Heterogeneous reactions involving HO$_2$ radicals and atmospheric aerosols

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The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

The thesis chapter on uptake to TiO$_2$ nanoparticles (Chapter 4) includes work published as follows:


I performed all the experiments and necessary analysis and interpretation of data to measure the uptake of HO$_2$ onto these particles, and wrote the drafts of the paper, and Anduix assisted with Scanning Electron Microscope (SEM) analysis of the particles. Heard, Seakins, Ingham and Baeza-Romero provided technical assistance, Chipperfield and Taverna performed the chemistry transport modelling to look at the impact of the uptake on these particles in the stratosphere, and all these authors contributed to writing of the paper.

The thesis chapter on uptake to meteoric smoke particles (MSP, Chapter 5) includes work published as follows:


I performed all the experiments and necessary analysis of data to measure the uptake coefficients onto meteoric smoke analogues using the aerosol flow-tube and contributed to the writing of the paper. Sandy James prepared the samples and performed other analyses on them, and drafted the paper, and the other authors provided technical assistance in the laboratory, modelled the impact of the uptake of HO$_2$ onto these particles in the upper atmosphere, or helped with the writing of the paper.

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The Arizonian Tigger Particle – “the most wonderful thing about tiggers is I'm the only one”

An SEM imagine of agglomerated particles of Arizona Test Dust magnified 120,000 ×
This work is dedicated to my Father, Paul Andrew Moon and is in memory of my late Grandmother, Brenda Campbell Moon.
Abstract
The hydroxyl radical (OH), along with the closely coupled species the hydroperoxyl radical (HO$_2$), have a profound effect on the concentration and distribution of most trace atmospheric species associated with climate change and poor air quality as they are essential to the daytime oxidizing capacity of the atmosphere. Tropospheric and mesospheric models that only consider gas-phase chemistry often over predict concentrations of HO$_2$ indicating that heterogeneous reactions with aerosols could be a possible sink. In order to investigate the kinetics of such reactions, the HO$_2$ uptake coefficient ($\gamma$(HO$_2$), i.e. the probability that HO$_2$ will collide and react within or on the surface of an aerosol) has been measured onto a variety of aerosols applicable to the troposphere, stratosphere and mesosphere using an aerosol flow tube experiment coupled to a highly sensitive HO$_2$ detector, known as Fluorescence Assay by Gas Expansion (FAGE), and a Scanning Mobility Particle Sizer (SMPS).

Deliquesced inorganic aerosols containing transition metal ions (TMI) have been shown to react rapidly with HO$_2$. Measurements of $\gamma$(HO$_2$) onto deliquesced inorganic aerosols doped with different concentrations of Cu(II), Fe(II), Mn(II), mixtures of Cu(II) and Fe(II) and I$^-$ are presented within this work. HO$_2$ uptake onto deliquesced inorganic aerosols doped with transition metal ions may not be as significant as previously thought. The Thornton expression, used in global modelling studies of HO$_2$ uptake, can predict $\gamma$(HO$_2$) at a relative humidity (RH) of 65%, however at a RH of 43%, near the efflorescence point ((NH$_4$)$_2$SO$_4$ = 37%), good agreement was only observed at higher concentrations of Cu(II) and Fe(II) (> 0.1 M) possibly indicating that HO$_2$ solubility decreases as HO$_2$ diffuses further into the bulk of the aerosol. It was expected that as deliquesced NaCl aerosols have a higher pH (7) that most HO$_2$ accommodated within the aerosols will dissociated to the more reactive species O$_2^-$. This should result in high values of $\gamma$(HO$_2$), however $\gamma$(HO$_2$) onto Cu(II)-doped NaCl aerosols was measured to be lower than $\gamma$(HO$_2$) onto Cu(II)-doped (NH$_4$)$_2$SO$_4$ aerosols with a lower pH, possibly due to the formation of [Cu(Cl)$_4$]$_2^-$ complexes which are repelled into the bulk of the aerosol by enhanced concentrations of Cl$^-$ ions within the interfacial layer. Measurements of $\gamma$(HO$_2$) onto Fe(II)-doped NaCl aerosols were relatively high and agreed with predictions made by the Thornton expression. When irradiated with UVA light, $\gamma$(HO$_2$) onto Cu(II)-doped (NH$_4$)$_2$SO$_4$ was lowered, however $\gamma$(HO$_2$) onto Cu(II)-doped NaCl remained the same. When the effect of irradiating Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols on $\gamma$(HO$_2$) was investigated, results indicated possible production of OH. Measurements of $\gamma$(HO$_2$) onto mixed Cu(II) and Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols could not verify the Mao hypothesis that an electron transfer reaction occurs between Cu(I) and Fe(III) resulting in the conversion of HO$_2$ to H$_2$O, rather than H$_2$O$_2$. However, values of $\gamma$(HO$_2$) did not simply equal the sum of $\gamma$(HO$_2$) onto Cu or Fe-doped aerosols individually, indicating that the presence of both TMI in the aerosol does alter
the chemistry of the aerosol in some way. Irradiation of Cu(II) and Fe(II)-doped aerosols resulted in an enhancement of $\gamma$(HO$_2$), possibly indicating an alternative mechanism than that proposed by Mao, where HO$_2$ is converted to H$_2$O via a photochemical mechanism. The presence of I$^-$ within NaCl aerosols does not result in a change of $\gamma$(HO$_2$), however when converted to I$_2$ by reaction with Cu(II) an enhancement of $\gamma$(HO$_2$) greater than when doped with Cu(II) alone was observed.

