<tr>
<td>17</td>
<td>0.69 ± 0.02</td>
<td>1.28 ± 0.08</td>
<td>27 ± 3</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>18</td>
<td>0.33 ± 0.3</td>
<td>–</td>
<td>1.6 ± 1.4(^b)</td>
<td>0.005 ± 0.004</td>
</tr>
<tr>
<td>19</td>
<td>0.74 ± 0.02</td>
<td>1.49 ± 0.08</td>
<td>63 ± 7</td>
<td>0.18 ± 0.06</td>
</tr>
<tr>
<td>20</td>
<td>0.68 ± 0.03</td>
<td>1.38 ± 0.09</td>
<td>36 ± 5</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>21</td>
<td>0.47 ± 0.06</td>
<td>1.45 ± 0.1</td>
<td>19 ± 3</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>22</td>
<td>0.69 ± 0.02(^a)</td>
<td>–</td>
<td>63 ± 7(^b)</td>
<td>0.20 ± 0.06</td>
</tr>
<tr>
<td>23</td>
<td>0.37 ± 0.007(^a)</td>
<td>1.46 ± 0.07</td>
<td>169 ± 19</td>
<td>0.58 ± 0.2</td>
</tr>
<tr>
<td>24</td>
<td>0.40 ± 0.02(^a)</td>
<td>1.62 ± 0.09</td>
<td>244 ± 30</td>
<td>0.66 ± 0.2</td>
</tr>
</tbody>
</table>

\(^a\)Measured under dark conditions.
\(^b\)Assuming average measured density of 1.42 ± 0.1 g cm\(^{-3}\).
compared to OH-initiated oxidation in high-NO\textsubscript{x} conditions. Meanwhile at low-NO\textsubscript{x} conditions, Henry et al. (2012) reports a significantly higher α-pinene SOA yield from OH oxidation compared to ozonolysis. Results from Griffin et al. (1999) are variable, with some monoterpenes, including α-pinene, showing a higher aerosol forming propensity upon ozonolysis, whilst other monoterpenes, such as β-pinene, sabinene and Δ\textsuperscript{3}-carene, yielding higher amounts of SOA in photooxidation experiments. A similar phenomenon is apparent when contrasting SOA yields from the ozonolysis study of Lee et al. (2006a) with the photooxidation study of Lee et al. (2006b), with some monoterpenes, including α-pinene, Δ\textsuperscript{3}-carene and α-terpinene recording higher yields in the ozonolysis experiments, whilst other monoterpenes, including β-pinene, myrcene and terpinolene, generating more SOA upon photooxidation. The remarkable aerosol forming ability of α-phellandrene observed upon ozonolysis, particularly under low mass loadings (<50 μg m\textsuperscript{-3}), cannot readily be discounted, with endocyclic conjugation present in α-phellandrene conducive to ELVOC formation upon ozonolysis (Jokinen et al., 2015). Figure 3.49 compares the aerosol yield curves of α-phellandrene with the monoterpenes α-pinene, β-pinene, Δ\textsuperscript{3}-carene, limonene and α-terpinene, whose data were collated from the studies of Hoffmann et al. (1997), Griffin et al. (1999) and Lee et al. (2006b). Results show yields are similar for most monoterpenes, particularly under low mass loadings, with α-phellandrene and limonene yielding the most aerosol at higher photooxidation aerosol loadings.

Limitations have been noted in the ability of the two-product model to cover the entire spectrum of volatilities for all chemical products, given it bins all compounds into only two semi-volatile products (Presto and Donahue, 2006; Boyd et al., 2015). For example, at high mass loadings, semi-volatile and volatile compounds can con-
Figure 3.49: Secondary organic aerosol yields for α-phellandrene compared to other monoterpenes. Data combines results from the studies of Hoffmann et al. (1997), Griffin et al. (1999) and Lee et al. (2006b), with curves showing the best resulting two-product model fits (Odum et al., 1996).

dense and potentially make up a large fraction of the aerosol. When a yield curve is fit to high mass loadings only, the parameters are likely to be biased towards semi-volatile and high volatility products. The two-product fit therefore cannot be used to predict yields at low mass loadings, where the SOA is mostly comprised of low-volatility products, and vice versa. Since the photooxidation yield curve generated as part of this study spans a wide range of organic mass loadings, the fitted parameters account for both the low-volatility products ($K_{om,1} = 0.46 \text{ m}^3 \text{ µg}^{-1}$) and the higher volatility products ($K_{om,2} = 3.9 \times 10^{-3} \text{ m}^3 \text{ µg}^{-1}$). Nonetheless, fitting yield data to the volatility basis set described in Donahue et al. (2006) shows that higher volatility products are favoured in the considered experiments. The fit coefficients are spread over five volatility bins, and are provided in Table 3.20.

Background particles were introduced in all experiments upon injection of α-phellandrene, however, for an unknown reason, the number of introduced particles was considerably higher in 2016 compared to 2013. One plausible explanation is that the injection box and/or injection line were significantly dirtier in 2016 compared to 2013. The contaminant particles had a mass concentration of around 1 µg m\(^{-3}\) in the 2016 experiments, compared to < 0.1 µg m\(^{-3}\) in 2013. The particles were small and consequently numerous, thus providing a large surface for absorptive partitioning to occur. A significant increase in particle number was still observed upon commencement of the 2016 reactions, showing fresh particle formation to be occurring, although the influence of the additional background particles is thought to explain why overall yields in 2016 experiments are higher than corresponding 2013 experiments (Wildt et al., 2014; Sarrafzadeh et al., 2016). Additionally, two
maxima were observed in the final size distributions in 2016. A local maximum was found at diameters similar to the 2013 experiments, thought to be the result of particles grown from freshly nucleated aerosol. A global maximum, which contained most of the aerosol mass, was found at diameters around twice the size of the local maximum, and is thought to be the result of growth of the background particles. No such phenomenon was observed in the 2013 experiments, suggesting a significant difference between the experiments. For this reason, experiments conducted in each campaign will be considered separately.

The fractional aerosol yields ranged from 0.005 to 0.26 in 2013, and 0.20 to 0.66 in 2016, despite all experiments starting with similar \( \alpha \)-phellandrene concentrations. Increasing the NO\(_x\) concentration was found to suppress aerosol yields, consistent with findings for other monoterpenes (Presto et al., 2005b; Ng et al., 2007a; Eddingsaas et al., 2012a; Wildt et al., 2014; Han et al., 2016; Zhao et al., 2017). By varying the NO to NO\(_2\) ratio, it was found that NO in particular was responsible for aerosol suppression (experiment 18 vs experiment 20) (Sarrafzadeh et al., 2016). Evidently the VOC/NO\(_x\) ratio or, more importantly, the VOC/NO and VOC/NO\(_2\) ratios, changes the product distribution with a significant impact on volatilities. Gas-phase measurements from the PTR-TOF provides evidence for this, with increased organic nitrate production in the high-NO\(_x\) and high-NO experiments, and increased acid production in the low-NO\(_x\) and high humidity experiments (Eddingsaas et al., 2012a).

Illustrating that later generation oxidation products are important for SOA growth, SOA mass is plotted as a function of consumed \( \alpha \)-phellandrene to produce time-dependent aerosol growth curves in Figure 3.50. Experiments 16, 19, 20, 22, 23 and 24 all trace dominant vertical growth profiles, suggesting that later generation oxidation products are important in determining the amount of SOA formed (Ng et al., 2006). Indeed, these experiments all report the highest SOA yields, suggesting that the chemistry dictating the higher-generation product distribution is critical in controlling the amount of SOA mass formed. However, differences in the vertical section of the growth curves indicate that secondary reactions contribute to SOA production to differing extents in the experiments, due to changes in physical and chemical conditions.
Decreasing the temperature by 10°C was found to increase the aerosol yield (experiment 19 vs experiment 17). This change can be explained by the Clausius-Clapeyron equation, with product saturation concentrations reducing with temperature. A larger number of product species therefore have the requisite gas-phase concentration for partitioning to be thermodynamically favourable (Pathak et al., 2007b; Jonsson et al., 2008). Therefore, all else being equal, a greater number of product species partition, whilst the equilibrium of previously saturated vapours shifts to drive further partitioning of these species. Nevertheless, kinetics must be considered, with different reactions having different temperature dependencies. A reduction in temperature will therefore lead to different production rates of the various products, and ultimately, a different composition of the particulate phase. The impact of changes in kinetics is unknown for the photooxidation of α-phellandrene. Pathak et al. (2007b) showed kinetics to be important in offsetting thermodynamic effects in the ozonolysis of α-pinene ozonolysis between 15°C and 40°C whilst, in the same temperature range for β-pinene, they found no observable kinetic effect (Pathak et al., 2008). A greater number of experiments are therefore required to accurately assess the role of thermodynamics versus kinetics in SOA formation from α-phellandrene.

In their study investigating the combined temperature and humidity dependence of SOA yield generated from the ozonolysis of β-pinene, von Hessberg et al. (2009) showed SOA yield to increase, rather than decrease, with increasing temperature at high humidities, indicating that water vapour may have a stronger influence on SOA formation than temperature. However, increasing the relative humidity to 52% in this study (experiment 21) made little difference to the observed aerosol yield (com-
pared to reference experiment 17). This is in contrast to the photooxidation study of Stirnweis et al. (2017), who found a clear increase in SOA yields for α-pinene with relative humidity. Stirnweis et al. (2017) concluded that water plays a central role in the partitioning of SOA compounds, either through changing the thermodynamic properties of the SOA (e.g. increasing absorptive mass, decreasing activity coefficients, non-reactive uptake), or by providing a reactive sink for semi-volatile vapours (e.g. increasing oligomer formation, reactive uptake). Therefore it is possible that water has a different impact on the product distribution for α-phellandrene compared to α-pinene, possibly due to reaction of stabilised Criegee intermediates.

α-Phellandrene has an additional double bond compared to α-pinene, and ozone was produced in high concentrations in most experiments (see Figure 3.43). It is therefore expected that ozonolysis plays a more significant role in this study compared to Stirnweis et al. (2017), with CIs already argued to be important SOA precursors (Section 3.5). Given reaction with water is an important SCI consumption channel (Johnson and Marston, 2008), increased removal of SCIs in experiment 21 can potentially offset any potential benefits of adding water. In support of this, Bonn et al. (2002) showed a decrease in particle number concentration and total aerosol volume with increasing humidity in the ozonolysis of select monoterpenes.

Whilst conventional thought is that NO\textsubscript{x} suppresses aerosol yields through changing the composition of the product distribution (Kroll and Seinfeld, 2008; Hallquist et al., 2009), recently it has been proposed that SOA suppression may largely be due to NO\textsubscript{x} inhibiting new particle formation, leading to a reduction in surfaces for organics to condense onto (Wildt et al., 2014; Sarrafzadeh et al., 2016; Zhao et al., 2017). Figure 3.51 shows that for experiments of differing VOC/NO\textsubscript{x}, there is a correlation between new particle formation and final aerosol yield. Furthermore, experiment 18, which had a relatively high starting NO concentration, showed the least new particle formation and correspondingly had the lowest aerosol yield. The enhanced new particle formation observed in experiment 19 under lower temperature conditions did translate into a respectively higher SOA yield. However, the same effect was not evident in experiment 21, with the higher rate of particle nucleation under humid conditions not materialising into net SOA. The discrepancy is likely explained by the reduced contribution of second generation SCIs, with the SOA growth curve for experiment 21 in Figure 3.50 showing minimal contribution of higher-generation products to the aerosol mass. New particle formation therefore provides a useful marker of the propensity of a system to yield SOA, although other factors remain important. The 2016 data supports the general trends discussed, with both new particle formation and final SOA yield correlating with VOC/NO\textsubscript{x}, and also VOC/NO ratios. However, due to the unconstrained impact of background particles in these experiments, the results are much more variable, and so no further
conclusions are made.

Sarrafzadeh et al. (2016) recently reported different NO\textsubscript{x} dependencies of SOA formation under different NO\textsubscript{x} regimes in the photooxidation of \( \beta \)-pinene. Under low-NO\textsubscript{x} conditions (VOC/NO\textsubscript{x} > 1.2), the authors report an increase in SOA mass with NO\textsubscript{x} concentrations, with the opposite SOA yield dependence observed at high-NO\textsubscript{x} conditions (VOC/NO\textsubscript{x} < 1.2). These observations suggest multiple influencing factors. Firstly, as discussed, NO\textsubscript{x} levels determine the fate of RO\textsubscript{2} radicals, by controlling the branching ratios between reactions with NO, HO\textsubscript{2} and RO\textsubscript{2} (Kroll and Seinfeld, 2008). Indirectly, a high NO concentration reduces the HO\textsubscript{2} concentration through Reaction 1.21, and recycles OH. Increased NO\textsubscript{x} concentrations also increases the production of O\textsubscript{3} and therefore the main photolytic OH source. At very high concentrations however NO\textsubscript{x} acts as an OH sink.

\[
\text{NO}_2 + \text{OH} \xrightarrow{M} \text{HNO}_3
\]

This juxtaposition of NO\textsubscript{x} driven OH production and consumption pathways was noted by Sarrafzadeh et al. (2016), who showed that OH concentration and SOA production were inextricably linked, and could explain the different SOA yield dependencies under high- and low-NO\textsubscript{x} regimes. Enhancement of SOA yields with increased OH concentrations has been observed in a number of other studies (Camredon et al., 2007; Eddingsaas et al., 2012a), who explained the effect through more efficient new particle formation and/or higher abundances of low-volatile vapours at the higher oxidant level. The higher yield observed in experiment 20, which started almost exclusively with NO\textsubscript{2}, compared to experiment 17, which had a similar VOC/NO\textsubscript{x} ratio, may therefore largely be due to increased OH radical production. This assignment of observed changes in SOA yields due to the impact of NO\textsubscript{x}, NO vs NO\textsubscript{2}, temperature or humidity is therefore complicated, as SOA yield is also likely linked to OH concentration, with a larger number of highly constrained experiments thus required to de-convolute the different effects.

The absence of a large number of first-generation products in the gas-phase measurements suggests some large loss mechanism, such as vapour partitioning to the Teflon walls. If the loss of SOA-forming vapours were occurring, then it would suppress SOA formation, resulting in understated yields. Vapours have been reported to experience reactive uptake onto walls, although the effect is only significant at high-humidities (Loza et al., 2010; Nguyen et al., 2016). While the process may influence reactive forming SOA compounds in experiment 21, it occurs on a timescale of hours and so is unlikely to affect the discussed experiments. This is in contrast to absorptive uptake (Zhang et al., 2014b; Yeh and Ziemann, 2015; La et al., 2016), which occurs on a timescale of around 10 minutes (Krechmer et al., 2016). Nonethe-

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less, through the high-reactivity of α-phellandrene and the rapid SOA production rates observed, it is anticipated that a sufficiently large particle condensation sink into which condensable gases can partition is formed, such that vapour wall losses are minimised (Boyd et al., 2015; Nah et al., 2017). It is noted that vapour wall losses were found to be minor in the oxidation of α-pinene, with SOA formation dominated by quasi-equilibrium growth (Zhang et al., 2014b; Nah et al., 2016a).

The carbon mass balance for each experiment is shown in Figure 3.52. It was calculated by summing the gas-phase yields of all product ions listed in Table 3.16, using a carbon number of 2.5 for m/z 59, along with SOA yields, incorporating elemental ratios measured by the AMS. Reported gas-phase yields pertain to specific time-points in each experiment relating to α-phellandrene consumption, with AMS yields and elemental concentrations thus calculated over this initial period. The carbon balance therefore describes the distribution of carbon directly from the consumption of α-phellandrene, providing a snapshot of the start of the experiment. Due to differing consumption rates of α-phellandrene in each experiment the time periods are different, with these noted in Figure 3.16, however over 80% of α-phellandrene was consumed in each experiment before recording of the carbon mass balance. This methodology is in contrast to the carbon mass balance shown for the ozonolysis experiments, which was reported for the whole experiment. Nevertheless, at least a quarter of carbon could be accounted for in each experiment upon α-phellandrene consumption, with carbon mass balances ranging from 27 – 59%.

Overall, the carbon distribution is quite similar in each experiment. A large fraction of the mass balance remains as α-phellandrene, with small products (< C₃), domi-
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Figure 3.52: Carbon mass balance for photooxidation experiments. Number above each bar denotes the reaction time (min) that the carbon mass balance captures, with more detail given in text.

nated by acetone/glyoxal, and large gas-phase products (other, unID) contributing similar amounts to the total carbon mass. SOA makes a mostly minor, albeit highly variable contribution, which is reflective of final SOA yields reported for each experiment. The missing carbon is thought to be derived from an inadequate description of the gas-phase. Firstly, the apparent lack of detection of first-generation products is noted, as they are expected to constitute a large fraction of the gas-phase in this initial period of the chamber experiments. Given each product is likely to contain somewhere between 7 to 10 carbons, this culminates in a large amount of missing carbon. Secondly, only the charged fragment in the PTR-TOF is detected. With considerable fragmentation observed upon calibration of the PTR-TOF, it is not unreasonable to assume that a non-negligible amount of carbon passes through as a neutral analyte. Furthermore, there exists uncertainty in the assignment of carbon numbers to all the detected ions, as well as uncertainty in the calibration of the PTR-TOF, particularly in assigned protonation rate coefficients. Despite this, the carbon mass balance provides a clear depiction of where carbon from α-phellandrene resides, adding context to the reported gas- and particle-phase yields.

Aerosol Composition

Aerosol composition was analysed by the AMS. Except for variable amounts of the NO$^+$ and NO$_2^+$ ions, which are dependent on NO$_x$, at peak SOA growth α-phellandrene photooxidation SOA exhibits similar spectra regardless of experimental
CHAPTER 3. EXPERIMENTAL

conditions. This is evident in Figure 3.53, which contrasts spectra from a high- and low-NO_x experiment, which incidentally corresponds to a low- and high-aerosol mass loading experiment respectively. The mass fragment C_2H_3O^+ is the largest in all experiments at peak SOA loading, followed by CO_2^+. Due to the calibrated fragmentation table (Section 3.2.5), the high CO_2^+ fraction correlates to large peaks at CO^+ and H_2O^+. In part, the consistency in spectra observed throughout the experimental dataset is due to the same fragmentation table being used for all photooxidation experiments. Indeed, the employed fragmentation factors represent a large source of uncertainty in this work, with values either being based on a limited set of standards (Allan et al., 2004; Aiken et al., 2008), or on the limited calibration work that comprises part of this study. More work is needed to constrain these ratios, particularly under varying experimental conditions. Other prominent ions include alkyl fragments, e.g. CH_3^+, C_3H_5^+, C_3H_7^+, C_4H_7^+, CHO^+ and the nitrate fragments, NO^+ and NO_2^+ which, as in the NO_2 oxidation study, are apportioned to the organic signal. Although gas-phase nitric acid is produced from the reaction of OH with NO_2 (Equation 3.37), at the low chamber humidities encountered, nitric acid is not expected to partition appreciably into the particle phase (Chhabra et al., 2011).

At higher mass-to-charge ratios, the signals at m/z 67 (C_5H_7^+), m/z 77 (C_6H_5), m/z 79 (C_6H_7) and m/z 91 (C_7H_7^+) are respectively large ions in α-phellandrene photooxidation SOA high-resolution mass spectra. These ions also comprise a large fraction of the AMS signal analysing SOA formed from the ozonolysis of α-phellandrene, of which an example is provided in Appendix E. These ions additionally make up a large fraction of spectra for SOA formed from monoterpene and sesquiterpene oxidation (Ng et al., 2007a; Shilling et al., 2009; Fry et al., 2011; Boyd et al., 2015; Chen et al., 2015; Nah et al., 2016b), whilst not being significant in the high-resolution mass spectra of isoprene and anthropogenically emitted (e.g. toluene, xylene, naphthalene) precursor SOA systems (Ng et al., 2008; Chhabra et al., 2010). Therefore, m/z 67, 77, 79 and 91 could potentially serve as fingerprint fragments for identifying SOA formed from monoterpene/sesquiterpene oxidation in ambient aerosol mass spectra. Interestingly, Kiendler-Scharr et al. (2009b) observed these ions to be prominent in SOA formed from eucalyptus (Eucalyptus globulus L.) emissions, suggesting the monoterpene, potentially α-phellandrene, derived species are significant constituents.

As shown in Figure 3.53, the nitrate fragments make a larger contribution to experiment 15, which had a VOC/NO_x ratio of 0.58, compared to experiment 16, which had a VOC/NO_x ratio of 4.6. Organic nitrates are generated both from the oxidation of α-phellandrene by the nitrate radical, and reaction of peroxy radicals with NO, with it noted that nitrate yields from peroxy radicals increase with size of
3.8. α-PHELLANDRENE PHOTOOXIDATION

Figure 3.53: High-resolution elemental mass spectra of α-phellandrene SOA formed under (a) high-NO\textsubscript{x} (experiment 15) and (b) low-NO\textsubscript{x} conditions (experiment 16). Spectra are taken at the peak of SOA growth.

the alkyl group (Arey et al., 2001). The addition of nitrate and alcohol groups have similar effects on vapour pressure (Capouet and Müller, 2006; Pankow and Asher, 2008; Compernolle et al., 2011), with reaction of monoterpenes with NO\textsubscript{3} observed to produce aerosol with significant yields in chamber studies (Hoffmann et al., 1997; Fry et al., 2009, 2014; Boyd et al., 2015). Consequently, particulate phase nitrates are thought to reflect gas-phase abundance.

The average ratio of NO\textsuperscript{+} to NO\textsubscript{2}\textsuperscript{+} in mass spectra ranged from 5.9 to 6.4, supporting apportionment of these ions to the organic signal (Fry et al., 2009; Farmer et al., 2010; Boyd et al., 2015; Kiendler-Scharr et al., 2016). This ratio is lower than what was observed during the NO\textsubscript{2} initiated oxidation experiments, suggesting a different distribution of nitrated products, although it is similar to what was reported during photooxidation of α-pinene and limonene in Zhao et al. (2017). Overall, the mass ratio of nitrate to organics in SOA formed in this study ranged from 3 – 7%. Estimating a total mass for organonitrates is difficult, since the average molecular mass is needed (Fry et al., 2013; Kiendler-Scharr et al., 2016). Molecular
weights of organonitrates proposed through the constructed gas-phase mechanism vary significantly (150 – 300 g mol$^{-1}$), however an average value of 200 g mol$^{-1}$, which represents an effective lower bound, is used to make results comparable with other chamber and field studies using this pseudo molecular weight (Xu et al., 2015; Kiendler-Scharr et al., 2016; Zhao et al., 2017). For this value, organonitrates are estimated to account for 10 – 23% of the total organic mass as measured by the AMS. The fraction of organonitrates in the total mass is within the range Zhao et al. (2017) reported for the photooxidation of α-pinene and limonene, although is less than what was reported during the NO$\text{2}$ initiated oxidation of α-phellandrene and what has been reported in chamber SOA formed from the reaction of nitrate radicals with monoterpenes (Fry et al., 2009, 2014; Boyd et al., 2015). The values are nonetheless consistent with organic nitrate fractions observed in SOA during field studies conducted in rural areas with large monoterpene emissions (Fry et al., 2013; Xu et al., 2015; Lee et al., 2016).