Measurements of $\gamma$(HO$_2$) onto TiO$_2$, a possible candidate aerosol for use within solar-radiation management (SRM) schemes, showed a positive dependence on Relative Humidity (RH) which correlated with the number of monolayers of water adsorbed onto the TiO$_2$ nanoparticle. This dependence suggests a mechanism by which HO$_2$ adsorbs to the surface of the TiO$_2$ particle by forming complexes with water molecules bound to bridging OH groups. The TOMCAT chemical transport model was used by Professor Chipperfield to predict the possible effects of HO$_2$ uptake (using an upper limit of $\gamma$(HO$_2$) = 1) onto the surface of TiO$_2$ nanoparticles on the stratospheric concentrations of HO$_2$ and O$_3$. The amount of TiO$_2$ used was chosen to achieve a similar cooling to that following the Mt. Pinatubo eruption, but the model predicted a very small loss of both stratospheric HO$_2$ and O$_3$. Upon illumination of airborne TiO$_2$ nanoparticles with UV light, significant quantities of HO$_2$ was formed within the gas-phase, thought to be the first direct observations of radicals emitted from the surface of airborne particles. The reaction is dependent on the presence of gas-phase O$_2$ and H$_2$O within the system. The production of HO$_2$ was shown to slow down as a function of time irradiated pointing towards a photochemical aging process occurring on the surface of the TiO$_2$ particles. The dependence of HO$_2$ production on O$_2$ and H$_2$O concentrations was determined, which shows a typical Langmuir adsorption saturation curve for O$_2$ suggesting it is the gas-phase reactant in this process. The addition of H$_2$O into the system inhibits the reaction and reduces the adsorption equilibrium coefficient for both species. Reduction of O$_2$ by photogenerated electrons is likely to be the initial step in this process followed by reaction with a proton. Hydrogen extraction from hydroxyl bridging groups (OH$_{br}$) groups by O$_2^-$ could explain the slow down observed in the rate of HO$_2$ production. Production of gas-phase OH radicals was investigated and showed OH was produced only when large concentrations of TiO$_2$ aerosols entered the aerosol flow tube, probably associated with the decomposition of H$_2$O$_2$ formed from reactive uptake. Although the production of HO$_2$ by TiO$_2$ aerosols initially would not be advantageous for its use within SRM schemes, the reaction ceases upon prolonged photocatalytic aging of the aerosol surface.