To better parameterise the composition of the entire SOA, it is useful to analyse bulk properties of the SOA. Despite having recently been revised by Canagaratna et al. (2015), the calibration factors of Aiken et al. (2008) are used for converting raw atomic ratios into elemental compositions to remain consistent with previously conducted ozonolysis work. The main criticism of the Aiken et al. (2008) method was that it underestimates CO$^+$ and H$_2$O$^+$ from many oxidised species. However, the contribution of both these ions with respect to CO$_2^+$ was calibrated and aptly corrected for in the fragmentation table, such that use of the Aiken et al. (2008) method is thought acceptable.

SOA is typically characterised in terms of changing intensities of the two most dominant oxygen-containing ions in the spectra: $m/z$ 44 (mostly CO$_2^+$) and $m/z$ 43 (mostly C$_2$H$_3$O$^+$). The CO$_2^+$ fragment is interpreted as a marker ion for organic acids in SOA, as it is known to form from the thermal decarboxylation of carboxylic acids (Aiken et al., 2007; Takegawa et al., 2007; Duplissy et al., 2011). Conversely, the fragment ion C$_2$H$_3$O$^+$ has been proposed to form from non-acid oxygen-containing organic compounds. In general, low-volatility oxygenated organic aerosol (LV-OOA) produces mass spectra dominated by the CO$_2^+$ mass fragment, whilst semi-volatile oxygenated organic aerosol (SV-OOA) produces mass spectra with C$_2$H$_3$O$^+$ as the dominant ion. The ratio of CO$_2^+$ to C$_2$H$_3$O$^+$ therefore provides a useful metric for assessing the degree of functionalisation in organic aerosol.

By plotting $f_{44}$ (ratio of $m/z$ 44 to total component spectrum) against $f_{43}$ (defined similarly), Ng et al. (2011) showed that oxygenated organic aerosol clustered into a triangular region. Data from LV-OOA tends to cluster in the top half of the ‘triangle plot’, and SV-OOA in the lower half.

Figure 3.54 illustrates the triangle plot (panel a) along with a van Krevelen dia-
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Figure 3.54: Triangle plot and van Krevelen diagram for SOA formed from α-phellandrene photooxidation.

(a) Triangle plot. The outline of the triangle proposed by Ng et al. (2011) is shown in grey.

(b) Van Krevelen diagram.

gram (panel b) for SOA derived from α-phellandrene photooxidation. The triangle plot was calculated using unit mass resolution (UMR) mass spectra data, and van Krevelen from high resolution (HR) mass spectra data. Experiment 18 is omitted from Figure 3.54b for clarity, with the low aerosol mass loading resulting in a noisy signal (Rollins et al., 2010). Consistent with results from the ozonolysis study, and findings for other monoterpenes (Shilling et al., 2009; Chhabra et al., 2011), as the SOA mass formed by α-phellandrene photooxidation increases, the O/C ratio and $f_{44}$ decrease due to enhanced partitioning of less oxidised semivolatile compounds into the growing OA medium. Photooxidation processes quickly overtake semivolatile partitioning however, and the oxidation state of the SOA increases, represented by increases in both O/C and $f_{44}$. This is evidenced by experiments moving towards
the top of the triangle plot in Figure 3.54a at the end of experiments.

The observed clustering of data in the lower half of the triangle classifies the SOA produced in these experiments as SV-OOA (Ng et al., 2011). This observation is characteristic of chamber studies, which typically do not reach the oxidant exposures achieved in the atmosphere (Kroll and Seinfeld, 2008; Hallquist et al., 2009), with other studies using AMS spectral factors to investigate monoterpene oxidation showing similar characterisation (Ng et al., 2010; Chhabra et al., 2011). Shilling et al. (2009) showed that in α-pinene ozonolysis $f_{43}$ increased with increasing particle mass loading, with Figure 3.55 showing the same effect to occur for α-phellandrene photooxidation SOA. Experiment 22, which had the highest NO$_x$ concentration, was an outlier to this general trend.

Figure 3.54b shows α-phellandrene photooxidation SOA to map a line with slope $= 0$ in van Krevelen space, implying the addition of oxygen with little loss of hydrogen. This observation is consistent with the mechanism of alkene oxidation, where oxygen can be added across double bonds with no loss in hydrogen. Therefore, condensible products are likely formed from reaction at one, or both, of the double bonds in α-phellandrene, with further decomposition through hydrogen abstraction channels yielding species that are too volatile (possibly due to fragmentation) to significantly impact the SOA mass. Moreover, involatile species are likely produced through the autoxidation process proposed by Crounse et al. (2013), whereby oxygen can be inserted into bonds without significant loss of hydrogen. This observation is in stark contrast to the study of Heald et al. (2010), who showed from a variety of ambient and laboratory measurements that SOA occupies a narrow range in van Krevelen space, tracing a line of slope $-1$, implying addition of a carboxylic acid group or equal amounts of hydroxy and carbonyl functional groups to a saturated chain. Chamber results from Chhabra et al. (2011), who investigated a large variety of SOA systems, showed more variation, producing a slope shallower than $-1$ in van Krevelen space. The authors concluded that ageing pathways in van Krevelen space are likely to be different for different species, given that not all SOA precursors resemble saturated chains. Results from α-phellandrene photooxidation seem to support this notion.

The van Krevelen plot shows elemental ratios, in general, change little during the course of an experiment, with the average elemental composition for each experiment listed in Table 3.21. The majority of data points are contained within an O/C ratio of 0.4 to 0.6, slightly higher than what was observed during the ozonolysis experiments in Section 3.5.1. Nonetheless, the O/C range is consistent with observations from α-pinene photooxidation (Chhabra et al., 2011; Pfaffenberger et al., 2013; Zhao et al., 2015a), and agrees with the O/C value in plant chamber SOA for monoterp-
Figure 3.55: H/C and O/C ratios and \( f_{43} \) for increasing organic particle mass loading, with general trends shown.

α-pinene dominated emission mixtures\(^5\) (Kiendler-Scharr et al., 2009b). It is interesting to note that experiment 19, which was conducted at the lowest temperature, had the lowest relative oxygen content, suggesting thermodynamically enhanced partitioning of less oxygenated products is occurring. Figure 3.54b shows the H/C ratio to vary between 1.55 to 1.70. This range is higher than a lot of the ozonolysis experiments, suggesting that a process with significant hydrogen loss, such as addition of a carbonyl, plays a larger role in SOA formation from ozonolysis compared to photooxidation (Zhao et al., 2015a). Figure 3.55 shows both O/C and H/C to have a slight dependence on SOA mass loadings (Shilling et al., 2009).

Table 3.21 also lists the fraction of oxygen originating from organic acids and organonitrate functionality, averaged over each experiment. The oxygen mass from organic acids was calculated by summing the oxygen mass contribution from \( \text{CO}_2^+ \) with those ions dependent on its signal, \( \text{O}^+, \text{HO}^+, \text{H}_2\text{O}^+ \) and \( \text{CO}^+ \), using the fragmentation table (Aiken et al., 2008). The oxygen mass from organic nitrates was determined by summing the oxygen mass contribution from \( \text{NO}^+ \) and \( \text{NO}_2^+ \). The oxygen contribution of each of these functionalities was then computed by comparing the calculated values to the total oxygen concentration, measured using the HR-mass loadings and elemental ratios. Table 3.21 shows that 44 – 60% of speciated oxygen is contained in acid groups, and 5 – 9% in nitrate groups. These values are similar to findings for isoprene, α-pinene and limonene photooxidation (Chhabra et al., 2011; Zhao et al., 2017). While acid and nitrate groups contain a significant amount of the oxygen content in oxidised SOA, a similar fraction does remain in other ions such as \( \text{C}_2\text{H}_3\text{O}^+ \).

\(^5\)O/C calculated from \( f_{44} \) using the method of Ng et al. (2010).


<table>
<thead>
<tr>
<th></th>
<th>Acid</th>
<th>Nitrate</th>
<th>Other</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.48</td>
<td>0.09</td>
<td>0.43</td>
<td>C(<em>1)H(</em>{1.55})O(<em>{0.49})N(</em>{0.03})</td>
</tr>
<tr>
<td>16</td>
<td>0.47</td>
<td>0.04</td>
<td>0.48</td>
<td>C(<em>1)H(</em>{1.62})O(<em>{0.46})N(</em>{0.02})</td>
</tr>
<tr>
<td>17</td>
<td>0.48</td>
<td>0.08</td>
<td>0.43</td>
<td>C(<em>1)H(</em>{1.59})O(<em>{0.49})N(</em>{0.03})</td>
</tr>
<tr>
<td>18</td>
<td>0.45</td>
<td>0.09</td>
<td>0.46</td>
<td>C(<em>1)H(</em>{1.56})O(<em>{0.62})N(</em>{0.04})</td>
</tr>
<tr>
<td>19</td>
<td>0.44</td>
<td>0.09</td>
<td>0.47</td>
<td>C(<em>1)H(</em>{1.55})O(<em>{0.44})N(</em>{0.03})</td>
</tr>
<tr>
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<td>0.47</td>
<td>0.08</td>
<td>0.45</td>
<td>C(<em>1)H(</em>{1.61})O(<em>{0.48})N(</em>{0.03})</td>
</tr>
<tr>
<td>21</td>
<td>0.52</td>
<td>0.07</td>
<td>0.41</td>
<td>C(<em>1)H(</em>{1.56})O(<em>{0.59})N(</em>{0.03})</td>
</tr>
<tr>
<td>22</td>
<td>0.60</td>
<td>0.07</td>
<td>0.32</td>
<td>C(<em>1)H(</em>{1.70})O(<em>{0.61})N(</em>{0.04})</td>
</tr>
<tr>
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<td>0.05</td>
<td>0.51</td>
<td>C(<em>1)H(</em>{1.65})O(<em>{0.47})N(</em>{0.03})</td>
</tr>
<tr>
<td>24</td>
<td>0.46</td>
<td>0.06</td>
<td>0.48</td>
<td>C(<em>1)H(</em>{1.65})O(<em>{0.57})N(</em>{0.03})</td>
</tr>
</tbody>
</table>

Table 3.21: Fraction of oxygen contribution in organic acid, organic nitrate and other functionalities, along with standardised elemental composition for SOA produced across each \(\alpha\)-phellandrene photooxidation experiment.

Under both low- and high-NO\(_x\) oxidation conditions the AMS data indicates similar bulk organic functionality. Of the 2013 experiments, SOA formed in experiment 21, which was conducted under the highest humidity, showed the largest acid contribution, consistent with gas-phase observations. Similarly, experiments 15 and 18 had the largest nitrate contribution, and experiment 16 the lowest, both in the gas- and particle-phases. Despite these observations, there was no systematic trend in gas-phase NO\(_x\) and particle nitrate concentration among the remaining experiments, suggesting the system is complex with multiple influencing factors.

Consistency both with and among the 2016 experiments is less obvious, potentially due to the unconstrained influence of background particles in these experiments. Nonetheless, despite NO\(_x\) family ions being included as part of the organic mass spectra, their oxygen content contribution is likely underestimated due to the inability of the AMS to detect nitrogen-bonded oxygen in –ONO\(_2\) functional groups (Farmer et al., 2010; Rollins et al., 2010). A similar issue may also be occurring for peroxides formed under low-NO\(_x\) conditions whereby, upon electron impact, the RO–OH bond severs, leaving the OH fragment undetected. This potentially is a reason why SOA elemental compositions observed under different NO\(_x\) regimes are similar (Chhabra et al., 2011).

### 3.8.3 Summary of Photooxidation Experiments

The photooxidation of \(\alpha\)-phellandrene was studied for the first time through ten chamber experiments, of varying VOC/NO\(_x\) conditions. These showed the degra-


dation of α-phellandrene to be an efficient NO\textsubscript{x}-cycler, with large concentrations of ozone produced in each experiment. The largest gas-phase organic signals were from formaldehyde (1–14%), acetaldehyde (2 – 9%), glyoxal/acetone (9 – 18%), methyl glyoxal (3 – 8%), formic acid (4 – 8%), acetic acid (3 – 7%) and the common fragment C\textsubscript{2}H\textsubscript{3}O\textsuperscript{+} (6 – 8%). NO\textsubscript{2}\textsuperscript{+} (2 – 11%) is also detected, from which it is inferred that nitrogen-containing organic products exist in the gas-phase. Yields of these small gas-phase products were found to be dependent on chamber oxidising conditions, and despite their low-molecular weight, were found to contain the majority of carbon mass in the gas-phase products. Signals at m/z 123, 139 and 151 were assigned as fragments of first-generation products, based on the temporal profiles, with all other remaining ions assigned to saturated second- and higher-generation products and their fragments. Based on m/z and a proposed chemical mechanism, structures for many of these ions have been assigned.

A homogeneous nucleation burst of fresh aerosol was observed in all experiments within a few minutes of irradiation, indicating formation of ELVOC species. The amount of new particle formation was observed to increase upon shifting from a RO\textsubscript{2} + NO dominated regime to a RO\textsubscript{2} + HO\textsubscript{2} or RO\textsubscript{2} regime, reducing the temperature and increasing the humidity, suggesting that the amount of OH radicals and peroxy radical propagation/re-arrangement reactions are important factors in ELVOC formation. The average effective SOA density was determined to be 1.42 ± 0.1 g cm\textsuperscript{-3}, with the SOA yield curve best fit by α\textsubscript{1} = 5.5 × 10\textsuperscript{-6}, α\textsubscript{2} = 1.0, K\textsubscript{om,1} = 0.46 m\textsuperscript{3} µg\textsuperscript{-1} and K\textsubscript{om,2} = 3.9 × 10\textsuperscript{-3} m\textsuperscript{3} µg\textsuperscript{-1}. SOA growth curves show both first- and higher-generation products to contribute to the particle phase, although the contribution of higher-generation products, and hence product volatility distribution, is highly dependent on experimental conditions. This is in stark contrast to the ozonolysis experiments, whose growth profiles tended to feature large vertical sections. Total SOA yield from α-phellandrene photooxidation is less than that observed during ozonolysis and higher than what was formed during NO\textsubscript{2} initiated experiments, and is quite similar to results from other monoterpenes presented in the literature. Aerosol formation is therefore more dependent on photooxidation conditions (e.g. VOC/NO\textsubscript{x}, OH concentration, temperature) compared to specific monoterpene structure, with the former having a greater impact on the composition of the product distribution. Nonetheless, correlation between aerosol yield and new particle formation was observed, with the amount of surface volumes initially available for partitioning also thought to be important.

Using a triangle plot the aerosol produced is classified as semi-volatile oxygenated organic aerosol. Whilst in van Krevelen space the SOA traces a slope of zero, suggesting oxygen is added with little loss of hydrogen, consistent with oxidation at the two double bonds in α-phellandrene. Organic nitrates are estimated to account for
10 – 23% of the total organic aerosol mass. Meanwhile 44 – 60% of speciated oxygen resides in acidic group, and only 5 – 9% in nitrate groups, with these values slightly dependent on VOC/NO\textsubscript{x} ratios. O/C, H/C and \textit{f}_{43} values were all found to have a weak dependence on SOA mass loadings. However in general, bulk organic functionality was found to be quite similar across the experimental dataset. The analysed photooxidation dataset will now be used to assist in mechanism construction and evaluation.
Chapter 4

Mechanism Construction and Evaluation

4.1 Mechanism Construction

The final component in characterising the tropospheric degradation of α-phellandrene is parameterisation of chemical degradation pathways in an explicit chemical mechanism. The gas-phase chemical mechanism, developed to be consistent with the MCM protocols (Jenkin et al., 1997; Saunders et al., 2003), although adjusted to incorporate recent theoretical and experimental findings, is integrated with an explicit representation of gas-particle partitioning. Mechanism construction is a compromise between chemical accuracy and size, with details of the specific construction methodology and various assumptions and estimative techniques used for determining unknown variables and parameters now provided. The complete degradation mechanism of α-phellandrene is provided in Appendix I. Names in this final chapter that are completely capitalised refer to either existing or newly developed species MCM code names. Structures for newly created products are provided along with the mechanism, whilst pre-existing structures can be viewed by searching code names in the MCM website (http://mcm.leeds.ac.uk).

4.1.1 Gas-Phase Construction

The complete gas-phase tropospheric degradation mechanism of α-phellandrene consists of 3601 reactions and 1187 closed-shell and radical species, of which 2150 reactions and 723 species are newly added. The scheme is therefore moderately detailed, but necessarily contains a number of simplifications, without which the mechanism could easily contain up to $10^8$ reactions (Aumont et al., 2005; Szopa et al., 2005). The degree of simplification changes depending on the importance of the product channel, and increases with successive generations (Jenkin et al., 1997; Saunders
et al., 2003). It is therefore highly unlikely that the mechanism contains all species that might be measured experimentally. Nonetheless, the mechanism provides a representation of the most important degradation routes, and is thus appropriate for describing the decomposition of α-phellandrene and its major products in the majority of systems where a representation of chemical detail is required. Furthermore, the constructed mechanism provides a reference benchmark against which reduced schemes can be developed and evaluated.

The mechanism includes chemistry initiated by reaction with OH radicals, O$_3$ and NO$_3$ radicals. The initial stages of mechanism construction are the most crucial, having the largest influence over mechanism evolution and product distribution. Therefore, important features of the various initiation pathways are now discussed.

**OH Initiation**

OH attack on α-phellandrene was represented with a rate coefficient of $3.2 \times 10^{-10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999). Of this, 27% is apportioned to H-abstraction (Peeters et al., 1999), and 73% to OH addition. As discussed in Section 3.8.1, OH addition to α-phellandrene yields six possible products (shown in Figure 3.41). Peeters et al. (2007) argue that the site-specific rate coefficients for OH addition depends on the stability of the radical product, with resonance stabilised radicals being more prevalent in conjugated systems than non-resonant analogues. Indeed, the SAR developed by Peeters et al. (2007) predicts that 67% of OH addition occurs at one of the outer carbons of the conjugated ring in α-phellandrene (carbons 3 and 6 in Figure 3.41). For this reason, the scheme was simplified by only considering OH addition to these two active sites. The SAR of Peeters et al. (2007) is used to assign branching ratios, with addition to carbon 3, which forms a tertiary and secondary radical, occurring 69% of the time, and addition to carbon 6, which forms two secondary radicals, assigned a branching ratio of 31%. Delocalisation of the nascent radical electron occurs mostly after the transition state, so the primary radical site, in the β-position, has a more dominant impact compared to the secondary radical site, in the δ-position. Consistent with the representation of isoprene in the MCMv3.2, and current representation of 1,3-butadiene in the MCM, the initial structure formed from addition is favoured with a weighting of 0.75, whilst the resonance canonical has a weighting of 0.25. The most recent update of the isoprene mechanism in the MCM (Jenkin et al., 2015) incorporates theoretical findings from Peeters and co-workers (Peeters et al., 2009, 2014), and represents the formation of cis- and trans-isomers of the allyl-stabilised hydroxalkenyl radical. Given its cyclic structure, rotation of the olefin moiety in the radical adduct would not occur in α-phellandrene, and so a similar representation is not adopted here. The two resonant products formed are
Figure 4.1: Simplified schematic showing the first-generation product distribution from the OH-initiated degradation of α-phellandrene, as represented in the constructed mechanism. The peroxy radicals, APHAO₂, APHCNO₃ and APHDO₂ are formed from sequential OH and O₂ addition, whilst APHEO₂ is formed from H-abstraction followed by O₂ addition. Relative product yields are given as percentages. Yields in green are for NOₓ free conditions. Yields in blue are for conditions with sufficient NO to provide an exclusive reaction pathway for RO₂ radicals.

quite similar to one another, having either a radical or hydroxy group at carbons 3 and 6. Given the similarity, and that the resonance products are respectively minor, the pathways are represented through one surrogate species to further simplify the chemical mechanism. Consequently, OH addition is represented through three distinct radical products, which are shown along with their branching ratios in Figure 4.1.

C–H bond strength calculations for α-phellandrene show abstraction from carbons 4 and 5 to dominate, with super-allyl-resonance existing in the generated radical products (Vereecken and Peeters, 2001). Of these two sites, H-abstraction from the CH group at carbon 5 is over 11 kJ mol⁻¹ more favourable. This difference in bond strength corresponds to over two orders of magnitude difference in reaction rate. Correspondingly, only abstraction from carbon 5 is represented in the mechanism. Although (super-)resonance structures exist, as a simplification for this minor pathway, only the initially-formed tertiary radical is represented. Despite ρ-cymene having been proposed as a possible product from the reaction of α-phellandrene with OH (Aschmann et al., 2011), its formation is not represented in the current mechanism.

Conventional chemistry outlined in the MCM protocol papers (Jenkin et al., 1997; Saunders et al., 2003) is used to dictate the fate of the generated peroxy radi-
icals, with the distribution of product species shown in Figure 4.1. In the absence of NO\textsubscript{x}, this includes a set of hydroperoxides formed from HO\textsubscript{2} terminating reactions of the peroxy radicals (APHAOOH, APHCOOH, APHDOOH and APHEOOH, accounting for 27.6% of the products); a set of hydroxy and dihydroxy species formed from a terminating channel of the peroxy radical permutation reactions (APHAOH, APHCOH, APHBOH and APHEOH, accounting for 18.5% of the products); and hydroxyketone species formed from the other peroxy radical permutation reaction terminating channel (APHCACO and APHDCO, accounting for 6.2% of the products). The propagating channel of the peroxy radical permutation reactions leads to the formation of oxy radicals, which decompose into the carbonyl products APHAAL (19.7%), APHCAL (9.1%), APHDAL (9.6%) and APHECO (9.2%). C–C bond scission in APHDO forms a vinyl-type radical, which decomposes into a carbonyl and acyl radical as described by MCM protocol (Jenkin et al., 1997). Reaction with O\textsubscript{2} is also included for APHDO, yielding APHDCO. Isomerisation reactions, including those discussed in Jenkin et al. (2015) for isoprene, are not considered for these initial oxy radicals, as the ring-structure prevents the correct geometry for intramolecular transfer from being attained.

Theoretical work by Peeters et al. (2009) and Da Silva et al. (2010) showed that 1,5-H atom shifts are favourable for $\beta$-hydroxy peroxy radicals in isoprene. Based on this, the pathway is included for APHAO2 and APHCO2, leading to the formation of APHAAL and APHCAL respectively, along with OH. Applied isomerisation rates are the same as for isoprene in the MCM (Jenkin et al., 2015). Peeters et al. (2009) additionally showed that cis-isomers of the $\delta$-hydroxy peroxy radicals in isoprene, analogous to APHDO2 in this work, undergo 1,6-H isomerisation reactions to produce resonant hydroxy hydperoxyalkenyl radicals. Such a pathway, however, is thought to be precluded by ring strain in APHDO2, and so is not represented in the current mechanism. Ring-closure reactions of unsaturated peroxy- and oxy radicals have been shown to be favourable for isoprene, $\alpha$- and $\beta$-pinene (Vereecken and Peeters, 2004), however are not considered in the current $\alpha$-phellandrene mechanism due to the strong structural dependence of barrier heights observed in the considered monoterpenes.

Formation of the same carbonyl products, namely APHAAL (29.2%), APHCAL (13.1%), APHDAL (14.1%) and APHECO (23.8%), is dominant under high-NO\textsubscript{x} conditions, due to NO-facilitated propagation of peroxy radicals. Nitrate formation also becomes relevant, with APHANO3, APHCNO3, APHDNO3 and APHENO3 (accounting for 19.9% of the products) formed from the NO-terminating channel. The branching ratios for the NO propagating and terminating channels in APHAO2, APHCO2 and APHDO2 are taken to be the same as limonene in the MCM (22.8%, Ruppert et al. (1999)). This value has support from the recent study of Teng et al.
(2015) for hydroxyperoxy radicals. The branching ratio for the nitrate forming channel for APHEO2, which has no β- or δ-OH, is taken from the MCM protocols.

It is important to note that the product distribution shown in Figure 4.1, which are the major first-generation products from OH initiation, are mostly predicted based on conventional chemical processes applied in the MCM. During photooxidation experiments, the PTR-TOF detected ions at m/z 169 and 171, whose masses correspond to proposed structures. Nonetheless, apart from this, no evidence for production of any of the species shown in Figure 4.1 currently exists.

### O₃ Initiation

O₃ attack was represented with a rate coefficient of $3.0 \times 10^{-15}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Calvert et al., 2000), based on the relative rate study of Shu and Atkinson (1994). Given the importance of the ozonolysis channel, all four possible excited Criegee intermediate products were represented. Guided by computational results (Chapter 2), attack at the less substituted double bond was represented 70% of the time, with equal weighting given to the two CI products (APH3OOA and APH4OOA). The remaining 30% proceeds through addition to the more substituted double bond, with 30% of this channel shown to form the primary CI APH1OOA, and 70% the secondary CI APH2OOA, based on the recommendation of Rickard et al. (1999) for tri-substituted olefins. The represented decomposition pathways of these four CIs to first-generation products is summarised in Figure 4.2.

Each excited CI was represented as having one stabilisation channel and a set of unimolecular rearrangement channels. The most computationally favourable vinyl hydroperoxide channel for each CI was represented. For APH2OOA and APH4OOA, this was the proposed allyl-resonance stabilised 1,6-hydrogen shifts, with the more stable tertiary radical represented as the ultimate radical site. For APH1OOA and APH3OOA, conventional 1,4-H shifts were represented. The weighting of these vinyl hydroperoxide channels were assigned to reflect experimentally observed OH yields ($35 \pm 12 \%$, Chapter 3.5.1), with a greater flux given to the two resonance stabilised pathways. This representation is in contradiction to Herrmann et al. (2010), who proposed no OH-forming channel from APH4OOA, due to the lack of available α-hydrogens. Subsequent conventional chemistry of the oxo-peroxy radicals generates a large number of species, as shown in Figure 4.2. Decomposition of APH2COTO2 to C7AL36CO additionally yields an isopropyl peroxy radical (IC3H7O2), which can decompose into acetone. This pathway is represented to occur with a flux less than 0.3%, consistent with the experimental acetone measurements of Reissell et al. (1999). The non-OH forming pathways yield either an epoxide (APH1EPOX, APH3EPOX), ester (APH2EST, APH4EST) or acid (C10AL1COOH) in low yields, reflecting predicted energy barriers. These products
Figure 4.2: Schematic showing the first-generation product distribution from the ozonolysis of \( \alpha \)-phellandrene as represented in the chemical mechanism. Relative product yields are given as percentages, corresponding to ozonolysis at 298 K, 1 atm and 10% RH, with complete OH radical scavenging.

were represented explicitly in the mechanism to maintain product identity (Jenkin et al., 2012), rather than through the non-OH generating decomposition channels shown in Jenkin et al. (1997).

Computational results predict SOZ formation to be the most favourable unimolecular reaction in the ozonolysis of \( \alpha \)-phellandrene. Subsequently, SOZ formation is represented as occurring with an initial rate of 0.3 s\(^{-1} \) from all stabilised CI, yielding the products APHSOZ1 (3.5%) and APHSOZ2 (8.4%). Setting of the initial rate is arbitrary, and open to future optimisation. The remaining flux occurs through traditional MCM stabilised CI pathways, that is bimolecular reactions with NO, NO\(_2\), CO, SO\(_2\) and H\(_2\)O to yield the dominant carbonyls APHAAL and APHCAL. Where the CI is primary, an additional acid-forming channel with water is also included (Jenkin et al., 1997; Saunders et al., 2003).
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NO$_3$ Initiation

Consumption of $\alpha$-phellandrene by the nitrate radical is only expected to be important at night. The reaction was represented with a rate coefficient of $7.3 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, based on the recommendation of Calvert et al. (2000). The preferred value of the room temperature rate coefficient represents the average of the relative rate studies of Atkinson et al. (1985) and Berndt et al. (1996). The recommended value is higher than what was measured by Martínez et al. (1999) using an absolute rate method, with the relative rate studies preferred, as an accurate determination of reactant concentrations is not required.

The large rate coefficient suggests that NO$_3$ adds across the double bonds. For conjugated dienes, such as $\alpha$-phellandrene, nitrate radical addition leads to the formation of $\beta$- and $\delta$-nitrooxy alkyl radicals (Skov et al., 1992; Calvert et al., 2000). Considering that consumption by the nitrate radical is a respectively minor tropospheric consumption pathway for $\alpha$-phellandrene, and the photooxidation experiments considered in this thesis are relatively insensitive to NO$_3$-initiated chemistry, only one addition channel is included. Using the nitrate radical SAR developed by Kerdouci et al. (2010), addition to the more substituted double bond in $\alpha$-phellandrene is estimated to occur at a rate 30 times faster than that to the less substituted double bond. Meanwhile, the distribution of $\beta$- and $\delta$-radicals is expected to be similar to what is formed from OH addition (Peeters et al., 2007), that is, the primary radical site is expected to have a larger influence compared to the secondary radical site. Addition to the external carbon of the more substituted double bond is therefore represented through a $\beta$-nitrooxy alkyl peroxy radical.

The main features of the NO$_3$-initiated degradation chemistry to first-generation products are summarised in Figure 4.3. The scheme is simplified with respect to

![Figure 4.3: Schematic of the first-generation product distribution from the addition of NO$_3$ to $\alpha$-phellandrene, as represented in the chemical mechanism.](image-url)
other initiation pathways. Reaction of the $\beta$-nitrooxy alkyl peroxy radical with NO is entirely radical propagating (Jenkin et al., 1997). Meanwhile the $\beta$-nitrooxy hydroperoxy product, NAPHAOOH, and the $\beta$-nitrooxy hydroxy product, NAPHAOH, are treated as minor species, with simplified OH reaction mechanisms to form products that are generated elsewhere in the mechanism. This representation is consistent with the other monoterpenes in the MCM.

**Higher Generation Chemistry**

The initiation chemistry described leads to the formation of first-generation oxygenated products of varying complexity and functionality, including carbonyl compounds, alcohols, hydroperoxides, organic nitrates, carboxylic acids, esters, epoxides, secondary ozonides and multifunctional compounds containing two or more of these functionalities. Many of these products contain a residual double bond, making them susceptible to attack from OH radicals, $O_3$ and NO$_3$ radicals. OH reaction rates for all species were calculated using the SAR developed by Kwok and Atkinson (1995), integrated with new parameters to account for alcohol (Bethel et al., 2001), hydroperoxide (Aumont et al., 2005) and PAN (Saunders et al., 2003) functional groups. The reaction of $O_3$ to unsaturated products was assumed to occur at a rate of $1.0 \times 10^{-16}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, based on experimental results (Chapter 3.5.1). All other kinetic parameters were taken from the MCM protocols (Jenkin et al., 1997; Saunders et al., 2003).

As described in detail by Jenkin et al. (1997) and Saunders et al. (2003), the further degradation of first and subsequent generation products is simplified in comparison to $\alpha$-phellandrene, in order to constrain mechanism size. Carbonyl compounds formed from the NO$_x$ catalysed chemistry (e.g. APHAAL, APHCAL, APHDAL, APHECO) are the major products under most conditions. These species, along with the two secondary ozonides, are degraded similar to $\alpha$-phellandrene, and include consumption by OH radicals, $O_3$, NO$_3$ radicals and photolysis, with some degree of simplification to limit the number of product channels represented. The alcohol, hydroperoxide, organic nitrate, carboxylic acid, ester and epoxide containing products are considered respectively minor, with their degradation chemistry significantly simplified (Jenkin et al., 1997; Saunders et al., 2003). The simplified chemistry, typically consisting of the major photolysis and OH initiated channels, aims to accurately reflect the lifetime of the products, maintain elemental mass balance, and fairly represent radical propagation and termination processes. Where possible, reaction pathways feeding minor channels back into major products were taken, regardless of whether this is the most preferable decomposition route. This typically involved radical attack at the non-carbonyl functionality, reducing it into a carbonyl. The same methodology, differentiating between major and minor prod-
ucts, is applied through successive product generations, with decomposition represented until smaller species already present in the MCM are formed. Comments explaining represented pathways for each reaction are provided with the mechanism in Appendix I.

### 4.1.2 Particle-Phase Construction

Gas-to-aerosol partitioning is explicitly incorporated into the mechanism for all non-radical compounds with a carbon backbone larger than five, numbering 458 products in total. Equilibrium partitioning theory of Pankow (1994) is assumed, which has widely been coupled with gas-phase chemical mechanisms to investigate and parameterise SOA formation in chamber experiments (Capouet et al., 2008; Jenkin et al., 2012; Camredon et al., 2010; Fry et al., 2011), and field studies (Johnson et al., 2006a,b; Lee-Taylor et al., 2011; Li et al., 2015). The model assumes a thermodynamic equilibrium exists between the gaseous and particulate phases for each compound:

\[
G_i + M \rightleftharpoons P_i, \quad K_{p,i} = \frac{[P_i]}{[G_i][M]} \tag{4.1}
\]

where \([G_i]\) (g m\(^{-3}\)) is the mass concentration of a semi-volatile species \(i\) in the gaseous phase, \([P_i]\) (g m\(^{-3}\)) the mass concentration of a semi-volatile species \(i\) in the particle phase, and \([M]\) (g m\(^{-3}\)) is the mass concentration of the total particulate matter into which partitioning can occur. The more commonly encountered form of the equilibrium expression, which was first proposed by Pankow (1994), is given in Equation 1.30.

A key thermodynamic property for describing gas-particle partitioning of a given organic compound is its vapour pressure. A fundamental assumption of Pankow (1994) is that the organic aerosol possesses an amorphous, liquid-like character. For \(\alpha\)-phellandrene derived SOA however, densities ranged from 1.28 to 1.9 g cm\(^{-3}\), suggesting that the aerosol likely exists in a waxy-solid like state (Kanakidou et al., 2005). However, the actual phase state of complex mixtures is debatable (O’Meara et al., 2014). Thermodynamic theory predicts that the melting point of an individual species is depressed in condensed phase mixtures of different compounds (Marcolli et al., 2004), however this effect remains poorly constrained (Koop et al., 2011). Laboratory measurements have observed both liquid-like (Cappa et al., 2008) and amorphous solid (most likely glassy)-like (Virtanen et al., 2010) states for mixed organic aerosol, with Renbaum-Wolff et al. (2013) showing viscosity of \(\alpha\)-pinene ozonolysis SOA to range from liquid to semisolid, or solid, across a range of atmospheric RH. Nonetheless, recent work by Ye et al. (2016) showed that the RH does not impact the exchange of semi-volatile compounds for \(\alpha\)-pinene ozonolysis SOA. Considering this, and that vapour pressure estimation methods for non-crystalline
solid states have not been presented in the literature, the sub-cooled\footnote{A sub-cooled liquid is a metastable liquid that exists if solidification does not occur at temperatures below that of the triple point.} liquid vapour pressure is used (O’Meara et al., 2014).

Excluding α-phellandrene, thermodynamic properties of the remaining 457 species considered for partitioning have not been experimentally measured. This is a general problem in the field, with experimental data unavailable for most organic compounds existing in the atmosphere. Consequently, vapour pressures in this thesis are estimated using the EVAPORATION (Estimation of VApour Pressure of ORganics, Accounting for Temperature, Intramolecular, and Non-additivity effects) method of Compernolle et al. (2011), based on the recommendation of O’Meara et al. (2014). All calculations were performed at 298 K using the online molecular property predictor UManSysProp (http://umansysprop.scaes.manchester.ac.uk, Topping et al., 2016), which accepts SMILES (Simplified Molecular Input Line Entry System) strings as input. EVAPORATION is based on the group contribution concept, that is, the notion that molecules can be broken down into specified functional groups, whose individual behaviours can be combined to provide an estimate for a property of the molecule as a whole. Compernolle et al. (2011) developed EVAPORATION using experimental data for 788 compounds, and uses 20 group and interaction contributions to estimate the vapour pressure of a molecule through the empirical formula:

\[ \log_{10}(p_{o,L}^i) = A_i + \frac{B_i}{T^{1.5}} \]  

(4.2)

where \(A_i\) and \(B_i\) are found from a mixture of additive and nonadditive group contributions accounting for size, topology, functionality and intramolecular group interactions. It is evident from Equation 4.2 that, unlike other vapour pressure estimative methods (e.g. Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Moller et al., 2008), a boiling point or any other molecular property is not required as an input. Moreover, the most critical aspect of EVAPORATION, at least with respect to its application in this thesis, is that compounds of atmospheric relevance were targeted in the minimisation process used to quantify group contributions. EVAPORATION is therefore able to resolve complex functionalities formed in the mechanism, such as peroxide, hydroperoxides, peracids and PANs. This is not necessarily the case for other available methods. For example, the method of Nannoolal et al. (2004, 2008) was developed to service chemical engineering, although an update by Compernolle et al. (2010) improved the breadth of application to the atmospheric sciences. EVAPORATION was subject to a critical assessment by O’Meara et al. (2014), who found the method to increasingly underestimate vapour pressure with decreasing volatility. Nonetheless, the authors found EVAPORATION to provide the most accurate vapour pressure values when compared with the methods of Lee and Kesler (1975),
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Myrdal and Yalkowsky (1997), Capouet and Müller (2006), Nannoolal et al. (2008), Moller et al. (2008) and Pankow and Asher (2008). Furthermore, O’Meara et al. (2014) showed EVAPORATION to most accurately predict SOA mass loadings, recommending it for use when estimating vapour pressures of SVOCs for atmospheric purposes.

The second important thermodynamic parameter required for representing gas-particle partitioning is the activity coefficient, which reflects the interaction of aerosol component $i$ with the remaining absorbing mixture. In this thesis the activity is formulated in relation to Raoult’s law, such that $\gamma_{org,i} = 1$ represents a pure compound with a mole fraction of one. Thus an activity coefficient greater than one indicates that a component is dissimilar to the bulk aerosol mixture (e.g. a long-chain alkane adsorbing into a mixture of polar multifunctional organics), and so will partition less into the aerosol phase. Conversely, an activity less than one indicates favourable mixing, resulting in enhanced partitioning into the aerosol phase. Activity coefficients were calculated for all 458 species using the AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficient) model (Zuend et al., 2008, 2011). AIOMFAC also uses a group contribution method, treating molecules as a collection of functional subgroups (e.g. CH$_3$, OH, CHO, COOH), before calculating activity by interacting each subgroup with every other subgroup in the mixture. Interactions are represented using expressions for long-range, mid-range and short-range interactions. The long- and mid-range interactions are important in inorganic and organic-inorganic mixtures (electrolyte solutions), with the former described by an extended Debye-Hückel expression and, together with the semi-empirical mid-range part, they form a Pitzer (1991)-like group contribution model. Short-range interactions are calculated using a slightly modified UNIFAC (UNIversal Functional Activity Coefficient) model (Fredenslund et al., 1975), using the revised parameter set of Hansen et al. (1991) for functional group interactions, Peng et al. (2001) for the COOH group of carboxylic acids, and Marcolli and Peter (2005) for alcohols/polyols. Therefore, for application in the current model, where inorganic ions are not considered, AIOMFAC reduces into UNIFAC. The UNIFAC-based group contribution method can successfully resolve a molecule so long as it is comprised of functional groups for which group-contribution parameters exist. With regards to products formed in the mechanism, limitations of UNIFAC exist for peroxides, hydroperoxide, peracids, organic nitrates and PAN compound classes. Despite UNIFAC parameters for these functionalities having becoming available (Compernolle et al., 2009), they remain incomplete, with interactions with all other common functional groups having not been parameterised. Instead, an analogy approach is used for representing interactions of these unknown compound classes (e.g. hydroperoxide to alcohol, peracid to carboxylic acid, nitrate to nitro) (Compernolle...
Activity calculations were performed using UManSysProp at a temperature of 298 K. All 458 species were assumed to be in the mixture. Relative molar concentrations were crudely assigned by partitioning species into four equal bins based on vapour pressures, and assigning these bins relative mole fractions of 1, 0.75, 0.5 and 0.25, with the highest value given to the least volatile 25%. This method will undoubtedly bias aerosol composition, although use of the group contribution method in AIOMFAC limits the impact, due to the similarity of functional groups existing in the different bins. Ideally, activity would be re-calculated with each time step in the model, iteratively correcting activities to reflect evolving composition until self-consistency is reached – however such a method greatly increases computational demand. By changing the mole fraction of all species to be equimolar, the activity of any given species varied by no more than ±8%. Larger uncertainties in the estimative techniques employed helps justify use of the current distribution method.

A kinetic parameterisation similar to that of Capouet et al. (2008) is used to integrate aerosol formation with the gas-phase mechanism. Adsorption and desorption of a compound $G_i$, as expressed in Equation 4.1, is parameterised by:

$$G_i + OA \xrightarrow{k_{on,i}} P_i$$

$$P_i \xrightarrow{k_{off,i}} G_i$$  \hspace{1cm} (4.3)

where $OA$ is concentration sum of all particle phase species $(OA = \sum_i P_i, \text{ molecules cm}^{-3})$, and $k_{on,i}$ and $k_{off,i}$ are the adsorption ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and desorption ($\text{s}^{-1}$) rates respectively. In the continuum diffusion limit, the maximum flux of a reactant gas $i$ to an aerosol droplet is given by, $J_{\text{diff},i}$ (mol m$^{-3}$ s$^{-1}$):

$$J_{\text{diff},i} = \frac{3D_{g,i}}{r^2}[G_i]$$  \hspace{1cm} (4.5)

where $D_{g,i}$ is the gas-phase diffusion coefficient of species $i$ (m$^2$ s$^{-1}$) and $r$ is the particle radius (Seinfeld and Pandis, 1998). Conversely, in the free molecular kinetic limit, the kinetic theory of gases sets an upper limit to the flux of a gas to the air-particle interface as, $J_{\text{kin},i}$ (mol m$^{-3}$ s$^{-1}$):

$$J_{\text{kin},i} = \frac{3\alpha_i c_i}{4r}[G_i]$$  \hspace{1cm} (4.6)

where $\alpha_i$ is the accommodation coefficient and $c_i$ the mean speed of species $i$. The two equations for fluxes under differing regimes can be combined to express the overall rate ($R_{on,i}$ (mol m$^{-3}$ s$^{-1}$)), that includes both gas-phase and interfacial mass.
4.1. MECHANISM CONSTRUCTION

transport (Schwartz, 1986):

\[ R_{on,i} = \left( \frac{r^2}{3D_{g,i}} + \frac{4r}{3\alpha_i c_i} \right)^{-1} \]  

(4.7)

The bracketed prefix in Equation 4.7 is the mass transfer rate coefficient \( (s^{-1}) \), which is used to define the absorption rate used in all calculations (Lelieveld and Crutzen, 1991):

\[ k_{on,i} = \frac{MW_{om}}{\rho N_A} \left( \frac{r^2}{3D_{g,i}} + \frac{4r}{3\alpha_i c_i} \right)^{-1} \]  

(4.8)

It is anticipated that the final model will display predictive characteristics, so the average photooxidation aerosol density \( (\rho = 1.42 \text{ g cm}^{-3}) \) is used universally, rather than tailoring the density to match experimental measurements for each simulation. The mean molecular weight of the condensed organic material \( (MW_{om}) \) is set to 200 g mol\(^{-1}\). Particle size is taken from the SMPS size bin with the largest mean volume over the first hour of each experiment, as this is when the majority of gas-particle partitioning occurs. Spherical particles are assumed. In the seven 2013 photooxidation experiments this corresponded to a radius of 42 ± 7 nm, whilst in the three 2016 experiments, due to added background contamination, a larger radius of 80 ± 15 nm is used. One shortcoming of the current method is that there is no incorporation of the size distribution of particles, or evolution of it throughout simulations. Nevertheless, based on sensitivity tests conducted by Stroud et al. (2004) and Kelly et al. (2010), the representation of uniform size is expected to have minimal impact when compared to experimental uncertainties. The group contribution method of Fuller et al. (1966, 1969) was used to calculate gas-phase diffusion coefficients for each compound in air at STP on the recommendation of Poling et al. (2001), who showed the method to provide the best agreement with experimental data when compared with other empirical and semi-empirical methods. Indeed recently, and pertinent to atmospheric studies, Tang et al. (2015) showed Fuller’s semi-empirical method to routinely estimate diffusivities to within 10% of experimental values for 157 common reactive organic compounds (e.g. hydrocarbons, alcohols, carbonyls, acids, amines, multifunctionals) in air. Fuller’s method proposes that the diffusivity of a trace gas G in a bath gas B can be estimated by:

\[ D_{GB} = \frac{1.00 \times 10^{-3} T^{1.75} \left( \frac{1}{MW_G} + \frac{1}{MW_B} \right)^{0.5}}{p \left( \left( \sum_G v_{i} \right)^{1/3} + \left( \sum_B v_{i} \right)^{1/3} \right)^2} \]  

(4.9)

where \( p \) is the pressure (atm) and the \( v_{i} \)’s are the dimensionless atomic diffusion volumes (cm\(^3\)), to be summed over the atoms, groups and structural features of each
diffusing species to give the diffusion volume of the entire molecule. Atomic diffusion volumes and the 1.75 exponent for temperature were determined from a nonlinear least-squares analysis of 512 experimental points, with the atomic diffusion volumes listed in Fuller et al. (1969) used in this thesis. Calculated diffusion coefficients ranged from $5.14 \times 10^{-6}$ to $8.20 \times 10^{-6}$ m$^2$ s$^{-1}$. A value of 0.2 was used for the accommodation coefficient for all compounds, based on the modelling studies of Bowman et al. (1997) and Stroud et al. (2004). This value results in mass transfer being dominated by the kinetic regime. Lastly, the mean speed of each compound in the gaseous phase was calculated from the Maxwell-Boltzmann distribution:

$$c_i = \sqrt{\frac{8RT}{\pi MW_i}}$$  (4.10)

The rate of condensation for a given species depends on the rate coefficient, $k_{on}$, along with its gas-phase concentration and the total aerosol mass concentration. Therefore, an increasing organic aerosol mass coupled with production of low-volatility products in the gas-phase chemical mechanism is what drives aerosol production in the model.