Meteoric smoke particles (MSP) provide the only significant surfaces within the mesosphere for heterogeneous reactions to occur. To investigate whether such reactions could, in some part, be responsible for the ‘HO$_x$ Dilemma’ measurements of $\gamma$(HO$_2$) onto analogues of MSP,
forsterite, olivine and fayalite, were conducted at a RH of 10%. These experiments showed forsterite to have the lowest reactivity with HO₂, similar to that of effloresced inorganic aerosols, and olivine and fayalite to have a similar reactivity that was more than an order of magnitude greater than that of forsterite, thus demonstrating that the presence of Fe within the MSP is required for significant reactivity with HO₂. Electronic structure calculations, conducted by Professor Plane, predicts that the difference in reactivity is associated mechanistic and energetic differences between the binding of HO₂ to Fe and Mg sites, however, the positive dependence of γ(HO₂) with RH and similar values of γ(HO₂) for olivine and fayalite suggests that OH bridging groups or complexing with water molecules adsorbed to such sites, as with TiO₂ nanoparticles, are adsorption sites for HO₂. Taking the measurements made in this work and the likely dependence of γ(HO₂) on temperature and RH, a value of 0.2 for γ(HO₂) was applied by Dr Sandy James in WACCM-CARMA. This modelling study predicted reductions in the HO₂ volume mixing ratio of up to 40% in the polar vortex. Impact to HO₂ budgets in the mesosphere was found to be dependent on latitude, giving agreement with the presence of MSPs in the polar night.
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<td>Aerosol Characterisation Experiment</td>
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<td>AIM</td>
<td>Aerosol Inorganic Model</td>
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<td>AIOMFAC</td>
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<td>APD</td>
<td>Acoustic Particle Disperser</td>
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<td>ARCTAS</td>
<td>Arctic Research of the Composition of the Troposphere from Aircraft and Satellites</td>
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<td>ATD</td>
<td>Arizona Test Dust</td>
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<tr>
<td>CARMA</td>
<td>Community Aerosol and Radiation Model for Atmospheres</td>
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<tr>
<td>CML</td>
<td>Carboxylate-Modified Latex</td>
</tr>
<tr>
<td>COMEAP</td>
<td>Committee on the Medical Effects of Air Pollutants</td>
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<td>COS</td>
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<td>CTM</td>
<td>Chemical Transport Model</td>
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<td>DMA</td>
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<td>HCCT-2010</td>
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<td>Hydrochlorofluorocarbons</td>
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<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
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<tr>
<td>$H_{eff}$</td>
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MCP  Micro-Channel Plate
MFC  Mass Flow Controller
MLS  Microwave Limb Sounder
MSP  Meteoric Smoke Particle
NAMBLEX  North Atlantic Marine Boundary Layer Experiment
NOx  Oxides of Nitrogen
OD  Outside Diameter
pptv  parts per trillion per unit volume
PSL  Polystyrene Latex
RH  Relative Humidity
ROS  Reactive Oxygenated Species
sccm  standard cubic centimeters per minute
SEM  Scanning Electron Microscope
SMPS  Scanning Mobility Particle Sizer
TMI  Transition Metal Ion
UK  United Kingdom
UV  Ultraviolet
UVA  Ultraviolet A (\(\lambda = 315 - 400 \text{ nm}\))
VOC  Volatile Organic Compound
WACCM  Whole Atmosphere Community Climate Model
\(\gamma(\text{HO}_2)\)  Hydroperoxyl Radical Reactive Uptake Coefficient
Chapter 1 – Introduction

This chapter briefly introduces the research subject background and the gap in current understanding of the science, hence the research questions to be answered. The aims and objectives of the study are presented and related to the research questions. Current literature related to this study is also presented.
1.1 Introduction and Background

Two of the main environmental challenges that the world faces in the 21st century are tackling climate change and improving the quality of the air that we breathe. Anthropogenic emissions of carbon dioxide (CO$_2$), carbon monoxide (CO), oxides of nitrogen (NO$_x$), methane (CH$_4$) and other volatile organic compounds (VOCs) into the troposphere are responsible for the warming the atmosphere (with the exception of CO and NO$_x$ directly) and have had a significant impact to human health and mortality. The hydroxyl radical (OH), along with the closely coupled species the peroxy radical (HO$_2$), have a profound effect on the concentration and distribution of most trace atmospheric species mentioned above as they are essential to the daytime oxidizing capacity of the atmosphere. These radicals can also affect climate change and air quality by initiating the formation of ozone (O$_3$) and secondary organic aerosols in the troposphere and also as a sink for CH$_4$. The radicals OH and HO$_2$ are often referred to collectively as HO$_x$ and are central to a complex cyclic process known as the HO$_x$ cycle. By developing a deep understanding of the chemistry associated with the HO$_x$ cycle we can further our knowledge of the lifetime and distribution of such chemical species in the atmosphere allowing us to predict with greater accuracy the effect human activity is having on climate change and air quality and enabling policy makers to create more informed policies that contain mitigation and adaptation measures that are targeted correctly and are cost effective.