From first-definitions, the equilibrium constant can be expressed as a ratio of the forward and reverse reactions. Incorporating correction factors for unit consistency, this ratio becomes:

$$K_{p,i} = \frac{N_A k_{on,i}}{10^6 MW_{om} k_{off,i}}$$  (4.11)

Assuming a dynamic equilibrium, $k_{off,i}$ is then calculated using values of the equilibrium constant (Equation 1.30) and $k_{on,i}$ (Equation 4.8).

### 4.2 Chamber Model Construction

$\alpha$-Phellandrene photooxidation chamber box models were constructed for solution in the FACSIMILE for Windows v.4 (MCPA Software Ltd.) kinetic modelling software package. The complete model contains the constructed $\alpha$-phellandrene gas-phase mechanism (Chapter 4.1), with relevant MCM organic and inorganic species extracts, product pools and generic rate coefficients, the complete set of auxiliary mechanisms specific to the GIG-CAS chamber (Chapter 3.4.3), photolysis rates in the chamber (Chapter 3.4.1), starting concentrations of all species including background VOCs (Table 3.15 and Appendix D), and physical parameters (e.g. temperature, pressure; used for defining concentrations and rate coefficients), as well as model specific information including variable and parameter lists, time controls, conversion constants, and information for those species whose concentrations are to be output. The complete model of experiment 15 is provided as an example in
Appendix I. FACSIMILE compiles the provided input, representing each species in the mechanism as a linear ordinary differential equation (ODE) of the form:

\[
\frac{\partial C_i}{\partial t} = P - L \times C_i - D
\]  

where \( C_i \) is the concentration of species \( i \), \( t \) is time, \( P \) is the instantaneous production rate of species \( i \) from photochemistry, \( L \times C_i \) is the instantaneous loss rate of species \( i \) from photochemistry, and \( D \) is the species independent dilution rate (Derwent et al., 2001). FACSIMILE then solves the ODE's numerically through integration with the algorithmic solver of Gear (1971).

Temperature and humidity are updated in the model every three minutes based on experimental measurements. The concentration of water is converted from relative humidity to molecules cm\(^{-3}\) using the method of Lowe and Ficke (1974). To crudely account for contaminant VOCs introduced with \( \alpha \)-phellandrene, \( \alpha \)- and \( \beta \)-pinene mechanisms are extracted from the MCM and set to 1.0% of the starting \( \alpha \)-phellandrene concentration, while cumene (isopropylbenzene) is extracted as a surrogate for \( p \)-cymene and set to 10% of the starting \( \alpha \)-phellandrene concentration. HONO is set to 1 ppb for all base case models.

Gas-particle condensation in the model is coded based on absorptive partitioning, which requires an initial non-zero absorptive mass to initiate aerosol growth. In each experiment this absorptive seed was set to the background aerosol concentration, as measured by the SMPS, assuming spherical particles, a density of 1.0 g cm\(^{-3}\) and a molar mass of 180 g mol\(^{-1}\). The background organic aerosol was incorporated into the model as a species named ‘BGOA’, with partitioning into these particles assumed to be identical to \( \alpha \)-phellandrene derived SOA (Leungsakul et al., 2005b). Only species derived from \( \alpha \)-phellandrene were considered for partitioning, with background contaminants represented exclusively in the gaseous phase. A calculation of SOA elemental composition (O/C, H/C, N/C) was incorporated using component chemical formula for each species. Atomic ratios, as opposed to mass ratios, are output, consistent with elemental ratios reported by the AMS (Aiken et al., 2007). Initially no condensed-phase reactions are considered in the model. Particle wall losses are represented explicitly, to keep the modelled absorbing mass consistent with what was experimentally inside the reactor. Particle deposition is represented as an irreversible process, with the average photooxidation first-order wall loss rate of \( 1.52 \times 10^{-4} \) s\(^{-1}\) applied uniformly for all particulate species. Once lost to the walls, particles are no longer considered as adsorbing.

Experimentally, gas-phase organics can be lost through four mechanisms (Saleh et al., 2013): (1) vapours can diffuse through small perforations in the Teflon walls; (2) highly adsorptive walls can act as sinks for vapours; (3) the walls can act as con-
densation sites for supersaturated vapours; and (4) as discussed in Chapter 3.5.1, vapours can partake in absorptive partitioning with the walls. Based on the stability of acetonitrile concentrations throughout the photooxidation experiments, no gas-phase dilution was represented in the model. Meanwhile, it can be argued that mechanisms two and three play a negligible role for modelling purposes in this study, as aerosol size reached equilibrium in each experiment. If loss of vapours through either mechanism were dominant, then gas-particle partitioning would continually be perturbed, resulting in a shift in aerosol size distribution to smaller diameters (e.g. Vaden et al., 2011). Absorptive partitioning has been shown to be an important phenomena in chamber experiments (Matsunaga and Ziemann, 2010; Zhang et al., 2014b; La et al., 2016), however the effect remains unquantified in the GIG-CAS chamber. Due to uncertainty regarding its impact during the α-phellandrene photooxidation chamber experiments, gas-wall absorptive partitioning is not modelled in this work. In this respect, all other factors notwithstanding (e.g. vapour pressure and activity estimation techniques, exclusive partitioning of compounds with more than five carbons, non-representation of condensed phase reactions), the model represents an upper bound for SOA formed, as experimental vapour losses would ultimately lead to reduced SOA yields.

4.3 Chamber Model Performance and Discussion

The performance of the α-phellandrene mechanism, and sensitivity to a number of mechanistic and parameter variations, are described in the following subsections. Model performance is evaluated with respect to three distinct output groups, each assessing different aspects of the model. The first groups consists of α-phellandrene, O₃, NO and NO₂. These compounds deliver crucial information on the ozone production and oxidative capacity of the system. The simplest measure of a model’s ability to capture the oxidative capacity of a system is through comparison of maximum ozone production (Bloss et al., 2005). However, as with chamber auxiliary mechanism evaluation, the quantity D(O₃ – NO) will be used as the main criterion for assessing model performance in this regard (Pinho et al., 2005, 2007).

The second group of compounds contains gas-phase organic reaction products, such as formaldehyde, formic acid, acetone, methyl glyoxal, APHAAL and APHAAL2. These species provide information on the accuracy of represented product channels, branching ratios for major reaction routes, the carbon budget and radical production in the α-phellandrene system. For instance, formaldehyde, glyoxal and methyl glyoxal have been identified as major radical sources in oxidation mechanisms (Bloss et al., 2005). However, compared to α-phellandrene and the inorganic products, these trace organic species have considerably higher experimental uncertainty.
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The third group contains compounds that constitute particulate matter. The loading of aerosol material, as well as its structural and elemental composition, is useful in validating the model’s representation of gas-particle partitioning. Conversely, with significant uncertainty surrounding the mechanism of SOA formation (Hallquist et al., 2009), the model provides a tool for understanding SOA formation characteristics from \( \alpha \)-phellandrene photooxidation.

Due to experimental uncertainties inherent to the various instruments and arising from chamber auxiliary mechanisms, smog chamber experiments are limited in their capacity to evaluate atmospheric chemical mechanisms (Stockwell et al., 1990; Carter et al., 2005; Hynes et al., 2005). This effect was evidenced by evaluation of the MCM propene mechanism in the GIG-CAS chamber (Chapter 3.4.3). Consequently, some model-experimental discrepancy is expected, with previous mechanism evaluation work taking deviations around \( \pm 25\% \) to be acceptable (e.g. Stockwell et al., 1990; Carter et al., 2005).

4.3.1 Gas-Phase Mechanism Evaluation

Modelling OH and HO\(_2\) concentrations in all experiments show chamber concentrations to be similar to those typically observed in the troposphere during the daytime; with OH concentrations of \( 0.2–10 \times 10^6 \) molecules cm\(^{-3}\) and HO\(_2\) concentrations of \( 0.3–20 \times 10^8 \) molecules cm\(^{-3}\) modelled (Stone et al., 2012, and references therein). Modelled NO\(_3\) reached concentrations up to 3.5 ppt in some experiments, significantly greater than what has been reported for the daytime troposphere (Geyer et al., 2003; Khan et al., 2015). Modelling of these oxidant concentrations, along with ozone, predicts that OH, O\(_3\) and NO\(_3\) on average consume 54\% (range 42 – 60\%), 45\% (range 39 – 57\%) and 1.0\% (range 0.3 – 1.4\%) of \( \alpha \)-phellandrene respectively across the ten photooxidation experiments.

One of the largest uncertainties in the model is the starting concentration of \( \alpha \)-phellandrene, which is reported with an experimental error of around 30\%. Such a large variation of the precursor VOC has a significant impact on NO\(_x\) recycling and consequently ozone formation in the model. Indeed, Appendix H.1 shows performance of the base case model having \( \alpha \)-phellandrene varied between its nominal, upper and lower experimental limits, against experimental measurements for all ten photooxidation experiments. The result is significant. By simply varying the starting \( \alpha \)-phellandrene concentration between its experimental uncertainty limits, \( D(O_3 - NO) \) across an experiment was found to have an average deviation of \( \pm 16\% \) to \( \pm 32\% \), compared to the model run with the quoted \( \alpha \)-phellandrene concentration. Moreover Figure H.1 shows, for all experiments modelled, \( D(O_3 - NO) \) can be brought into better agreement with measured data by altering the starting \( \alpha \)-
phellandrene concentration within its uncertainty limits. For experiments 15, 16, 20 and 21, changing the starting α-phellandrene concentration can bring simulated D(O₃ – NO) into good agreement (average deviation < 10%) with experiment data.

Across all experiments the mean absolute deviation of simulated D(O₃ – NO) from the initial model compared to observation is 47%. No NOₓ dependency was observed, contrary to findings for the α-pinene MCM mechanism, for which better performance at higher VOC/NOₓ ratios has been reported (Saunders et al., 2003; Pinho et al., 2007). In general, the initial model overpredicts the oxidative capacity of the system in the 2013 dataset, whilst underpredicting it through the 2016 dataset. Given experimental conditions were similar for both campaigns, with known variations such as differing lighting conditions and auxiliary mechanisms accounted for, the findings make it difficult to reconcile the constructed mechanism with the current experimental dataset. This is because incorporating mechanistic variations to reduce NOₓ cycling will improve agreement for some experiments, whilst proving detrimental to others. Furthermore, given the impact of varying the starting α-phellandrene concentration within experimental uncertainty, it would be remiss to make large mechanistic changes to improve the model, as these may instead be compensating for inaccuracy in precursor concentration.

The following analysis therefore assumes the nominal α-phellandrene concentration reported by the PTR-TOF to be correct, with mechanistic features of interest varied to assess the impact of their change. Scope for mechanistic advancement is limited, as the α-phellandrene mechanism is newly developed and thus contains many of the recent advances in general mechanism construction, as well as updated computational and experimental findings from this thesis regarding α-phellandrene’s degradation. Nonetheless, by comparing the D(O₃ – NO) concentration against experiment for minor mechanistic changes, critical points in the mechanism can be identified for exploration in future mechanistic refinement.

The primary mechanistic parameters investigated are listed in Table 4.1, with impact on D(O₃ – NO) shown in Figure 4.4. Mechanisms M₁ to M₅ explore model sensitivity to varying mechanistic parameters consistent with reported uncertainty ranges, while mechanism variant M₆ explores the impact of simplifying the mechanism. To test compounding effects the collective implementation of a number of mechanistic variations is then assessed in mechanism M₇. The primary aim is to assess the magnitude of impact of each variation however, given that the majority of simulations overpredict the chamber oxidative capacity, refinements are geared towards reducing NOₓ recycling and thus ozone formation. If an alternate scenario is desired, one can simply alter each variant to its opposing limit to increase the simulated oxidative capacity.

APHAAL and APHCAL are the two major first-generation products produced
Mechanism Description $\Delta D(O_3 - NO)^a$

$M_0$ Proposed $\alpha$-phellandrene photooxidation mechanism. 0

$M_1$ $M_0$ with rate of OH addition to APHAAL and APHCAL halved. Abstraction channels are appropriately scaled. -3.9%

$M_2$ $M_0$ with nitrate yield from initial OH attack increased to 30%. -8.6%

$M_3$ $M_0$ with OH radical yields from second-generation CIs decreased from 15 to 8%. -1.4%

$M_4$ $M_0$ with rate of $O_3$ addition to unsaturated first-generation products decreased from $1.0 \times 10^{-16}$ to $3.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. -4.9%

$M_5$ $M_0$ with initial OH abstraction from $\alpha$-phellandrene reduced from 8.64 to $5.44 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Addition channels are appropriately scaled. -2.5%

$M_6$ $M_0$ with only one OH channel (addition channel ‘A’) and two ozonolysis channels (labelled ‘3’ and ‘4’) represented. -8.2%

$M_7$ Combination of mechanisms $M_1$, $M_2$, $M_3$, $M_4$ and $M_5$. -20.0%

$M_8$ $M_7$ with SOA (scaled) implementation. –

*aAverage deviation with respect to mechanism $M_0$ over all photooxidation simulations.*

Table 4.1: Summary of mechanistic variations tested against the $\alpha$-phellandrene photooxidation experiments and resulting impact on oxidative capacity.

in the photooxidation of $\alpha$-phellandrene (see Figure 4.1). The decomposition of these products therefore has a significant impact on the final product distribution. Consumption by OH is their primary fate, with reaction rates and branching ratios calculated from SAR (Kwok and Atkinson, 1995). For both species, addition to the double bond is the major reaction site, with abstraction of an aldehydic hydrogen represented as occurring 29% and 58% (29% from either aldehyde group) of the time for APHAAL and APHCAL respectively. The first mechanism, $M_1$, therefore investigates the impact of changing these branching ratios, by halving the rate of addition in both products. Increasing the proportion of acyl peroxy radicals formed was found to lower $D(O_3 - NO)$, through forming a higher proportion of closed-shell products. The average variation of $D(O_3 - NO)$ from implementing this mechanistic variation across all ten photooxidation simulations was reduction by 3.9% (range – 4.8 to –2.7%) with respect to mechanism $M_0$.

The formation of nitrates from peroxy radicals has a large impact on the chemistry on the system by inhibiting an NO-to-NO$_2$ conversion, terminating the OH regeneration catalytic cycle, and providing a nitrogen reservoir. As described in the mechanism construction, nitrate yields from the initially formed peroxy radicals were set analogously to limonene in the MCM (Ruppert et al., 1999), except for APHEO2, which was assigned branching ratios based on MCM protocols. The
other monoterpene investigated in the study of Ruppert et al. (1999) were α-pinene, β-pinene and myrcene, which had respective nitrate yields of 24%, 25% and 29%. Using the same experimental method, Nozière et al. (1999) reported a nitrate yield for α-pinene of 18 ± 9%, while more recently Rindelaub et al. (2014) reported a nitrate yield of 26 ± 7% from α-pinene. A nitrate yield of 30% is therefore investigated as a tentative upper limit, to reduce radical propagation in mechanism variant M2. As expected, Figure 4.4 shows implementation has the largest effect on earlier time points. Across all experiments, D(O3 – NO) was reduced on average by 8.6% (range −13.5 to −4.9%) with respect to mechanism M0.

Experimental results discussed in Chapter 3.5.1 report OH yields from the ozonolysis of α-phellandrene’s first-generation products of 15 ± 7%. Based on demonstrated sensitivity of miscellaneous alkenes (Pinho et al., 2006) and α- and β-pinene (Pinho et al., 2007) photooxidation simulations to ozonolysis radical yields, the effect of reducing first-generation ozonolysis OH yield to its lower experimental limit of 8% was investigated in mechanism M3. This lower yield is consistent with the study of Herrmann et al. (2010), who reported an OH yield of 8 – 11% for ozonolysis of the second double bond in α-phellandrene. As shown in Figure 4.4, implementation has only a minor influence on D(O3 – NO), reducing its value on average by 1.4% (range −2.1 to 0.7%) with respect to mechanism M0. Conversely, if the reaction rate of first-generation products with ozone is reduced to its lower experimental limit (3.0 × 10−17 cm³ molecule⁻¹ s⁻¹, M4), an average D(O3 – NO) reduction of −4.9% (range −11.7 to 28.5%) is observed. Experiment 16 was found to be an outlier, being the only simulation where the mechanistic variation was found to increase the oxidative capacity of the system. This suggests that under high-NOx conditions, cumulative consumption of first-generation products by ozone results in more efficient radical propagating pathways than OH initiated channels. Meanwhile, under low NOx conditions, such as those found in experiment 16, the represented first-generation ozone initiated pathways have a lower impact on the model oxidative capacity compared to OH initiated pathways. It is therefore important to validate mechanistic changes under a variety of VOC/NOx conditions. Removing the low-NOx experiment, D(O3 – NO) was reduced on average by 8.5% (range −11.7 to −5.5%) with respect to mechanism M0. Importantly, compared to other mechanistic variations, implementation of M4 had the largest effect at latter time points in the model.

Based on the study of Peeters et al. (1999), one H-abstraction channel was included in the representation of OH attack on α-phellandrene. The pathway results in significantly different chemistry compared to the three corresponding OH addition routes. The impact of varying the OH attack distribution is therefore investigated in mechanism M5, by lowering the addition channel to the lower limit of 17% reported by Peeters et al. (1999), whilst proportionally increasing the addition channels to
Figure 4.4: Deviation of simulated D(O₃ – NO) from experimental observations in the ten α-phellandrene photooxidation experiments, for the different mechanistic variations listed in Table 4.1. Deviation is defined as (model – experiment)/experiment, and is shown for three different time points in each experiment.

maintain overall reactivity. Implementation resulted in a small average D(O₃ – NO) decrease of –2.5%, with the impact fairly consistent across the simulated experiments (range –3.7 to –1.4%). Evidently the chemistry evolving from APHEO2 contains
more NO-to-NO₂ conversions than the peroxy radicals formed from the addition pathways, stemming from a reduced nitrate forming channel and direct formation of an isopropyl radical through oxy-radical decomposition.

To further probe the impact of the various initiation routes, only the primary OH initiation channel (‘A’ stream) and ozonolysis to the most reactive double bond (channels ‘3’ and ‘4’) are included in mechanism M₆. Figure 4.4 shows that simplifying the mechanism, for the most part, has a minor impact on simulated D(O₃ – NO), averaging –8.2% (range –20.4 to 6.5%) with respect to M₀ across the ten photooxidation experiments. Only in experiment 16, which had the lowest NOₓ, did M₆ simulate a higher oxidative capacity with respect to M₀. This finding is further supported by simulations in which O₃ addition was only represented to occur at the least substituted double bond (channels ‘3’ and ‘4’). These models showed an average deviation of less than 1% compared to the base model M₀, indicating similar chemistry from ozone addition to either double bond. Given the similarity in output, the finding suggests that, when reducing computational costs is favourable over a detailed chemical species representation, various α-phellandrene initiation channels can be removed to significantly reduce the size of the mechanism with little impact on simulated results.

Overall, the implemented mechanistic variations result in modest changes to the simulated oxidative capacity. It is therefore likely that a number of mechanistic adjustments would have to be simultaneously executed to produce a sizeable change in model output. Mechanism M₇ was constructed to test this, by incorporating mechanism changes M₁–₅. As expected, Figure 4.4 shows mechanism M₇ had the largest impact on D(O₃ – NO), with an average deviation of –20.0% (range –26.4 to 7.7%) with respect to M₀. Moreover individual impacts appear to be additive, that is, the sum of changes due to individual mechanism refinements is similar to the collective implementation of all refinements – a useful property for future mechanism sensitivity testing and/or refinement.

For all 2013 experiments, the ad hoc optimised M₇ mechanism best simulates the chamber oxidative capacity. The refined mechanism is therefore used to model all ten photooxidation experiments, with the simulated α-phellandrene, O₃, NO and NO₂ concentrations compared with experimental data in Figure 4.5. Complete model performance is quite variable. α-Phellandrene consumption is well simulated in all but experiment 18, suggesting that the employed rate coefficients and initial reactant precursor formation mechanisms are well parameterised. Ozone temporal profiles are adequately simulated in experiments 15, 20 and 21, overpredicted in experiments 17, 18 and 19, and underpredicted in experiments 16, 22, 23 and 24. Therefore, the model’s ability to capture NOₓ recycling under different experimental conditions still requires improvement. The observed discrepancy may not be entirely chemical. For
example, experiments 17 and 24 both have nearly identical physical and chemical starting conditions (e.g. temperature, humidity, VOC, NO$_x$), yet the simulated output is vastly different, with 163 ppb of ozone predicted at the 200 minute mark of experiment 17, compared to 107 ppb of ozone at the same time point in experiment 24. This discrepancy is entirely attributable to the different photolysis rates utilised when modelling the two separate campaigns. Despite exhibiting variable ozone predictive characteristics, NO consumption is reasonably well represented across the dataset, although it does become more erroneous in experiments with higher initial NO concentrations (e.g. experiments 18 and 22). Meanwhile, NO$_2$ production and consumption is well simulated in experiments 15, 23 and 24, whilst concentrations are underestimated by differing amounts in the remaining experiments. General underestimation of NO$_2$ suggests some NO$_x$ loss mechanism and/or nitrogen sink is overrepresented in the model.

The underprediction of NO$_2$ is not unique to α-phellandrene simulations however, having previously been reported in both the 2012 (Appendix C) and 2016 (Chapter 3.4.3) GIG-CAS propene photooxidation models. It is possible that the discrepancy is purely due to some fault in the model’s representation of NO$_x$ formation and loss processes (e.g. photolysis rates, wall losses, radical offgassing). That being said, the chemiluminescence detector used to monitor NO and NO$_2$ concentrations inside the chamber is prone to a false positive bias with other nitrogen containing compounds. Most notably, the molybdenum catalyst inside the NO$_x$ analyser is known to reduce compounds including NO$_3$, HNO$_3$, N$_2$O$_5$ and organonitrates, and to a lesser extent HONO, PANs and particle phase nitrates (Grosjean and Harrison, 1985; Fehsenfeld et al., 1987; Williams et al., 1998; Dunlea et al., 2007). Atmospheric concentrations of these potential interferents are generally low relative to NO$_2$, however this is not necessarily true under the chamber conditions reported. The NO$_2$ reading may therefore, to some unknown extent, reflect the concentration of nitrogen containing species inside the reactor in addition to NO$_2$ – explaining why simulated NO$_2$ concentrations are lower than experiment for both propene and α-phellandrene. Indeed, for each experiment, summing simulated NO$_2$ with NO$_3$, HNO$_3$, HONO, N$_2$O$_5$, organonitrates and PANs yields a concentration greater than the experimental NO$_2$ reading, making the argument, at least, plausible.

Several other mechanistic and model variations were also investigated, although these are not reported in Table 4.1 or Figure 4.4 due to relative model insensitivity ($\Delta D$(O$_3$ – NO) < 1%). These include increasing the non-radical propagating Norrish type II photolysis channel by 20 fold; re-distributing branching ratios of OH addition to α-phellandrene to include 35% of the resonant ‘D’ pathway; removing or doubling the concentration of surrogate contaminants cumene, α-pinene and β-pinene; and lastly modifying the chamber auxiliary mechanism to represent
Figure 4.5: Comparison of experimental (shaded) and M₇ simulated (lines) time dependencies of α-phellandrene (orange), O₃ (green), NO (blue) and NO₂ (red) in all ten photooxidation experiments. Grey shading in experiments 22, 23 and 24 denotes time periods where chamber lighting was switched off.
initial HONO concentration within stated uncertainty limits. The first two variations show non-critical points in the α-phellandrene mechanism, with the Norrish type II photolysis channel only represented for a small number of species in the mechanism, and products of the three OH addition channels exhibiting quite similar photo-degradation. The latter two variants indicate that the concentration of α-phellandrene is sufficient in the models/experiments, such that its oxidation dictates the system’s oxidative capacity. The magnitude of variation used for cumene exceeds that of the background VOC concentrations, suggesting that background VOCs too are unlikely to have much of an impact over the time frame of experiments. Adjusting the rate coefficient for SOZ formation by a factor of two either way (0.15 to 0.6 s$^{-1}$) was found to have a small impact on the simulated oxidative capacity. The change however becomes more important under low-NO$_x$ conditions, with average deviation in oxidative capacity in experiment 16 being around ±5%.

Evidently the competitive dynamics of SCI radical terminating channels also has an influencing role on NO$_x$ recycling.

Finally, as discussed in Chapter 3.7, the high reactivity of α-phellandrene with NO$_2$ has led researchers to propose that its reaction may be of potential importance in smog chamber experiments (Reissell et al., 1999; Bernard et al., 2013). This is because concentrations of NO$_x$ (and therefore NO$_2$) used in chamber experiments tend to be higher than those typically found in the ambient. For this reason, reactions and associated chemistry for the reaction of NO$_2$ with α-phellandrene have been developed and incorporated into the existing mechanism, as described in Appendix G.1. Similarly, reaction of unsaturated compounds with O($^3$P), formed predominantly by photolysis of NO$_2$, is not normally of great significance in the atmosphere. However, due to elevated levels of NO$_x$, Pinho et al. (2005, 2006, 2007) showed the reaction to be non-negligible during smog chamber experiments. The reaction of α-phellandrene with O($^3$P) is therefore incorporated into the mechanism based on analogy with other studies (Cvetanović, 1987; Paulson et al., 1992b; Luo et al., 1996; Alvarado et al., 1998; Calvert et al., 2000), as described in Appendix G.2.

Overall, the introduction of NO$_2$ and O($^3$P) initiation channels had a minor impact on simulated results. The largest change was found for inclusion of the O($^3$P) channel in experiment 22, the experiment having the largest starting NO$_x$ concentration (354 ppb), in which the average simulated D(O$_3$ – NO) concentration was reduced by 1.4%. Therefore, under most, if not all experimental conditions, inclusion of the two supplementary initiation pathways are not required. This is because, whilst the reaction rate of NO$_2$, and most likely O($^3$P), with α-phellandrene is anomalously high, so too is reaction with other more common atmospheric oxidants generated during photooxidation (e.g. OH, O$_3$, NO$_3$). The differential in reaction rates and/or precursor concentrations in the simulated α-phellandrene experiments...
is therefore insufficient for reaction with NO\textsubscript{2} or O\textsuperscript{3P} to have a significant impact. Nonetheless, use of a surrogate rate coefficient for O\textsuperscript{3P} (with γ-terpinene) in the mechanism is noted, with the actual α-phellandrene + O\textsuperscript{3P} rate coefficient required before assessing the true impact of the O\textsuperscript{3P} initiation reaction.

In the gas-phase, the second important group of compounds to consider for mechanism evaluation is organic products. Unfortunately, as concluded by the analysis of propene during chamber characterisation, the comparison of PTR-TOF measurements with model predictions is not a reliable measure of mechanism performance without accurate calibration of the PTR-TOF using standards. For interest, modelled yields of a number of smaller species that were experimentally reported in Chapter 3.8 are provided in Table 4.2. Experimental quantification is considered more accurate for these products, as they were either directly calibrated or have better parameterised rate coefficients and fragmentation patterns. Yields were determined using the same methodology employed during experimental analysis, that is, by plotting product formation against α-phellandrene consumption over the initial part of each experiment. Formaldehyde and acetone yields from α-phellandrene are consistent with what was experimentally reported. However, time profiles shown in Appendix H.2 show formaldehyde to be systematically overpredicted in 2013 experiments and acetone underpredicted in all experiments, suggesting a poor representation of formation of these products from higher generation chemistry in the mechanism. Glyoxal formation was predicted to be minor compared to acetone in the model (<4%), suggesting reported experimental yields at m/z 59 are predominantly attributable to acetone. If true, then the experimental and modelled acetone yields from the photooxidation of α-phellandrene in this work are slightly higher than the 8 ± 4 % yield reported by Reissell et al. (1999). The remaining prominent low molecular weight carbonyl species, acetaldehyde and methyl glyoxal, had yields which were consistently under-represented in the model compared to experiment.

Modelled formic and acetic acid yields are significantly lower than what was found experimentally, suggesting a missing channel forming acidic groups from small organic radicals in the mechanism. However, given that essentially all chemistry for species with less than 3 carbons was extracted from the MCM, the discrepancy is thought not to lie with the newly constructed reactions. Alternatively, the large differential indicates that the m/z 47 and 61 signals in the PTR-TOF are primarily attributable to fragments of larger acidic species, highlighting the need for better constrained product data.

Simulated time-profiles for a select number of heavier organic products are also shown in Figure H.2 in the Appendix. Concentrations of APHAAL and APHCAL both show the characteristic formation and decay profiles of unsaturated first-generation products, which was used to argue the non-attribute of the m/z 169
ion in both photooxidation and ozonolysis experiments to major predicted first-
generation products. Second-generation species, whose molecular weights match
ions detected by the PTR-TOF, are also plotted; APHAAL2 (m/z 129) and C613AL
and C613CO (m/z 115). The simulated concentration of major first- and second-
generation products are typically significantly greater than what the PTR-TOF
reports, supporting significant fragmentation and/or loss of these functionalised
species during sampling and detection. Validation of model accuracy with respect
to gas-phase organic products is therefore not performed, with more reliable exper-
imental data first required.

Despite the model exhibiting variable performance in its ability to simulate O₃
production, an ozone isopleth is constructed to check if the concept of VOC and NOₓ
limited regimes is applicable to the system. The isopleth is constructed from 400
equidistant data points, spaced over initial α-phellandrene and NOₓ concentrations
ranging from 0 to 100 ppb. These concentrations are thought typical of chamber
experiments. Initial NOₓ was represented as 3 parts NO to 1 part NO₂. Relative
humidity was set to 10% in all simulations. No chamber auxiliary mechanism, back-
ground or contaminant species were included to make the result directly attributable
to α-phellandrene. Photolysis parameters from the 2013 campaign were used.

As the VOC/NOₓ ratio strongly increases during the course of an experiment,
the maximum ozone concentration obtained over a 12 hour simulation is plotted in
Figure 4.6 as a function of initial α-phellandrene and NOₓ concentration. The max-
imum ozone concentration in the simulated chamber experiments shows behaviour
analogous to that depicted in isopleths calculated for atmospheric conditions. At
low-NOₓ concentrations, ozone production is NOₓ limited, with an increase in NOₓ

<table>
<thead>
<tr>
<th>No.</th>
<th>Formaldehyde (HCHO)</th>
<th>Acetaldehyde (CH₃CHO)</th>
<th>Formic acid (HCOOH)</th>
<th>Acetone (CH₃COCH₃)</th>
<th>Acetic acid (CH₃CO₂H)</th>
<th>Methyl glyoxal (MGLYOX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>6.4</td>
<td>0.17</td>
<td>0.005</td>
<td>11</td>
<td>0.0007</td>
<td>2.4</td>
</tr>
<tr>
<td>16</td>
<td>2.4</td>
<td>0.09</td>
<td>0.004</td>
<td>8.4</td>
<td>0.04</td>
<td>1.3</td>
</tr>
<tr>
<td>17</td>
<td>4.5</td>
<td>0.12</td>
<td>0.004</td>
<td>11</td>
<td>0.003</td>
<td>2.5</td>
</tr>
<tr>
<td>18</td>
<td>7.4</td>
<td>0.13</td>
<td>0.004</td>
<td>11</td>
<td>0.001</td>
<td>2.2</td>
</tr>
<tr>
<td>19</td>
<td>5.1</td>
<td>0.13</td>
<td>0.004</td>
<td>11</td>
<td>0.002</td>
<td>2.5</td>
</tr>
<tr>
<td>20</td>
<td>4.3</td>
<td>0.15</td>
<td>0.005</td>
<td>11</td>
<td>0.003</td>
<td>2.5</td>
</tr>
<tr>
<td>21</td>
<td>5.9</td>
<td>0.15</td>
<td>0.005</td>
<td>11</td>
<td>0.002</td>
<td>2.3</td>
</tr>
<tr>
<td>22</td>
<td>11</td>
<td>0.22</td>
<td>0.009</td>
<td>12</td>
<td>0.0003</td>
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</tr>
<tr>
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<td>0.15</td>
<td>0.005</td>
<td>11</td>
<td>0.0006</td>
<td>0.7</td>
</tr>
<tr>
<td>24</td>
<td>4.1</td>
<td>0.18</td>
<td>0.009</td>
<td>10</td>
<td>0.006</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 4.2: Modelled gas-phase molar yields (%) for major species detected dur-
ing photooxidation experiments using mechanism M₇. Comparative experimental
results are provided in Table 3.17.
Figure 4.6: Constructed ozone isopleth for an α-phellandrene–NOx system under chamber conditions using mechanism M7. The maximum ozone concentration (in ppb) during the simulation is plotted as a function of the starting α-phellandrene and NOx concentrations. Starting positions of the α-phellandrene photooxidation experiments discussed in Chapter 3.8 are shown by black diamonds, except for experiment 22 which lies outside the plotted range.

bringing the system to a region of maximum ozone productivity. At higher NOx concentrations, the system becomes VOC limited, with ozone concentration decreasing as NOx is further increased. The black diamonds in Figure 4.6 show that experiments were conducted under both regimes. It is known that ozone production is most sensitive to mechanistic parameters under VOC limited scenarios, making high NOx experiments ideal for studying the robustness of chemical mechanisms with respect to O3 production. However, for the validation of atmospheric models, chamber experiments with low-NOx concentrations that better reflect atmospheric conditions are preferred. The constructed isopleth can therefore be used to guide development of future chamber experiments under different regimes.

4.3.2 Condensed Phase Evaluation

The initial SOA parameterisation underpredicted peak mass loadings by one to two orders of magnitude (10 to 440 times). A species-independent scaling factor (SF) and scaling constant (SC) were therefore implemented to values of $k_{on}$ and $k_{off}$ respectively, with the former to increase partitioning into, and the latter to decrease partitioning out of, the aerosol phase. The scaling factor therefore accounts for inherent uncertainties in estimated properties pertaining to the gas-aerosol flux (e.g. mean molecular speed, diffusion coefficient, accommodation coefficient, particle diameter), whilst the scaling constant accounts for additional errors in estimated properties and assumptions used in determining the gas-aerosol partitioning coeffi-
4.3. CHAMBER MODEL PERFORMANCE AND DISCUSSION

cients (e.g. vapour pressure, activity, condensed phase reactions).

To highlight variability in estimative techniques, Figure 4.7 compares vapour pressures estimated at 298 K in this study ($p_{o, EVAPORATION}$, Compernolle et al. (2011)), with those estimated using the method of Nannoolal et al. (2008) combined with the method of Nannoolal et al. (2004) for estimating boiling points ($p_{o, Nan,Nan}$), and the method of Myrdal and Yalkowsky (1997), combined with either the method of Stein and Brown (1994) ($p_{o, MY,SB}$) or Joback and Reid (1987) ($p_{o, MY,JR}$), for boiling point estimation, for all $\alpha$-phellandrene photooxidation products considered for partitioning. $p_{o, Nan,Nan}$ was recommended as the preferred vapour pressure estimation method in the comprehensive evaluation of Barley and McFiggans (2010), whilst in their assessment O’Meara et al. (2014) recommended Myrdal and Yalkowsky (1997), along with the EVAPORATION method. The trend line of $p_{o, Nan,Nan}$ compares most similarly with $p_{o, EVAPORATION}$, with $p_{o, MY,SB}$ increasingly underestimating and $p_{o, MY,SR}$ overestimating the vapour pressure for less volatile compounds. The mean absolute error in log $p_o$ of the three methods, with error being taken as deviation from $p_{o, EVAPORATION}$, are 0.91, 0.86 and 1.2 atm respectively for $p_{o, Nan,Nan}$, $p_{o, MY,SB}$ and $p_{o, MY,SR}$. That is, each method tends to deviate from $p_{o, EVAPORATION}$ by around an order of magnitude for $\alpha$-phellandrene photooxidation products, consistent with method deviation reported for simulated $\alpha$-pinene photooxidation products (Valoroso et al., 2011). Given proportionality of absorption and desorption rates on component variables, decisions made in choosing specific estimative methods consequently have a profound impact on SOA modelling.

The uncertainty present in implementation of gas-to-particle partitioning provides merits for rate constant scaling. Previous studies simulating aerosol formation in chamber experiments have used similar techniques to that used in this study. For example, Jenkin (2004) applied an empirical scaling constant of around 120 to all desorption rate coefficients to accurately simulate aerosol formation in $\alpha$-pinene and $\beta$-pinene chamber ozonolysis experiments. Similar factors were also used by Chen and Griffin (2005) and Chan et al. (2009) in modelling $\alpha$-pinene ozonolysis. Jenkin et al. (2012) considered scaling constants to reduce vapour pressure values by up to 20, in simulating SOA production from the photooxidation of $\beta$-caryophyllene; however, the authors found this change was unable to reproduce experimentally observed SOA during the initial stages of their experiments. Meanwhile, Johnson et al. (2004, 2005) used scaling factors ranging from 5 to 80 to increase all gas-to-particle partitioning coefficients to simulate SOA formation during aromatic photooxidation. Other studies have reported similar discrepancies between estimated partitioning coefficient components and apparent partitioning coefficient components (Kamens and Jaoui, 2001; Barley and McFiggans, 2010; O’Meara et al., 2014).

Using values of SF ranging from 8 to 40, and SC values ranging from 0.036 to
0.28, it was possible to obtain reasonable simulations of aerosol production and loss inside the chamber for each experiment, as shown in Figure 4.9. The 2016 experiments required a larger scaling factor, due to larger SOA diameters reducing the absorption rate constants in these experiments. The 2016 models also respectively required smaller scaling constants, due to the larger aerosol loadings recorded during the campaign (see Chapter 3.8.2). Implementation was found to have a minor impact on the system oxidative capacity (mechanism M8 in Figure 4.1), with the majority of species preferentially residing in the gaseous phase. For each simulation, the contribution of unsaturated and saturated products is also reported. As expected, the initially formed aerosol in each experiment is dominated by unsaturated products, which are in general first-generation, although saturated products, which are almost always higher-generation species, make a sizeable contribution by the time peak SOA loading is reached. Nonetheless, unsaturated products tend to remain the dominant constituent of aerosol over the conducted simulations. This representation is in mixed agreement with the SOA growth curves presented in Figure 3.50.

Figure 4.8 shows the 15 most prominent SOA species across all experiment simulations after 2 hours. Collectively, these 15 products on average constitute 73% of the SOA by mass, although the variability in aerosol composition across the simulated experiments shown in Figure 4.9 is noted. Of these top contributors, ten are unsaturated products, receiving important contributions from the carbonyls C93CHO6CO, APHAAL and APHAAL, and the acids C101ALCOOH and C10AL1COOH. In-
4.3. CHAMBER MODEL PERFORMANCE AND DISCUSSION

Indeed, these five products alone, on average, comprise 38% of the simulated SOA across all experiments after 2 hours. The presence of two first-generation acids among the largest contributing aerosol species is promising, with C101ALCOOH and C10AL1COOH having been identified as an important constituent of SOA formed in the ozonolysis of α-phellandrene (N13, Chapter 3.5.2). Products with five carbon atoms were cumulatively found to comprise less than 0.1% of the SOA by mass, supporting the exclusion of smaller compounds from aerosol modelling. In general, peak aerosol loading is well represented in the current SOA parameterisation, however performance is variable once loss processes dominate, with models of some experiments capturing decay better than others. In particular, SOA loss in a number of simulations (e.g. experiments 16, 17, 23, 24) is too rapid compared to measurement. Rather than being loss related, these experiments are thought to be missing a significant contribution from saturated SVOCs in the simulation.

Figure 4.9 also compares experimental and simulated elemental compositions for each experiment. The H/C ratio is reasonably well simulated in each experiment, however both O/C and N/C ratios are systematically under-predicted compared to
4.3. CHAMBER MODEL PERFORMANCE AND DISCUSSION

Figure 4.9: Results of SOA model simulations of the ten photooxidation chamber experiments. The left panel shows simulated time evolution of SOA mass loading; red dots are experimental results, dark shading the simulated first-generation product contribution and light grey shading simulated higher-generation product contribution. The central panel shows experimental (shading) and simulated (lines) aerosol composition; H/C in blue, O/C in green and N/C in red. The right panel shows model predictions of SOA functional composition, with total contribution of alcohol and/or carbonyl containing species in the aerosol phase represented by blue, hydroperoxides containing species by yellow, acid containing species by green, nitrates containing species by red, and PAN containing products by orange.
AMS measurements. This suggests that the predicted SOA is not sufficiently function- 

tionalised, which may somewhat explain the need for scaling factors to achieve the 

required aerosol mass. For instance, increasing the prevalence of acids, hydroperox- 

ides or nitrates with respect to carbonyl and alcohol groups would increase the 

O/C and N/C ratio without significantly impacting the H/C ratio. Whether this is 

a result of a poorly represented gas-phase, of which the aerosol phase is a reflection, 

or systematic overestimation of vapour pressures of more functionalised species is 

unknown. Of the 788 compounds used in evaluating the EVAPORATION vapour 

pressure estimation method, only 34 were multifunctional compounds, and so the 

latter conjecture cannot be ruled out. Indeed, Barley and McFiggans (2010) ob- 

served that predicted vapour pressures of multifunctional compounds were 100 to 

1000 times more volatile than required to contribute significantly to organic aerosol 

– although they did not consider the EVAPORATION method used here. Alterna- 

tively, O/C and N/C ratios could be increased through a greater simulation of higher-

generation products, which are typically fragmented with respect to α-phellandrene 

and so tend to have a higher functional state. Both O/C and N/C were simulated 

to slowly increase over the course of a simulation, with less functionalised species 

preferentially desorbing once loss processes became dominant.

Lastly, the functional group distribution of the simulated organic aerosol mass is 

investigated. Products are distributed into six main groups for compositional anal- 

ysis; carbonyls and alcohols, hydroperoxides, carboxylic acids, peracids, nitrates and 

PANs. Species consisting of a hydrocarbon backbone with only aldehyde, ketone 

and/or alcohol functional groups are placed in the first category, whilst those con- 

taining at least one of any other of the functional groups are placed accordingly. 

The complete list of species comprising each compositional group is provided in Ap- 

pendix I. Peracids were found to make a negligible contribution to the aerosol mass, 

due to their low gas-phase abundance, and so are not considered further in this dis- 

cussion. The contribution of the remaining groups for each experiment are shown 

in Figure 4.9. This shows the majority of experiments have simulated aerosol which 

is dominated by carbonyls and acids. The interplay between these two species has 

a weak loading dependence (or more accurately scaling factor and constant depen- 

dence), with the relatively less volatile carbonyl containing species becoming more 

influential at higher aerosol mass concentrations. Nevertheless, experiment 21 was 

found to have the largest acid contribution, which is attributable to high humidity 

favouring acid production. The aerosol composition in experiment 16, which had 

the highest VOC/NO_x ratio, was dominated by hydroperoxides. This reflects the 

higher simulated HO_2 concentrations in this experiment, and shows hydroperoxide 

formation to become more favourable in the model as NO_x concentrations decrease. 