Suspended in the atmosphere are many liquid and solid phase particles known as aerosols. These aerosols also play an important role within air quality and climate change. The Committee on the Medical Effects of Air Pollutants (COMEAP) calculated that in 2008 the burden of anthropogenic aerosols had an effect on UK mortality of around 29,000 deaths at typical ages. This burden represents an average loss of life expectancy of approximately six months. Aerosols can directly affect the radiative balance of the atmosphere through absorption and scattering of sunlight and indirectly via interactions with clouds, where they serve as cloud condensation nuclei or ice nuclei which go on to form cloud droplets or ice crystals. The contribution of aerosols from anthropogenic sources to the total anthropogenic radiative forcing of the atmosphere is the dominant source of uncertainty within climate model projections. However, aerosols can also indirectly affect air quality and climate change via heterogeneous uptake of HO$_2$ and many other gases. Heterogeneous uptake is a term used to describe the process where a chemical species is adsorbed on to the surface or accommodated within a particle that is in a different phase to it. It can then either remain within or on the surface of the particle, go on to react with other chemical species within or on the surface of the particle, react with another chemical species within the gas-phase if adsorbed onto the surface of the particle or desorb back into the atmosphere. A chemical box model is a tool
that predicts the concentration of an atmospheric species within a box representative of the atmosphere within the study area based on a complex mechanism of gas-phase chemical reactions where transport processes are simplified. Purely gas-phase chemical box models have been shown to often over-predict concentrations of HO$_2$ in comparison with field measurements, in some part, due to heterogeneous uptake by aerosols not being considered. By including heterogeneous uptake into such models better agreement can be gained. During the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ACRTAS) campaign it was shown that aerosols within the Arctic led to around a 30% decrease of OH and HO$_2$ with heterogeneous loss being considered the dominant sink for these species above altitudes of 5 km. Heterogeneous uptake of OH by aerosols is thought to have a negligible effect to gas-phase concentrations of OH as its chemical lifetime is significantly shorter than HO$_2$. Heterogeneous uptake of HO$_2$ by aerosols is parameterised within numerical models as the reaction uptake probability coefficient, $\gamma$(HO$_2$), i.e. the probability of reaction given a collision with the aerosol surface. Jacob suggested a general value of 0.2 for $\gamma$(HO$_2$) would be acceptable for use within numerical models, however, this approach has since been shown to be too crude as this parameter is highly sensitive to a number of variables (e.g. chemical composition, relative humidity and temperature) and is a relatively large value compared with laboratory experiments. Deliquesced inorganic aerosols have been shown to yield relatively higher $\gamma$(HO$_2$) values than effloresced inorganic aerosols and the presence of copper ions and to a lesser extent iron ions increases the reaction probability significantly to its upper kinetic limit.

Although understanding of heterogeneous uptake of HO$_2$ is progressing, much remains uncertain and there is often variation in literature $\gamma$(HO$_2$) values. Values of $\gamma$(HO$_2$) have been determined for a variety of aerosols, however, there are still many different types of aerosols to undergo experimentation. There is still uncertainty regarding the reaction mechanism of reactive uptake of HO$_2$ and hence the products of the reaction that are partitioned back into the atmosphere. In addition to this, there are a limited number of measurements taken under varying atmospheric parameters such as temperature and RH and many early experiments have been undertaken at HO$_2$ concentrations that are not atmospherically relevant.