More broadly, the result is supportive of high hydroperoxide concentrations found
in SOA formed during low-NO$_x$ experiments (Docherty et al., 2005; Xia et al., 2008; Li et al., 2016). Despite having variable VOC/NO$_x$ ratios, the joint contribution of nitrates and PANs to SOA in the remaining experiments is fairly consistent (ca. 5 – 7%), with relative amounts of each varying depending on available NO and NO$_2$. Simulated values are lower than the range 10 – 23% experimentally observed (Chapter 3.8.2). However the current model does not predict increased nitrate or PAN formation under high NO$_x$ conditions (e.g. experiment 22), which is similar to observed experimental invariance (Table 3.21). The current aerosol parameterisation is therefore able to capture many of the trends experimentally observed for different VOC/NO$_x$ conditions.
To further probe the effect of VOC/NO\textsubscript{x}, Figure 4.10 shows the fraction of a selection of species containing acid, hydroperoxide, nitrate or PAN functionality with respect to their chemical group, for experiments having three different VOC/NO\textsubscript{x} ratios. This shows that, along with a general shift in distribution of functional groups, the species composition within each group also changes with oxidation conditions. The acids are dominated by the major first-generation products C101ALCOOH and C10AL1COOH under all VOC/NO\textsubscript{x} conditions tested. Within the hydroperoxide functional group, the contribution of C102OH1OOH and C63CO1COOH decreases dramatically as the VOC/NO\textsubscript{x} ratio increases, due to an increase in hydroperoxide products formed through the ozone initiated channels. Similarly, the nitrate signal is dominated by C96CO1NO3, although C916CO5NO3 makes a sizeable contribution at VOC/NO\textsubscript{x} ratios of around unity and APH2COTNO3 under low-NO\textsubscript{x} conditions, due to differing prevalence of OH and O\textsubscript{3} initiated channels. PANs are generally dominated by C106O1PAN, followed by C103O7PAN, which makes a comparatively larger contribution under low-NO\textsubscript{x} conditions.

The magnitude of implemented SF and SC is somewhat linked to total aerosol loading inside the reactor, suggesting that the scaling approach is a crude fix, rather than a measured adjustment to account for estimated inaccuracies. Indeed, the entire dataset cannot be accurately fitted with one set of SF and SC parameters, although the inexplicably high SOA yields in 2016 compared to the 2013 campaign has already been noted. The current representation of aerosol formation is therefore unable to consistently simulate the intricacies of aerosol production and/or loss across the different starting experimental conditions. Either key parameters involved in the estimation of partitioning properties are subject to significant errors, or absorptive partitioning of products generated in the mechanism is not an accurate depiction of SOA formation. Apart from the aforementioned uncertainties in estimated properties, other potential flaws in the model’s representation of experiment are in:

1. Micro-physical processes. No diffusion limitations, aerosol nucleation or coagulation processes were implemented in the model. The model implicitly assumes that these processes are not rate limiting; with sensitivity testing showing the model to be insensitive to initial BGOA. In addition, semi-volatile gas-phase losses to reactor walls are not considered. The initial model underpredicts aerosol formation, with inclusion of SVOC deposition only going to further reduce SOA yield. Nevertheless, loss of SVOCs to the walls of the GIG-CAS reactor through absorptive partitioning is expected to be small in these experiments, due to rapid SOA formation providing a more competitive condensation sink (Boyd et al., 2015; Nah et al., 2017). Once rates of vapour wall losses are known for the GIG-CAS chamber, however, it would be advisable to include
the process in the model for complete parameterisation.

2. Aerosol composition. All aerosol considered in the model system is assumed to be in one well-mixed phase. This is thought to be a reasonable assumption, given the purely organic nature of the aerosol and similarity in component activities (Zuend and Seinfeld, 2012). Furthermore, aerosol is assumed to be dry and free of any water phase, which is considered valid for most experiments, given the low RH conditions (Cocker et al., 2001a; Roldin et al., 2014). Prisle et al. (2010) showed that water in the organic phase only has a weak impact on equilibrium vapour pressures and activity coefficients in organic systems, whilst water itself is known to contribute little to the aerosol mass (< 5%, Kamens et al. (1999)). Therefore, treating aerosol as purely organic is thought to only have a small impact on SOA modelling, with the model able to account for the impact of increasing RH through mechanistic channels (Jonsson et al., 2008; Stirnweis et al., 2017). There is, however, underlying uncertainty in the activity of organics, which, to be modelled accurately, should be updated in conjunction with changing SOA composition throughout and in each experiment.

3. Gas-phase chemical mechanism. The MCM is a near explicit chemical mechanism, necessarily containing a number of systematic simplifications to constrain mechanism size. The most influential simplification, with regards to SOA formation, is thought to be the treatment of ‘minor’ reaction products (e.g. acids, hydroperoxides, nitrates, PANs), of which simplified chemistry preferentially attacking the functional site is represented (Jenkin et al., 1997; Saunders et al., 2003). Whilst limiting size, this representation reduces the prevalence of multi-functional products. For instance, diacids found in ozonolysis filter samples are not formed through the current MCM parameterisation. The current mechanism also omits degradation chemistry arising from acyl oxy radicals, which are assumed to exclusively decompose to liberate CO$_2$. Re-arrangement reactions to form a δ-peroxy carboxylic acid are therefore not considered which, if included, would increase the prevalence of low-volatility species and increase the relative oxygen content of products resulting in a higher O/C ratio.

4. Condensed phase reactivity. No condensed phase or heterogeneous reactions are considered in the model. Assuming that products from condensed phase reactions are less volatile than the their precursor reactants, implementation would increase SOA yield. Indeed, scaling factors have been proposed as being, at least in part, ad hoc corrections for condensed phase accretion reactions (Jenkin, 2004; Chan et al., 2009; Camredon et al., 2010). Given the ubiquity of
Impact of Condensed-Phase Accretion Reactions

Due to the large number of potential monomers, and numerous ways they can be coupled together, the distribution of oligomeric molecules is complex, even when produced from a single precursor VOC. As such, mechanisms representing oligomerisation reactions have remained largely conceptual. For example, in modelling SOA from the ozonolysis of α-pinene, Jenkin (2004) modelled gaseous dimerisation and subsequent transfer into the aerosol phase of 22 C$_{8-10}$ bi- and multi-functional acids; Camredon et al. (2010) considered a first-order irreversible dimerisation process for each SVOC formed; Zuend and Seinfeld (2012) explicitly modelled two surrogate dimers; Trump and Donahue (2014) considered dimerisation from three acidic monomers; and Roldin et al. (2014) explicitly represented dimer formation from monomers, however simplified the mechanism, by lumping dimers based on formation pathway and assuming a mass of 400 g mol$^{-1}$ for each.

To simplify accretion parameterisation, all condensed phase species are considered as potential monomer units, as each compound contains at least one carbonyl, alcohol, peroxy or acidic group – with these functionalities generally considered as being able to participate in oligomer forming reactions (e.g. Figure 1.10). This multifunctional monomer pool is then reacted with condensed phase hydroperoxide and acid containing species, to reversibly produce a symmetric dimer. This representation is likely to overestimate oligomer formation, as it is unlikely that all monomers represented favourably react with one another. Nonetheless, the assumption has some backing from theoretical work, with aldol condensation, diol esterification, peroxyhemiacetal and acid–acid dimerisation having been shown to be thermodynamically favourable accretion processes (Barsanti and Pankow, 2004, 2005, 2006; DePalma et al., 2013). Experimentally, Heaton et al. (2007) observed oligomers within seconds in the reaction of monoterpenes with ozone, further suggesting that there is no intrinsic kinetic barrier to dimer formation. Given thermodynamic favour, dimerisation processes are likely rapid enough to form substantial dimer mass on short timescales (i.e. the length of chamber experiments). All dimers are assumed to be non-volatile in the model. Oligomeric components of SOA have also been considered potential nucleating agents (Heaton et al., 2007; Kristensen et al., 2014; Witkowski and Gierczak, 2014; Zhao et al., 2015b). To represent this, all C$_{8-10}$ hydroperoxide and acid-containing compounds are reacted with a pool containing
these species, to form a symmetric dimer which is assumed to instantaneously condense. This is based on theoretical work by DePalma et al. (2013), who showed gas-phase formation of covalently bound peroxyhemiacetal and non-covalent acid dimers to be thermodynamically favourable. Despite experiments finding evidence of trimers and higher-order oligomers in the oxidation of other monoterpenes (e.g. Hallquist et al., 2009), these species are not included as a simplification measure. Considering dimers are represented as non-volatile, the inclusion of higher order oligomers would have little impact on model output. It is noted that this simplified approach is based on a variety of assumptions concerning dimer formation, and is unlikely to be physically correct. Nonetheless, it introduces gas-to-particle transfer and condensed-phase retention processes that displays an overall second-order rate dependence on the concentration of multifunctional species, and is therefore at least notionally representative of the possible effects that dimerisation has on the system.

The kinetic representation of condensed-phase dimerisation was implemented using peroxyhemiacetal formation information provided in Ziemann and Atkinson (2012); that is, a second-order rate coefficient of $0.5 - 70 \text{ M}^{-1} \text{ h}^{-1}$ $(2.3 \times 10^{-25} - 3.2 \times 10^{-23} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1})$, and equilibrium constant of $0.16 - 120 \text{ M}^{-1}$ $(2.7 \times 10^{-22} - 2.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1})$. However, it is noted that hydroperoxide and acid dimerisation are unlikely to occur at the same rate, with values to be optimised using experimental data to provide different dimerisation responses based on simulated gas-phase and aerosol composition. To transition kinetics from a monodisperse to condensed phase representation in the model, the average photooxidation aerosol density $(1.42 \text{ g cm}^{-3})$ was used with an assumed average constituent mass of $200 \text{ g mol}^{-1}$. These values provide a total monomer concentration of $4.3 \times 10^{21}$ molecules cm$^{-3}$ in the aerosol phase, which is used in a pseudo first-order reaction parameterisation. Concentrations of individual monomers were expressed as a fraction of this monomer pool, using concentrations formed in the model. Condensed phase diffusion effects are assumed to be a non rate-limiting factor. Given experimental evidence indicates that uniform SOA composition is achieved on timescales of less than an hour, this approximation is thought valid (Trump and Donahue, 2014). Gas-phase dimerisation was initially implemented using the optimised rate coefficient found in the modelling study of Jenkin (2004); $1.5 \times 10^{-32} e^{(14770/T)} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.

The result of simulations including dimerisation reactions are variable, with SOA production highly sensitive to the inferred parameters. Model SOA output from experiments 15, 16 and 17, which were conducted at three different VOC/NO$_x$ ratios, are shown in Figure 4.11. For consistency, the same dimerisation input parameters were used in all three models, that is, the condensed-phase dimerisation rate coefficient was reduced to $3 \times 10^{-32}$ and $2 \times 10^{-32} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for acid and
Figure 4.11: Simulated time evolution of SOA mass loading in experiments 15, 16 and 17, using models incorporating dimer formation. The contribution of dimers to the simulated mass is shown by dark grey shading. Experimental measurements are denoted by red dots.

Hydroperoxide dimerisation respectively. This significant reduction is likely due to an over-representation of potential monomer units. Equilibrium constants were both set to two orders of magnitude smaller than this. The gas-phase dimerisation rate coefficient proposed by Jenkin (2004) was kept the same. In general, Figure 4.11 shows the model to underpredict SOA mass. Dimers were simulated to constitute a significant fraction of the SOA by mass in each experiment. Increasing the gas-phase dimerisation rate coefficient had little impact on aerosol loadings, suggesting that the value is at an upper limit. Meanwhile, increasing the propensity of condensed-phase dimerisation, or decreasing the reverse dimer decomposition rate, increased aerosol formation, but at a cost to the accuracy of simulated time profiles. In particular, changes resulted in an increasingly significant dimer fraction at the start of the simulation and/or reduced dimer losses, yielding a flatter SOA mass profile through the duration of the experiment. This effect is evident by comparing the simulated time profiles of experiment 15, which has a respectively large simulated dimer fraction, with experiment 16, which does not. Given all experiments are modelled with the same dimerisation parameters, differing yields show the impact of gas-phase volatilities, with correlation between simulated loadings and hydroperoxide production observed.

Evidently the current implementation of dimer formation does not provide an accurate depiction of experimental measurements. It is possible then that dimers are not influential in the α-phellandrene photooxidation system. For instance, Kristensen et al. (2014) observed that despite dimer precursors being present, dimers were not formed during their photooxidation study on α-pinene. Alternatively, the gas-phase mechanism could be providing a poor representation of dimer precursors, or oligomerisation occurs through unrepresented, more substantial pathways. Based on simulated time profiles, the problem again appears to lie with higher generation compounds, with SOA mass contribution after the initial burst not well represented. Whilst not discussed in this thesis, a (more) explicit ozonolysis chemical mechanism was constructed and integrated with a similar parameterisation of gas-particle par-
tioning, including autoxidation and dimer formation processes. This was able to capture SOA formation when modelling the ozonolysis experiments discussed in Chapter 3.5.1. The problem is therefore unlikely to be related to coding but, rather, in the representation of either SVOC formation in the gas-phase mechanism or accretion processes during the photooxidation of α-phellandrene. A notable difference between the ozonolysis and photooxidation models is the incorporation of autoxidation reactions to form ELVOCs (Ehn et al., 2014; Jokinen et al., 2015), and reaction of stabilised CIs to form oligomers (Kristensen et al., 2014; Zhao et al., 2015b), both of which have been proposed as being important aerosol-forming pathways in ozonolysis experiments. However, given the large number of competing channels for peroxy radicals and SCI during ‘polluted’ photooxidation experiments, these pathways are not considered relevant – although a number of 1,5-H isomerisations are represented in the gas-phase mechanism for alkoxy radicals. However, there is evidence of ozone heterogeneously adding to condensed-phase unsaturated products of limonene, with the SCI products of this reaction then able to form oligomers (Maksymiuk et al., 2009). Given α-phellandrene is also doubly unsaturated, the impact of heterogeneous processes is something which should be considered in the future. Implementation would additionally improve currently modelled O/C, which, if dimerisation were to involve dehydration, would further decrease (Ziemann and Atkinson, 2012).

Whilst integration of dimerisation in the model represents the possible effects it can have, optimisation of SOA mass reduces to the same scenario; scaling of variable parameters. Whether it is adjusting scaling factors and constants for condensation and evaporation rates, or tuning gas-phase and condensed-phase dimerisation rate coefficients, the underlying issues likely remain the same. More complex modelling of the intricacies involved in SOA formation and evolution was never in the scope of this dissertation, and so further investigation into more advanced physical and chemical processes such as aerosol coagulation and size evolution, diffusion limitations between the gas phase, particle surface and particle bulk phase, non-equilibrium partitioning, acid catalysis, heterogeneous uptake, non-ideal interactions and phase splitting into multilayer (potentially organic and aqueous) aerosol was not conducted. To better understand which processes (e.g. gas-phase chemistry, particle-phase reactions, particle-phase state, aerosol dynamics) are influencing aerosol formation and properties, more complex aerosol models will need to be constructed. Moreover, the current model would necessarily have to be extended if experimental conditions changed (e.g. inorganic seeds were introduced). With regards to the current model, it is recommended that more experimental work concerning accretion reactions during photooxidation be conducted, both from α-phellandrene to identify possible dimer products, and more generally to better constrain kinetic processes.
and parameters. This way, the model can be more accurately used to determine if oligomerisation is important for SOA mass formation, or if there is some other misunderstood or misrepresented process existing in the model.

## 4.4 Modelling Summary

A chemical mechanism describing the tropospheric degradation of α-phellandrene has been developed for the first time, tying in knowledge from theoretical and experimental components of this thesis with MCM protocols. The gas-phase mechanism describes in moderate detail the complete degradation of α-phellandrene, initiated by reaction with OH radicals, O₃ and NO₃ radicals. The mechanism contains 3601 reactions and 1187 closed-shell and radical species, of which 2150 reactions and 723 species are newly added. Consumption of α-phellandrene by NO₂ and O(^3P) was found not to be important during these experiments, although the mechanisms are provided should they be required in future simulations. The gas-phase mechanism was integrated with a kinetic parameterisation of gas-to-particle partitioning for 458 multi-functional, closed-shell oxidation products.

The performance of the mechanism was evaluated against the photooxidation chamber experiments. Unfortunately, uncertainties in experimental measurements, particularly in gas-phase organic concentrations, prevented confident optimisation of the constructed mechanism. Instead, sensitivity testing was used to locate critical mechanistic features that can be targeted during future refinements, including: branching ratios for OH addition and abstraction channels to α-phellandrene and major first-generation products, first-generation nitrate yields, rate of O₃ addition to unsaturated products, OH radical yields from first-generation ozonolysis and SOZ formation rates from α-phellandrene SCI. As an example, a number of these mechanistic refinements were implemented together to best simulate results from the 2013 experimental campaign. The ‘optimised’ mechanism was then able to consistently recreate α-phellandrene and NO time profiles within uncertainty bounds of key parameters in the model, whilst results for O₃ and NO₂ were more variable. Simulated yields and time profiles for most organics show considerable deviation from experiment measurements, although this is likely to be as much an issue with experiment as it is with the constructed mechanism.

Initial implementation of gas-to-particle partitioning was found to consistently underpredict SOA mass loadings. This was accounted for through use of two scaling factors, which were argued to account for uncertainties in estimated or assumed properties (e.g. vapour pressures, activities, accommodation and diffusion coefficient), or by inclusion of gas- and condensed-phase accretion reactions. In the former parameterisation, an increase in $k_{on}$ of up to 40 times and a decrease in $k_{off}$ of
up to 28 times was required to simulate aerosol production. Compositional analysis shows aerosol in each experiment to be dominated by a small number of species, the majority of which are unsaturated, with elemental ratios showing these species to be insufficiently functionalised. Functional distribution of condensed products shows that SOA from α-phellandrene changes with VOC/NO\textsubscript{x}, reflecting relative gas-phase abundances of hydroperoxides, acids, nitrates and PANs. When integrated with accretion reactions, focusing on dimerisation of hydroperoxides and organic acids, the model was unable to accurately simulate SOA mass loadings. This does not rule out the impact of oligomers in α-phellandrene photooxidation SOA, with more complex aerosol modelling deemed necessary to determine which aspects of SOA formation, evolution and loss are currently poorly represented or constrained.

The constructed mechanism therefore provides an initial representation of α-phellandrene’s tropospheric degradation, which is currently able to capture some general experimental features. More importantly however, it provides a benchmark from which reduced mechanisms can be evaluated, and future theoretical, experimental and modelling development can build.
Chapter 5

Conclusion and Future Work

5.1 Conclusion

This thesis presents the first comprehensive study into the tropospheric degradation of α-phellandrene. The main body of the thesis has been separated into three chapters, with each discussing the use of a different investigative method for examining the decomposition of α-phellandrene; namely, computational techniques, smog chamber experiments, and mechanism development and modelling. Summaries were provided throughout the thesis, either at the end of published material or after discussion of distinct pieces of work. The aim of this final chapter is therefore not to rewrite previous conclusions but, rather, synthesise findings from the entire thesis before presenting avenues for improvement and future research.

The ultimate aim of this project was parameterisation of α-phellandrene’s atmospheric degradation through a detailed chemical mechanism. From the outset, however, with little prior research or available literature on this BVOC, it was recognised that a multi-faceted, multi-institutional approach was needed, requiring use of a number of investigative techniques. First, a computational investigation into the ozonolysis mechanism of α-phellandrene, a pathway known to have considerable mechanistic variability depending on precursor structure, was undertaken. Using high-level composite G4(MP2) theory, the potential energy surface for unimolecular decomposition from all four Criegee intermediate products (eight considering conformation isomerism) was mapped to first-generation products. Results showed ozone addition to the least substituted double bond in α-phellandrene is preferred, with the hydroperoxide channel generally favoured for excited syn-CIs, the ester or ‘hot’ acid channel for excited anti-CIs, and secondary ozonide formation for thermalised CIs. Furthermore, cyclic conjugation present in α-phellandrene enabled two novel rearrangement processes to occur for specific CIs, namely, resonance stabilised 1,6-H migrations and epoxide formation. The resonance stabilised H-migration was
especially interesting, as it both lowered the energy barrier for the hydroperoxide channel, and allowed it to occur in CIs without access to conventional 1,4-H migration pathways. Findings from the theoretical study were subsequently implemented during construction of the ozonolysis portion of the chemical mechanism. With approximately 50% of α-phellandrene simulated to be consumed by ozone in the photooxidation experiments, computational parameterisation of the ozonolysis mechanism proved important.

Secondly, allotted facility access allowed 11 ozonolysis, 3 NO₂-initiated, and 10 photooxidation chamber experiments to be conducted at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences’ smog chamber facility. The campaigns provided the first comprehensive experimental investigation into the degradation of α-phellandrene, in addition to datasets for mechanism evaluation. The majority of ozonolysis experiments were conducted with cyclohexane as an OH radical scavenger, and determined gas-phase yields for a number of major products, OH yields of 35 ± 12 % and 15 ± 7 % for α-phellandrene and its unsaturated first-generation products, a rate coefficient of $1.0 \pm 0.7 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction of unsaturated products with ozone at 298 K, and parameterised a number of aerosol properties including a one-product fit to the very high yields, to which first- and higher-generation products contributed, an average effective density of $1.42 \pm 0.2$ g cm$^{-3}$, bulk elemental composition and oxidation state. Nucleation was observed almost instantaneously in all experiments, suggesting that the endocyclic conjugation present in α-phellandrene is conducive to rapid formation of highly-condensible products, with the addition of CI scavengers found to suppress new particle formation. Filter samples taken during chamber experiments were analysed at the University of York, UK, with 21 product or product groups identified from chromatograms. These included polyfunctional first- and second-generation species containing one or more carbonyl, acid, alcohol and hydroperoxide functionalities, with key reaction pathways identified. Oligomeric peaks were observed, with suppression of these upon introduction of an SCI scavenger, and double bond equivalency factors, supporting dimerisation through stabilised CIs. Photooxidation chamber experiments were conducted at a variety of different oxidation conditions ($0.16 \leq$ VOC/NO$_x$ $\leq 4.6$), which showed α-phellandrene to be an efficient cycler of NO$_x$. Yields for a number of smaller oxidation products were determined, with fragments of larger products assigned based on mechanistic theory. Significant aerosol, albeit less than ozonolysis, was produced, with nucleation observed to increase upon shifting from an RO$_2$ + NO to an RO$_2$ + HO$_2$ or RO$_2$ dominated regime, with final yield showing a nucleation dependence. The SOA produced, having an average density of $1.42 \pm 0.1$ g cm$^{-3}$, was classified as semi-volatile oxygenated organic aerosol, with organic nitrates estimated to account for 10 – 23% of the SOA by mass. NO₂-initiated
smog chamber experiments were conducted for completeness, with the gas- and particle-phase somewhat parameterised, however results are thought not to be relevant outside the most extreme of conditions. Whilst endocyclic conjugation present in \(\alpha\)-phellandrene makes it highly reactive, and results in reactive first-generation and highly functionalised second-generation products, that collectively contribute to large SOA yields, for the most part, however, general experimental trends in gas- and particle-phase properties from \(\alpha\)-phellandrene oxidation are consistent with what has been reported for other monoterpenes.

Experimental results from this study and the literature were then integrated with the theoretical findings to construct a chemical mechanism describing the tropospheric degradation of \(\alpha\)-phellandrene, consistent with the Master Chemical Mechanism protocols. The complete mechanism contains 3601 reactions and 1187 closed-shell and radical species, of which 2150 reactions and 723 species were newly added. Gas-to-particle partitioning was explicitly represented for 458 multifunctional, closed-shell oxidation products. The mechanism was incorporated into a model of the GIG-CAS chamber system, and evaluated against the suite of photooxidation experiments. Unfortunately, poorly constrained experimental data, in particular gas-phase organic measurements from the PTR-TOF, and inconsistencies in SOA yields between the two different photooxidation campaigns, prevented confident assessment of the constructed mechanism and model. Indeed, the PTR-TOF additionally proved problematic in the experimental assessment, with a lack of available standards preventing accurate quantification of products. Furthermore, possible sampling losses, drift tube fragmentation, and a lack of kinetic data restricted the accuracy of secondary calibration methods. Sensitivity testing was therefore used to identify mechanistic features that resulted in non-negligible changes to the simulated oxidative capacity, when varied within set uncertainty limits. Notable parameters include: OH branching ratios of major first-generation products, first-generation nitrate yields, and first-generation ozonolysis rates and resultant radical production. Nonetheless, the constructed model was able to capture a number of observed gas-phase features. Aerosol formation was found to be systematically underpredicted, with some adsorption and evaporation rates having to be scaled by over an order of magnitude to generate loadings experimentally observed. This suggests some large misrepresentation of gas-to-particle partitioning in the current model, with more complex aerosol modelling necessary to identify the source of error (e.g. gas-phase mechanism, estimated properties, condensed phase reactions, aerosol dynamics and phase state). Along with model advancement, the current mechanism also requires a better constrained experimental dataset for more robust testing and evaluation. The mechanism thus provides a foundation on which future theoretical, experimental and modelling research can build.
5.2 Research Improvements and Future Avenues of Investigation

Given the difficulties encountered whilst conducting research comprising this thesis, a number of recommendations that would either improve, or extend, various aspects of the current investigation are now presented. However, before enacting any of the recommendations, more field studies are first required to better ascertain the abundance, and consequent importance of α-phellandrene in local environments. In particular, Eucalypt forests are thought to have potentially high α-phellandrene emissions, and so are recommended as potential sites for field studies targeting α-phellandrene. Eucalypt forests have received little attention compared to boreal and tropical forests, however initial research has shown intense and frequent aerosol nucleation events (Lee et al., 2008; Suni et al., 2008) and large monoterpene emissions (Emmerson et al., 2016), making Eucalypt forests of more general scientific interest.

Recommendations are now listed under the investigative technique to which they are pertinent.

Computational Study

1. **RRKM analysis.** The computed PES currently provides an overview of all ozonolysis reaction pathways, with barrier heights indicating relative favourabilities for the different channels. The natural extension of this is to conduct a statistical kinetic RRKM/master chemical equation analysis for the entire PES (e.g. Zhang and Zhang, 2005; Nguyen et al., 2009b). This will transform energy barriers into unimolecular rate coefficients, allowing more accurate branching ratios and thus product yields to be assigned.

2. **OH initiated PES.** Several non-traditional peroxyl radical chemistry pathways, arising from reaction of OH radicals with isoprene and α-pinene, have been identified through theoretical studies (Vereecken and Peeters, 2004; Vereecken et al., 2007; Da Silva et al., 2010; Nguyen et al., 2010; Peeters et al., 2009, 2014). Of these, 1,5-H atom shifts for β-hydroxy peroxy radicals has been incorporated into the α-phellandrene mechanism by analogy. Nonetheless, the impact of exotic unimolecular processes can only be determined by examining the full degradation mechanism of the pertaining compound, as process favourability often strongly depends on precursor structure. Given the importance of OH radicals in the troposphere, a complete computational investigation into the reaction of α-phellandrene with OH radicals should therefore be conducted. Scope should include assessing relative reactivity of addition sites at the two
double bonds, and favourability of proposed non-traditional pathways; including reversibility of O$_2$ addition, ring-closure of intermediate peroxyl- and oxy radicals, H-shifts in peroxyl- and oxy radical intermediates, effect of resonance stabilisation in nascent β-hydroxy radicals, and the likelihood of \(p\)-cymene formation from H-abstraction channels.

**Experimental Study**

With the highly complex nature of atmospheric chemistry and wide range of experimental techniques available to study reactions and processes, the following are suggestions on how future research can build on what has been accomplished in this project.

3. *Experimental conditions.* An immediate and intuitive extension of the current study is to conduct further smog chamber experiments under a wider variety of conditions. In this project, only two ozonolysis experiments were performed without an OH radical scavenger, one of which had NO$_2$ added, only two ozonolysis experiments had an SCI scavenger added, and only one photooxidation experiment was conducted at a temperature different to \(\sim 298\) K or with humidity that wasn’t dry. These are insufficient to draw conclusive findings. A more systematic approach should therefore be implemented to investigate the impact of different parameters on gas and aerosol properties in the oxidation of \(\alpha\)-phellandrene. Furthermore, the range of oxidation conditions could be extended in the different experiments by adjusting precursor concentrations (e.g. different VOC/NO$_x$ ratios), or by introducing inorganic seed particles. The system can be probed further by changing conditions during an experiment, for example by ramping up temperature to assess the competitive role of thermodynamics and kinetics in aerosol formation (Pathak et al., 2007b), actively diluting samples to investigate evaporation and reversibility of partitioning (Grieshop et al., 2007), changing lighting conditions to investigate diurnal effects and/or SOA ageing (Donahue et al., 2012a; Nah et al., 2016b), and introducing more oxidants at later time points to parameterise the influence of higher-generation products (Fry et al., 2011). However, the aforementioned experiments represent a significant time investment, with a highly instrumented, operational facility (all instruments calibrated and running optimally) limited to around 3 to 4 experiments per week. Given consistency of many macroscopic \(\alpha\)-phellandrene properties with other monoterpenes, particularly those relating to SOA (e.g. density, composition, responses to temperature, humidity, SCI scavenging and NO$_x$), analogous information can provisionally be inferred from other monoterpene experiments (e.g. Pathak et al., 2008; Jons-
CHAPTER 5. CONCLUSION AND FUTURE WORK

son et al., 2008; Shilling et al., 2009; Saathoff et al., 2009; Eddingsaas et al., 2012a; Kristensen et al., 2014; Draper et al., 2015; Sarrafzadeh et al., 2016; Stirnweis et al., 2017; Zhao et al., 2017).

4. **NO$_3$ and OH initiated reactions.** The present investigation studied the ozonolysis, NO$_2$-initiated reaction and photooxidation of α-phellandrene. However, the reaction of NO$_3$ with monoterpenes has received increased attention in the literature as a significant source of nocturnal SOA (e.g. Ng et al., 2017). In general, yields are higher than photooxidation and ozonolysis studies, however yields among monoterpenes have been variable, with anomalously low monoterpene SOA yields in some studies and high yields in others (Fry et al., 2009, 2011; Draper et al., 2015; Boyd et al., 2015; Nah et al., 2016b). Given the high aerosol yields for α-phellandrene with other oxidants, it is possible that the reaction of α-phellandrene with NO$_3$ is an important nocturnal source of organic aerosol, however experimental testing is required to support this. The reaction is also a major pathway for the production of organic nitrates, and may serve as a NO$_3$ reservoir or sink. The simplified reaction conditions, like in ozonolysis, also allow for a more comprehensive analysis which can be used to better parameterise the NO$_3$-initiated mechanism, and identity of nitrates formed during photooxidation experiments.

A similar simplification approach can be applied to the OH initiated reaction, by using photolysis of H$_2$O$_2$ as the oxidant source (e.g. Eddingsaas et al., 2012b,a). In doing so, an essentially zero-NO$_x$ experiment can be performed, making results directly attributable to OH addition and subsequent HO$_x$ driven chemistry. It would be useful in these OH initiated experiments, and more broadly in photooxidation studies, to interface the GIG-CAS chamber with an instrument to measure OH radical concentrations (along with other radicals like HO$_2$). For example, the HIRAC chamber at the University of Leeds measures OH radicals using laser induced fluorescence (LIF) through the Fluorescence Assay by Gas Expansion (FAGE) technique (Heard and Pilling, 2003). Given that results presented in this thesis suggest that SOA yields may be linked to the concentration of OH, these measurements will provide further insight into SOA formation pathways, along with additional experimental data to constrain models.

5. **SOA chemical composition.** The detailed filter sample and analysis methodology proved successful for identifying molecular composition of key constituents of ozonolysis SOA. It would therefore be beneficial to extend the method to SOA formed during photooxidation studies. This should identify important photooxidation products, and thus aerosol forming channels under different
oxidation conditions. The presence, and subsequent importance of oligomers can also be assessed. Not only will findings be of experimental interest, but they can also be used to better parameterise the mechanism. One drawback of filters is that sampling occurs over a long time period, with results therefore reflecting an average composition. Time-resolved aerosol measurements would therefore be useful, particularly in assessing which species are pertinent to new-particle formation and initial aerosol growth. One instrument that has shown greater time-resolution is a particle into liquid sampler (PILS), which collects particles into water for subsequent analysis (Hallquist et al., 2009; Pereira et al., 2014). Coupling to the GIG-CAS chamber should therefore be investigated.

6. α-phellandrene sample. Canister sampling methodology showed the bottle of α-phellandrene supplied by Aldrich contains minor contaminant monoterpenes, which to an unknown extent interfered with the m/z 137 PTR-TOF signal. To better constrain experiments, it is therefore necessary to determine sample purity. One way this can be achieved is by diluting a sample and running it though a HPLC-MS system. Once known, it would then be useful to make up α-phellandrene standards, to calibrate analytical instruments.

7. Experimental methods. A number of issues were noted with the current experimental set-up. Firstly, α-phellandrene induced a false positive bias in the photometric ozone analyser. An instrument operating on a different measurement technique, such as the Aeroqual portable gas monitors discussed in Chapter 3.2.1, should therefore concurrently be used, to provide more reliable ozone measurements and test the accuracy of employed data correction techniques. Alternatively, if sufficient separation between ozone and α-phellandrene absorption bands exists, then Fourier-transform infrared (FTIR) spectroscopy could be used to reliably monitor concentrations of both species (e.g. Winterhalter et al., 2009).

Secondly, modelling suggests that the NO₂ signal from the chemiluminescence NOₓ analyser may be experiencing interference from other nitrogen-containing species inside the reactor (e.g. NO₃, HNO₃, N₂O₅, organonitrates). Spectroscopic techniques such as LIF (Thornton et al., 2000), cavity ring-down spectroscopy (CRDS) (Osthoff et al., 2006), differential optical absorption spectroscopy (DOAS) (Platt and Perner, 1980; Stutz and Platt, 1996), and tunable diode laser absorption spectroscopy (TDLAS) (Li et al., 2004), that directly measure NO₂ without any chemical conversion, could be employed in tandem to provide more accurate NO₂ and thus overall NOₓ measurements. Intercomparison studies have shown these instruments to perform well with
one another and chemiluminescent analysers (Harder et al., 1997; Thornton et al., 2003; Fuchs et al., 2010), however set-up and operation does require more expertise. Alternatively, the use of post-processing techniques for data correction could be investigated (e.g. Ordóñez et al., 2006; Steinbacher et al., 2007).

Thirdly, and perhaps most critically, the facility is currently unable to reliably detect and quantify large organic products from α-phellandrene’s oxidation, particularly those products that are unsaturated. This is problematic, as product time profiles are critical to identifying mechanistic pathways and validating chemical mechanisms. The lack of available standards is noted, and a definite point for improvement, however currently these are not commercially available for major α-phellandrene degradation products. Beyond this, there appeared to be some large loss mechanism of functionalised products either during sampling, or PTR-TOF and GC/MS analysis. It would be difficult to shorten FEP tubing due to the partition dividing the reactor from the adjacent room containing the instruments, although sample lines could be heated to reduce losses (Ehn et al., 2014).

For online analysis, the PTR-TOF demonstrated considerable fragmentation, even at reduced drift tube energies for hydrocarbons. It is therefore thought that larger, functionalised products are fragmenting upon protonation, with known fragment ions having been detected (e.g. $m/z$ 43). Use of alternative, less-energetic chemical ionisation methods is therefore recommended. For example, chemical ionisation mass spectrometry (CIMS) using ions larger than hydronium, has successfully been used to detect, identify and quantify gaseous reaction products in chamber experiments. Utilised reagent ions include $\text{CF}_3\text{O}^-$ (CIT-CIMS; Paulot et al., 2009a; Eddingsaas et al., 2012b; Crounse et al., 2013), $\text{CH}_3\text{C(O)}\text{O}^-$ (NI-PT-CIMS; Veres et al., 2008; Lopez-Hilfiker et al., 2015), I$^-$ (TD-CIMS; Slusher et al., 2004; Boyd et al., 2015) and $\text{NO}_3^-$ (CI-API-TOF; Jokinen et al., 2012; Ehn et al., 2014), with the different techniques often selective towards different analyte classes (Nozière et al., 2015). Furthermore, coupling of a filter inlet for gases and aerosols (FIGAERO) to a CIMS instrument would enable online monitoring of both gaseous and particle phases (Lopez-Hilfiker et al., 2014). The last method, CI-API-TOF, has been used to identify ELVOCs in the gas-phase. It is important to note however that the described state-of-the-art CIMS instruments are all expensive, and require specific expertise for operation. Meanwhile, in the PTR-TOF, Duncianu et al. (2017) showed hydroxyl and ketonitrates to have a high affinity towards NO$^+$, suggesting that other ionisation modes in
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the PTR-TOF should be explored.

Potential issues with, and solutions to, improving the offline canister-based monitoring method were discussed in Chapter 3.4.3. Other methods that exist for capturing VOCs, include: Teflon or Tedlar (polyvinyl fluoride) bags (Jaoui et al., 2016), although these are known to experience heightened sample artefact and analyte losses; derivatisation (e.g. dinitrophenylhydrazine (DNPH)), although this method is specific to certain analyte classes; and absorbent resins such as Tenax (Matsunaga and Ziemann, 2010; Rindelaub et al., 2014), which again are specific and do not capture all compounds equally. Therefore, a suite of offline measurements would likely be needed in order to capture the broad spectrum of reaction products formed. Improvements in online detection methods are therefore favoured, despite structural information not being made available by these techniques.

The remaining experimental recommendations necessitate improved product identification for their successful implementation.

8. First-generation nitrate yields. Nitrate yields in the chemical mechanism are set analogous to other monoterpenes, with model performance showing sensitivity to the parameter. Given that variation is observed between different monoterpenes (Ruppert et al., 1999), and even between different studies on the same monoterpene (Nozière et al., 1999; Aschmann et al., 2002; Rindelaub et al., 2014), it would be useful to parameterise the yield of first-generation nitrates for α-phellandrene. The cited literature can be referred to for methods on how to do this.

9. Validate theoretical findings. The theoretical study provided useful insight into the ozonolysis mechanism, nonetheless it would be reassuring to experimentally validate its predictions. Complicating matters is that a number of predicted products are isomeric (e.g. first-generation SOZs, acids and esters), with mass spectrometry therefore unable to resolve which chemical pathways were undertaken. Indeed, this was the advantage of undertaking the computational study. Nevertheless, techniques such as FTIR can be used to identify SOZ bands (Winterhalter et al., 2009), and so confirm whether SOZ formation is favourable under atmospheric conditions. NI-PT-CIMS is sensitive towards organic acids, and so the $\text{CH}_3\text{C(O)O}^-$ ion could be used to quantify acid-forming channels. More generally, first-generation products, formed through the newly proposed 1,6-hydrogen shift channel, result in a higher proportion of fragmented products, with identification of a number of these using more sensitive instruments able to help justify the pathways existence. Alternatively, specific hydrogens could be replaced with deuterium to ascertain
relative branching ratios. Modelling of these different experiments can then constrain branching ratios and kinetics used in the chemical mechanism, with remaining isomeric products summed in simulations (Jenkin et al., 2012).

10. **GIG-CAS gas-wall partitioning.** The potential impact of gas-wall partitioning of semi-volatile organic vapours was discussed a number of times throughout this thesis (e.g. Chapter 3.5.1), with the effect remaining unparameterised in the GIG-CAS chamber. Considering the large potential impact it could have on the conducted and future experiments, a study into quantifying its effect and determining parameters relevant for analysing chamber experiments and modelling (e.g. time scales, chamber wall equivalent mass concentration) should be conducted. A method for doing this was recently published by Krechmer et al. (2016).

**Mechanism and Modelling Study**

11. **Mechanism improvements.** Being newly constructed, following theoretical and experimental phases of this research, the scope for mechanistic adjustments to the α-phellandrene reaction scheme is limited. Nonetheless, the impact of the following changes would be of interest, and should be subject to gas- and particle-phase sensitivity testing: (a) acyl peroxy radical rearrangements, which are currently exclusively represented to decompose (Saunders et al., 2003); (b) re-arrangement reactions of peroxy radicals, especially those formed from initial OH attack (Vereecken and Peeters, 2004); (c) epoxydiol formation from unsaturated hydroperoxides (Paulot et al., 2009b; Jenkin et al., 2015); and (d) reattainment of non-carbonyl functional groups (e.g. acids, nitrates, PANs) through successive generations.

12. **SOA model improvements.** As discussed in Chapter 4.3.2, poor model performance with respect to SOA modelling may be due to an unrepresentative gas-phase mechanism, or deficiencies in model parameterisation – with construction of more complex models recommended. Proposed parameter inclusions will not be repeated, although it is suggested that the model constructs of Zuend and Seinfeld (2012), Roldin et al. (2014) and Beardsley and Jang (2016) be referred to.

13. **ROPA analysis.** In order to gain a deeper understanding of dominant sources and sinks for any given species or intermediate with time, the model can be coupled with a rate of production analysis (ROPA, http://mcm.leeds.ac.uk/MCMv3.3.1/tools.html). ROPA de-convolutes pathways, branching ratios and yields to give contributing factors of primary species to the formation of target
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products in the model. Implementation would thus allow for determination of critical points (reactants and/or pathways) in the model that can be subject to optimisation to improve modelled yields.

14. *Mechanism simplifications.* Modelling showed simplification measures not to have a significant impact on performance. This property should be evaluated further. Additionally, a Common Representative Intermediate (CRI) mechanism (Jenkin et al., 2008; Watson et al., 2008) detailing α-phellandrene’s degradation was developed during this project (not presented in this thesis). The constructed mechanism outlines α-phellandrene’s reaction with OH radicals, O₃ and NO₃ radicals through 99 new reactions and 30 new species, however, to date, has not been thoroughly evaluated with respect to the explicit mechanism or experiment, or integrated with an aerosol forming module (Utembe et al., 2009). Due to its reduced size, the CRI parameterisation has been implemented into larger atmospheric modelling systems, including providing a representation of chemistry for the Weather, Research and Forecasting model (WRF; Archer-Nicholls et al., 2014). Evaluation and refinement of the constructed α-phellandrene CRI mechanism is therefore recommended.

15. *Pollutant creation potentials.* In general, high ozone formation was observed during photooxidation chamber experiments, with the model able to somewhat capture this. To better parameterise the ozone forming ability of α-phellandrene with respect to other VOCs (in particular ethylene), its photochemical ozone creation potential (POCP) should be determined in a photochemical trajectory model (e.g. Derwent et al., 1998; Cheng et al., 2010; Lam et al., 2015). α-Phellandrene’s relative SOA formation potential can also be estimated in a similar manner (Derwent et al., 2010), although this has somewhat been achieved experimentally by comparing SOA yield curves.

Despite experimental issues and time constraints preventing a more robust mechanism evaluation, the overall project remains highly successful in providing the first comprehensive description of α-phellandrene’s degradation. The computational study provided the first insight into the chemical mechanism of α-phellandrene, with two newly proposed CI pathways likely to be important in other conjugated systems. Experiments provided the first comprehensive dataset detailing α-phellandrene’s degradation, with aerosol yields and properties adding to the growing body of knowledge on atmospheric aerosols. In particular, identification of SCI as important aerosol precursors is supportive of recent literature championing this channel as an important nucleation source. Finally, mechanism development was a useful endeavour in consolidating all known literature data on α-phellandrene’s degradation,
and provides the first complex parameterisation of α-phellandrene’s tropospheric decomposition, with exploration indicating points of interest. Through collective implementation of a number of the recommended improvements, it will be possible to more confidently assess the performance of α-phellandrene’s chemical mechanism, and further optimise it. This will enable support for eventual inclusion in the MCM, where it will be made freely available to the scientific community, and thus for use in ambient models to better understand the role α-phellandrene, and reactive BVOCs, play in influencing tropospheric chemistry.
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Appendices
Appendix A

Guangzhou Air Pollution

Figure A.1: Set of photos highlighting poor air quality experienced in Guangzhou.
Appendix B

PTR-TOF Equation Derivation

Derivation of equation used for calculating volume mixing ratios of ions detected in the PTR-TOF. Derivation is adapted from House (2008).