### 1.2 Aims and Objectives of the Study

The study will attempt to provide experimental data to help answer the following research questions:

1. “How do aerosols influence the oxidative capacity of Earth’s atmosphere?”
2. “How would solar-radiation management schemes involving stratospheric injection of particles affect lower stratospheric chemistry?”
These questions will be addressed through the following objectives:

- Determine how the presence of transition metal ions within deliquesced inorganic aerosols affects the kinetics and reaction products of heterogeneous uptake of HO₂;
- Investigate whether heterogeneous reactions between HO₂ and deliquesced sea salt aerosols doped with iodide (I⁻) can account for discrepancies between modelled and observed mixing ratios of HO₂ in the marine environment;
- Investigate the feasibility of stratospheric injection of TiO₂ particles as a possible solar-radiation scheme with regards to heterogeneous reactions involving HO₂; and
- Determine whether reactive uptake of HO₂ onto meteoric smoke particles can account for the discrepancy between modelled and observed mixing ratios of HO₂ in the mesosphere, known as the HO₄ dilemma.

1.3 Delivery Plan

The above objectives will be investigated using a number of experimental and computational modelling studies:

- Measurement of γ(HO₂) onto aerosols and production of HO₂ from aerosol surfaces using a kinetic aerosol flow tube experiment coupled to a highly sensitive Laser Induced Fluorescence detector known as Fluorescence Assay by Gas Expansion (FAGE) and a Scanning Mobility Particle Sizer (SMPS); and
- Engage with atmospheric modellers (see section 1.5) to interpret the impact of laboratory measurements to atmospheric composition using the TOMCAT off-line three-dimensional (3D) chemical transport model (stratospheric chemistry) and the Whole Atmosphere Community Climate Model (WACCM) coupled with the Community Aerosol and Radiation Model for Atmospheres (CARMA) (mesospheric chemistry).

1.4 Thesis Plan

The objectives of this study aim to provide new insight into the mechanism and magnitude of HO₂ uptake and production by aerosols relevant to a comprehensive range of atmospheric environments, from the troposphere to the mesosphere. The study focuses on those aerosols in these environments that have been shown to contribute significantly to heterogeneous reactions with HO₂ radicals, where new studies into such reactions have been identified as being necessary by previous publications, or where such aerosols are relatively abundant and model-measurement comparison of HO₄ is poor.
Chapter 1 – Introduction

1.5 Project Management

Modelling of stratospheric O₃ and HO₂ concentrations were conducted by Giorgio Taverna and Professor Martyn Chipperfield using the TOMCAT model. The TOMCAT modelling work was supported by the EU StratoClim project (FP7 grant 603557). The model simulations were performed on the University of Leeds and N8 HPC system.

Modelling of mesospheric HO₂ concentrations were conducted by Dr Sandy James and Dr Wuhu Feng. This work was supported by funding from the European Research Council (project 291332—CODITA).

1.6 Model-Measurements Comparison of Atmospheric HO₂

In order to test current understanding of atmospheric chemistry, predictions made with numerical box models constrained to the conditions measured during the field campaign are compared with measurements made within the field. OH and HO₂ are ideal target molecules to test our understanding of atmospheric chemistry as their short chemical lifetime means that their concentrations are only controlled by local in situ chemistry and not by transport processes. Studies that compare HO₂ field measurements with numerical box model simulations often show that purely gas-phase chemistry models can significantly over-predict concentrations of HO₂ indicating that a sink of HO₂ has not been considered. Heterogeneous uptake is often cited as a potential unconsidered HO₂ sink in these studies, thus providing the motivation for this work.