A large number of trace gas components \((R_i)\) undergo reaction with \(H_3O^+\) ions in the PTR-TOF drift tube:

\[
R_i + H_3O^+ \xrightarrow{k_i} R_iH^+ + H_2O \tag{B.1}
\]

The rate equation for the reaction of \(H_3O^+\) with \(i\) trace gas species is:

\[
- \frac{d[H_3O^+]}{dt} = [H_3O^+] \sum_i k_i [R_i] \tag{B.2}
\]

By rearranging and integrating Equation B.2 between times \(t = 0\) and \(t = t\), an expression for \([H_3O^+]\) can be developed. \(\sum_i [R_i]\) is treated as a constant since only a small fraction of the total trace gas concentration reacts (due to a much larger concentration when compared to \(H_3O^+\)).

\[
\int_0^t \frac{1}{[H_3O^+]} d[H_3O^+] = - \sum_i k_i [R_i] \int_0^t dt \tag{B.3}
\]

\[
ln[H_3O^+]_t = - \sum_i k_i [R_i] t + ln[H_3O^+]_0 \tag{B.4}
\]

\[
[H_3O^+]_t = [H_3O^+]_0 e^{-\sum_i k_i [R_i]} \tag{B.5}
\]

where \([H_3O^+]_0\) and \([H_3O^+]_t\) represent the concentration of \(H_3O^+\) at time \(t = 0\) and \(t = t\) respectively. The desired result is the concentration of a single trace gas species \((R_a)\). The rate equation for the reaction of a single species is:

\[
\frac{d[R_a H^+]}{dt} = k_a [R_a][H_3O^+] \tag{B.6}
\]

Substitution of Equation B.5 into B.6 gives:

\[
\frac{d[R_a H^+]}{dt} = k_a [R_a][H_3O^+]_0 e^{-\sum_i k_i [R_i]} \tag{B.7}
\]
Rearranging and integration of Equation B.7 produces:

\[
[R_aH^+]_t = \frac{k_a[R_a]}{\sum_i k_i[R_i]}[H_3O^+]_0(1 - e^{-t\sum_i k_i[R_i]}) \tag{B.8}
\]

Rearranging B.4 yields:

\[
\sum_i k_i[R_i] = -\frac{1}{t}\ln\left(\frac{[H_3O^+]_t}{[H_3O^+]_0}\right) \tag{B.9}
\]

Substituting Equation B.9 into B.8 gives:

\[
[R_aH^+]_t = -\frac{k_a[R_a]}{ln\left(\frac{[H_3O^+]_t}{[H_3O^+]_0}\right)}\frac{[H_3O^+]_0(1 - e^{-t\sum_i k_i[R_i]})}{[H_3O^+]_0} \tag{B.10}
\]

Total product formation at a time ‘t’ is given by:

\[
\sum_i [R_iH^+] = [H_3O^+]_0 - [H_3O^+]_t \tag{B.11}
\]

Substitution of Equation B.5 into B.11 and simplifying yields:

\[
\sum_i [R_iH^+] = [H_3O^+]_0(1 - e^{-t\sum_i k_i[R_i]}) \tag{B.12}
\]

Substituting this result into Equation B.10 and making \([R_a]\) the subject:

\[
[R_a] = \frac{1}{k_a t \sum_i [R_iH^+]}[R_aH^+]_t \ln\left(\frac{[H_3O^+]_0}{[H_3O^+]_t}\right) \tag{B.13}
\]

Substituting for \([H_3O^+]_0\) using Equation B.11:

\[
[R_a] = \frac{1}{k_a t \sum_i [R_iH^+]}[R_aH^+]_t \ln\left(1 + \frac{\sum_i [R_iH^+]_t}{[H_3O^+]_t}\right) \tag{B.14}
\]

Since \([H_3O^+] \gg \sum_i[R_iH^+]\), the logarithmic term can be expanded into its Maclaurin Series (B.15), with the non-linear terms becoming negligible.

\[
\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \ldots \text{ for } x \leq |1| \tag{B.15}
\]

Leading to.

\[
[R_a] = \frac{1}{k_a t [H_3O^+]_t} \tag{B.16}
\]
This formula calculates concentration, with volume mixing ratio calculated from:

$$[R_a] = \frac{1}{k_a t} \frac{[R_a H^+]_t}{[H_3O^+]_t} 10^9 \frac{N}{N}$$  \hspace{1cm} (B.17)$$

where $N$ is the number density of particles in the drift tube. A multiplicative factor of $10^9$ converts the result into units of ppb. The number density can be expressed using the ideal gas law as:

$$N = \frac{\text{(molecules/V)}_d}{N_A} = \frac{N_A P_d}{R \ T_d}$$  \hspace{1cm} (B.18)$$

where $N_A$ is Avogadro’s number, $R$ is the ideal gas constant and $P_d$, $V_d$ and $T_d$ are the pressure, volume and temperature inside the drift tube respectively. Substituting in the formula for number density into Equation B.17 gives:

$$[R_a] = \frac{10^9 \ [R_a H^+]_t}{k_a t} \frac{R \ T_d}{[H_3O^+]_t \ N_A P_d}$$  \hspace{1cm} (B.19)$$

Reaction time is based on the residence time of H$_3$O$^+$ ions in the drift tube, since these have much shorter residence times compared to trace species. Reaction times can then be calculated from:

$$t = \frac{L_d}{v_d}$$  \hspace{1cm} (B.20)$$

where $L_d$ is the length of the drift tube and $v_d$ is the drift velocity. The drift tube velocity of an ion in an electric field is given by:

$$v_d = \mu E$$  \hspace{1cm} (B.21)$$

where $\mu$ is the ion mobility and $E$ the electric field strength. Ion mobilities are commonly reported as reduced mobilities ($\mu_0$), which are ion mobilities corrected for standard gas density.

$$\mu_0 = \mu \frac{N_0}{N} = \mu \frac{T_0}{T_d} \frac{P_d}{P_0}$$  \hspace{1cm} (B.22)$$

where $N_0$, $T_0$ and $P_0$ are the number density, temperature and pressure at STP. Combining Equations B.20 – B.22 yields the following expression for reaction time:

$$t = \frac{L_d \ T_0 \ P_d}{\mu_0 E \ T_d \ P_0}$$  \hspace{1cm} (B.23)$$

In a ‘uniform’ field such as that found in the drift tube, the magnitude of $E$ is related to the potential difference applied.

$$E = \frac{U_d + U_{dx}}{L_d}$$  \hspace{1cm} (B.24)$$
APPENDIX B. PTR-TOF EQUATION DERIVATION

Where $U_d$ is the drift tube voltage and $U_{dx}$ is the extraction voltage at the end of the drift tube. Substituting both B.23 and B.24 into Equation B.19 yields:

$$[R_a] = \frac{10^9 \mu_0 (U_d + U_{dx}) [R_a H^+]_t \frac{R}{(H_3O^+)_t} \frac{T_d^2}{N_A T_0} P_0}{k_a L_d^2} \ (B.25)$$

In the real world concentrations at the drift tube exit are affected by instrument inefficiencies. Transmission coefficients ($T$) are therefore used to relate detected ion counts to theoretical drift tube exit concentrations.

$$([H_3O^+]_d = [H_3O^+] T_{H_3O^+}) \ (B.26)$$

$$([R_a H^+]_d = [R_a H^+] T_{R_a H^+}) \ (B.27)$$

where () denotes detected ion count rates and [ ]$_d$ the theoretical concentrations at the drift tube exit. Thus Equation B.25 becomes:

$$[R_a] = \frac{10^9 \mu_0 (U_d + U_{dx}) (R_a H^+)_t \frac{R}{(H_3O^+)_t} \frac{T_d^2}{N_A T_0} P_0 T_{H_3O^+}}{k_a L_d^2} \ (B.28)$$
Appendix C

2012 Propene–NO\textsubscript{x} Chamber Characterisation Experiment

A number of chamber calibration experiments were conducted post GIG-CAS chamber construction in 2012 (Wang et al., 2014). This included a propene–NO\textsubscript{x} experiment, of which the raw experimental data provided for modelling. The experimental method was conducted following the methods discussed in Chapter 3 with the same instruments used. Propene was monitored exclusively through the canister sampling technique however, using GC-FID for detection. Formaldehyde and acetaldehyde were measured directly by sampling air through a Sep-Pak DNPH-Silica cartridge (Waters Corporation, USA) and passing the sample through HPLC (HP1200; Agilent Technologies, USA) with a 360 nm UV detector (Tang et al., 2003). The detection of carbonyls using this method was not available during later visits to the GIG-CAS chamber. Starting conditions for the 2012 propene characterisation experiment are provided in Table C.1.

The experiment was modelled using the auxiliary mechanism proposed in Chapter 3.4. A starting HONO concentration of 5 ppb was required to optimise model performance, with results shown in Figure C.1. Overall good agreement was achieved, with O\textsubscript{3}, NO, propene and HCHO accurately represented. The peak NO\textsubscript{2} concentration is overpredicted, with consumption after the peak occurring more rapidly than experimental measurements. The shorter experimental length should be noted, with the model predicting NO\textsubscript{2} to be almost completely consumed over 300 minutes, similar to results from the 2016 characterisation experiment. A large NO\textsubscript{2} sink therefore remains overrepresented in the propene mechanism. Nonetheless modelled D(O\textsubscript{3}–NO) is within 4% of the experimental value at the end of the experiment, comfortably within the limits of accuracy of chamber simulations (Stockwell et al.,

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>RH (%)</th>
<th>NMHCs (ppb)</th>
<th>C\textsubscript{3}H\textsubscript{6} (ppm)</th>
<th>NO (ppb)</th>
<th>NO\textsubscript{2} (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>propene–NO\textsubscript{x}</td>
<td>298.3</td>
<td>6.2</td>
<td>17.0</td>
<td>878</td>
<td>215</td>
</tr>
</tbody>
</table>

Table C.1: Starting conditions for the 2012 propene–NO\textsubscript{x} characterisation experiment.
APPENDIX C. 2012 PROPENE–NO\textsubscript{X} CHAMBER CHARACTERISATION EXPERIMENT

Figure C.1: Time profiles from the 2012 propene–NO\textsubscript{X} characterisation experiment. Black lines and closed black diamonds show experimental measurements, with open circles model simulations.

(a) O\textsubscript{3}, NO and NO\textsubscript{2}  
(b) C\textsubscript{3}H\textsubscript{6} and HCHO  
(c) D(O\textsubscript{3}–NO)

1990; Carter et al., 2005). The considered auxiliary mechanism therefore provides a suitable representation of chamber dependent processes, and so is used in evaluating the proposed \(\alpha\)-phellandrene degradation mechanism against 2013 photooxidation data.
Appendix D

Background Chamber Contaminants

<table>
<thead>
<tr>
<th></th>
<th>2013</th>
<th>2015</th>
<th>2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>2272</td>
<td>2829</td>
<td>2220</td>
</tr>
<tr>
<td>Ethene</td>
<td>924</td>
<td>936</td>
<td>1147</td>
</tr>
<tr>
<td>Ethyne</td>
<td>1166</td>
<td>817</td>
<td>1249</td>
</tr>
<tr>
<td>Propane</td>
<td>7839</td>
<td>5205</td>
<td>6429</td>
</tr>
<tr>
<td>Propene</td>
<td>391</td>
<td>716</td>
<td>544</td>
</tr>
<tr>
<td>Isobutane</td>
<td>2034</td>
<td>1732</td>
<td></td>
</tr>
<tr>
<td>1-butene</td>
<td>124</td>
<td>343</td>
<td>2236</td>
</tr>
<tr>
<td>n-butane</td>
<td>2464</td>
<td>2912</td>
<td>111</td>
</tr>
<tr>
<td>Isopentane</td>
<td>532</td>
<td>952</td>
<td>3863</td>
</tr>
<tr>
<td>n-pentane</td>
<td>318</td>
<td></td>
<td>3124</td>
</tr>
<tr>
<td>Isoprene</td>
<td>261</td>
<td></td>
<td>2352</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>116</td>
<td></td>
<td>197</td>
</tr>
<tr>
<td>n-hexane</td>
<td>3088</td>
<td>139</td>
<td>2540</td>
</tr>
<tr>
<td>n-heptane</td>
<td></td>
<td>563</td>
<td></td>
</tr>
<tr>
<td>m/p-xylene</td>
<td>297</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.2</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>CO</td>
<td>0.36</td>
<td>0.50</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table D.1: Average concentrations for the main background constituents in the reactor matrix for 2013, 2015 and 2016. NMHC concentrations are given in ppt, CO and CH$_4$ concentrations are given in ppm.
Appendix E

High-Resolution Aerosol Mass Spectra for α-Phellandrene Ozonolysis SOA

Figure E.1: High-resolution mass spectra of α-phellandrene ozonolysis SOA taken at peak SOA loading in experiment 5. (a) shows elemental composition and (b) family groups. Similar high-resolution mass spectra were observed in remaining ozonolysis experiments.
Appendix F

Gas-Phase Yields from Monoterpene Photooxidation Experiments

For comparison, products yields from a range of different monoterpenes are presented with reference to α-phellandrene. Data are taken from the study of Lee et al. (2006b). Both the experimental design and analysis procedures of Lee et al. (2006b) are similar to what was conducted in this thesis, with the reported yields thought to provide a suitable comparison. Product yields from other studies for the monoterpenes listed here can be found in Lee et al. (2006b) (and references therein), however, most of these have differing radical precursors and/or reaction conditions. Nonetheless, these comparisons are included simply to present the range of yields observed elsewhere for other monoterpenes, and have no impact on the results or discussion of the present study.

<table>
<thead>
<tr>
<th>Monoterpene</th>
<th>VOC/NO$_x$</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Formic acid</th>
<th>Acetone</th>
<th>Acetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>limonene</td>
<td>1.1</td>
<td>43 ± 5</td>
<td>0.7 ± 0.1</td>
<td>5.0 ± 0.6</td>
<td>0.4 ± 0.1</td>
<td>3.2 ± 0.4</td>
</tr>
<tr>
<td>myrcene</td>
<td>0.9</td>
<td>74 ± 8</td>
<td>0.7 ± 0.1</td>
<td>4.5 ± 0.5</td>
<td>22 ± 2</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>3-carene</td>
<td>0.8</td>
<td>35 ± 4</td>
<td>1.6 ± 0.2</td>
<td>5.4 ± 0.6</td>
<td>9.3 ± 0.9</td>
<td>5.1 ± 0.6</td>
</tr>
<tr>
<td>α-pinene</td>
<td>1.1</td>
<td>16 ± 2</td>
<td>1.4 ± 0.2</td>
<td>4.5 ± 0.5</td>
<td>6.3 ± 0.6</td>
<td>3.4 ± 0.4</td>
</tr>
<tr>
<td>terpinolene</td>
<td>1.1</td>
<td>23 ± 3</td>
<td>0.7 ± 0.1</td>
<td>3.5 ± 0.7</td>
<td>20 ± 2</td>
<td>1 ± 0.2</td>
</tr>
<tr>
<td>β-pinene</td>
<td>2.1</td>
<td>49 ± 6</td>
<td>0.6 ± 0.1</td>
<td>8.2 ± 0.7</td>
<td>7.9 ± 0.7</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>γ-terpinene</td>
<td>1.1</td>
<td>17 ± 2</td>
<td>1.2 ± 0.2</td>
<td>8.2 ± 0.8</td>
<td>5.3 ± 0.5</td>
<td>4.5 ± 0.5</td>
</tr>
<tr>
<td>α-terpinene</td>
<td>1.0</td>
<td>7.8 ± 2</td>
<td>0.7 ± 0.1</td>
<td>6.1 ± 1</td>
<td>3.1 ± 0.4</td>
<td>2 ± 0.3</td>
</tr>
<tr>
<td>α-phellandrene$^a$</td>
<td>0.16 – 4.6</td>
<td>1.2 – 14</td>
<td>1.7 – 9.3</td>
<td>4.0 – 7.8</td>
<td>9.5 – 18</td>
<td>2.8 – 6.9</td>
</tr>
</tbody>
</table>

$^a$This study.

Table F.1: Comparison of major monoterpene gas-phase photooxidation product yields (%). Data taken from Lee et al. (2006b).
### Table F.2: Comparison of minor monoterpene gas-phase photooxidation product and fragment ion yields (%). Data taken from Lee et al. (2006b).  

<table>
<thead>
<tr>
<th>Monoterpene</th>
<th>VOC/NO₂</th>
<th>m/z 111</th>
<th>m/z 113</th>
<th>m/z 123</th>
<th>m/z 141</th>
<th>m/z 155</th>
</tr>
</thead>
<tbody>
<tr>
<td>limonene</td>
<td>1.1</td>
<td>1 ± 0.2</td>
<td>1 ± 0.2</td>
<td>21 ± 4</td>
<td>1.3 ± 0.3</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>myrcene</td>
<td>0.9</td>
<td>9.3 ± 2</td>
<td>32 ± 7</td>
<td>5.5 ± 1</td>
<td>0.6 ± 0.2</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>3-carene</td>
<td>0.8</td>
<td>1.7 ± 0.4</td>
<td>2 ± 0.4</td>
<td>26 ± 6</td>
<td>4.5 ± 1</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>α-pinene</td>
<td>1.1</td>
<td>1 ± 0.2</td>
<td>0.9 ± 0.2</td>
<td>3.6 ± 0.7</td>
<td>1 ± 0.2</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>terpinolene</td>
<td>1.1</td>
<td>29 ± 6</td>
<td>2.8 ± 0.6</td>
<td>1.7 ± 0.4</td>
<td>1.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td>2.1</td>
<td>0.7 ± 0.2</td>
<td>0.4 ± 0.1</td>
<td>1.1 ± 0.2</td>
<td></td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>γ-terpinene</td>
<td>1.1</td>
<td>0.4 ± 0.1</td>
<td>1 ± 0.2</td>
<td>17 ± 4</td>
<td>2.2 ± 0.5</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>α-terpinene</td>
<td>1.0</td>
<td>0.6 ± 0.1</td>
<td>0.6 ± 0.2</td>
<td>7.2 ± 2</td>
<td>0.9 ± 0.4</td>
<td>3.4 ± 1</td>
</tr>
<tr>
<td>α-phellandrene*</td>
<td>0.16 – 4.6</td>
<td>0.16 – 1.0</td>
<td>0.03 – 0.97</td>
<td>0.14 – 0.60</td>
<td>0.04 – 0.52</td>
<td>0.01 – 0.09</td>
</tr>
</tbody>
</table>

*This study.
Appendix G

α-phellandrene Mechanism Extensions

G.1 NO$_2$ Initiation

NO$_2$ addition to α-phellandrene was represented with a rate coefficient of $1.3 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, based on the study of Atkinson et al. (1984). As discussed in Section 3.7.1, the reaction proceeds via addition to either of the double bond. To simplify the mechanism, only the channel which is thought to be most favourable is represented—that being addition to carbon 3 in Figure 3.35. Furthermore, only the direct nitroalkyl peroxy radical is considered (APHELLNO2), with resonant structures ignored.

The main features of the NO$_2$-initiated degradation chemistry are summarised in Figure G.1. Reaction of APHELLNO2 with NO is considered entirely propagating, consistent with the simplification assumed in the MCM for nitrate initiated chemistry. Meanwhile, closed-shell products are treated as minor products, considering reaction with OH to form pre-existing products as the only pathway. Ultimately the simplification measures result in the mechanism converging onto the first-generation product APHAAL, which is formed through previous OH, O$_3$ and NO$_3$ initiated pathways. In total 20 new reactions and 8 new radical and closed-shell species are included to incorporate the NO$_2$ initiation channel, with the mechanism available in Appendix I.

G.2 O($^3$P) Initiation

The reaction of O($^3$P) atoms with α-phellandrene has never been studied, with the proposed mechanism based on analogy. The reaction is represented with a rate coefficient of $8.57 \times 10^{-11}$ molecules cm$^{-3}$ s$^{-1}$, based on the study of γ-terpinene by Luo et al. (1996). The mechanism of O($^3$P) alkene attack proceeds predominantly through addition to the olefin bond, forming an excited triplet biradical adduct which can decompose, isomerise, or be collisionally stabilised to form an oxirane (Cvetanović, 1987; Calvert et al., 2000). Oxirane yield has been reported to increase with molecular size, with Alvarado et al. (1998) finding α-pinene oxide to be formed in a yield of 77% from reaction of O($^3$P) with α-pinene. Based on this, and to keep the mechanism simple, the epoxide APHELLOX was exclusively represented.
as the product from the α-phellandrene + O(^3P) reaction. Based on the findings of Paulson et al. (1992b) for isoprene, attack at the more substituted double bond is thought to be the favoured route and so is represented in the mechanism.

Reaction of APHELLOX occurs through conventional MCM chemistry described in Chapter 4.1, with the chemistry summarised in Figure G.2. Given the O(^3P) initiation channel is only expected to be minor, APHELLOX is treated as a minor product, that is, only its reaction with OH radicals is considered. Further simplifications are taken with closed-shell products, so that they re-form pre-existing species in the mechanism. Ultimately the products APHDAL, C101256O and C102OH1CO3 are formed through the various channels, with these species all existing in the initial α-phellandrene mechanism. In total 32 new reactions and 14 new radical and closed-shell products are added to incorporate O(^3P) initiation. The complete set of reactions can be viewed in Appendix I.
Figure G.1: Schematic detailing reaction of NO\(_2\) with \(\alpha\)-phellandrene as represented in the chemical mechanism. Species in dashed boxes are new stable products formed, whilst that in the solid box previously exists in the constructed chemical mechanism.

Figure G.2: Schematic detailing reaction of O\((3P)\) with \(\alpha\)-phellandrene as represented in the chemical mechanism. Species in dashed boxes are new stable products formed, whilst those in solid boxes previously exist in the constructed chemical mechanism.
Appendix H

Supplementary Model Output
H.1 Effect of $\alpha$-phellandrene on Model Output

Figure H.1: Comparison of experimental (black) and mechanism $M_0$ modelled (green) D(O$_3$ – NO) concentrations, with $\alpha$-phellandrene concentrations set to reported PTR-TOF values (solid line) and their respective upper (dotted line) and lower (dashed line) limits. Varying the initial $\alpha$-phellandrene concentration within its reported experimental uncertainty is shown to have a significant impact on model output.
H.2 Gas-phase Organic Products

Figure H.2: Comparison of experimental (shaded) and mechanism M7 simulated (lines) time dependencies of formaldehyde (orange), acetone (green), APHAAL2 (m/z 129, red) and combined C613AL and C613CO (m/z 115, cyan), for the ten photooxidation experiments. The combined signal of APHAAL and APHCAL (blue) is also included to show the magnitude and nature of simulated time profiles of major first-generation products. Grey shading in experiments 22, 23 and 24 denotes time periods where chamber lighting was switched off.
Appendix I

Supplementary Files

This thesis is accompanied by two supplementary files that are too large to be included with the printed version. These are:

1. An excel file titled, ‘Mackenzie-Rae_Felix_2017_Appendix_I1.xlsx’. This file contains: the complete degradation mechanism of α-phellandrene, with accompanying descriptions for each reaction included; structures of all newly proposed species, with SMILES and IUPAC International Chemical Identifier (InChI) strings provided; relevant parameters for SOA coding, and subsequent calculations for \( K_{pi,j} \), \( k_{un,i} \) and \( k_{off,i} \) for SOA contributing species; and lists of species comprising the various products pools.

2. A FAC file titled, ‘Mackenzie-Rae_Felix_2017_Appendix_I2.fac’. This file contains the complete α-phellandrene photooxidation chamber model for experiment 15, as an example. Headings are provided throughout, detailing the various components of the input file.