Mace Head, Ireland, has been the location for numerous field campaigns that intend to investigate the chemistry occurring within the clean marine boundary layer in the Northern Hemisphere ¹⁰-¹². Five day back trajectories produced during the NAMBLEX (North Atlantic Boundary Layer Experiment) campaign showed that for the majority of the time air at this location was of oceanic origin that has travelled across the Atlantic from North America, Greenland and the Tropics. Prior to the NAMBLEX campaign were the EASE96 (East Atlantic Summer Experiment) and EASE97 (Spring) campaigns during which the University of Leeds Fluorescence Assay by Gas Expansion (FAGE) instrument was deployed to conduct field measurements of OH and HO₂ radicals. During these campaigns midday concentrations of 2.0 - 6.0 × 10⁶ molecule cm⁻³ and 0.5 - 3.5 × 10⁸ molecule cm⁻³ were measured for OH and HO₂ respectively ¹². A constrained photochemical box model that used the Master Chemical Mechanism (MCM) substantially over-predicted concentrations of OH and HO₂ by a factor of 2.4 and 3.6 respectively indicating that the HO₂ chemistry in this environment was not fully understood ¹¹.
During 2002 the NAMBLEX campaign featured a number of improvements, such as measurements of more OH sinks (e.g. oxygenated VOCs) along with HO\textsubscript{2} co-reactants IO and BrO and aerosol composition and size distribution, also OH and HO\textsubscript{2} were measured simultaneously rather than sequentially. As previously, a box model based on the MCM was used to predict concentrations of OH and HO\textsubscript{2} during this campaign \textsuperscript{13}. Each simulation increased in its complexity starting from considering just clean marine boundary layer chemistry to adding hydrocarbons, oxygenates, peroxides, iodine and bromine. Heterogeneous uptake of HO\textsubscript{2} was considered in all models, although its calculation differed. Base models used the simpler free-molecular expression for heterogeneous uptake which assumes all aerosols have the same properties, whereas, the more complex models used the transition regime expression (E1.1) to calculate more precise rate coefficients for aerosol uptake which considers gas-phase diffusion control, which is dependent on the gas-phase diffusivity ($D_g$), and uptake control, which is dependent on the mass accommodation coefficient ($\alpha$, defined as the probability that reversible uptake of a gas-phase species will occur upon collision of that species with an aerosol). This treatment could be used as the NAMBLEX campaign featured more detailed aerosol measurements.

\[
L k^{-mt} = \int_0^\infty \left( \frac{dV(r)}{dr} \times k_{mt}(r) \right) dr 
\]

\[
= \int_0^\infty 4\pi r^3 \frac{dN(r)}{dr} \times \left( \frac{r^2}{3D_g} + \frac{4r}{3\alpha} \right)^{-1} dr 
\]

where $L$ is the total aerosol volume, $k^{-mt}$ is the mass transfer coefficient, $r$ is the radius of droplet, $\overline{v}$ is the mean molecular velocity and $N(r)$ and $V(r)$ are the number density and volume of particles with radius smaller than $r$.

The process of uptake of the gas-phase species and reaction in the aerosol is parameterised by the reaction uptake coefficient ($\gamma$); the probability that a gas-phase molecule collides with the aerosol and reacts within it. Values for reactive uptake coefficient for HO\textsubscript{2}, $\gamma$(HO\textsubscript{2}), were calculated using E1.2\textsuperscript{14}.

\[
\gamma$(HO\textsubscript{2}) = 1.40 \times 10^{-8} e^{\left(\frac{3780}{T}\right)} 
\]

Values for $\gamma$(HO\textsubscript{2}) were changed to 1.0, the upper limit, in order to determine the sensitivity of the model to this parameter. The values of $\gamma$(HOI) and $\gamma$(HOBr) are important as they govern the partitioning of HOX ($X = Br, I$) between photolysis (see section 1.7) and heterogeneous loss, which affects predictions of OH. Both were set to 0.6, however, values of 0.06 were used as a lower case to also check sensitivity of OH predictions to this parameter. Limitations within the treatment of heterogeneous uptake in this study were that the effect of chemical...
composition was only partly considered and did not consider the reactivity of the atmospheric species within the aerosol, nor did it consider the products desorbed.

The base model simulations (i.e. no halogen chemistry and heterogeneous uptake characterised by the free-molecular expression) over-predicted the concentration of HO$_2$ by around a factor of two. Changing the treatment of heterogeneous uptake from the free-molecular expression to the transition regime expression made no significant change as the value of $\gamma$(HO$_2$) was too low ($\approx 0.006$), however, the effect of the transition regime expression, when the model is constrained to BrO chemistry, was much greater. Changing $\gamma$(HO$_2$) to its theoretical maximum (i.e. $\gamma$(HO$_2$) = 1) had a dramatic effect on the concentrations of HO$_2$ predicted, reducing them by up 40% reaching good agreement with measured values. With regards to HO$_2$ uptake, the study concludes that agreement of model predictions and measured data is greatest when both halogen and heterogeneous uptake of HO$_2$ by sea-salt particles are considered. This study makes it apparent that further characterisation and understanding of the processes involved with HO$_2$ uptake are central to improving the description of HO$_x$ chemistry in the troposphere, particularly in the marine boundary layer. The same conclusion was reached when steady state analysis of OH and HO$_2$ during the same NAMBLEX field campaign was conducted.

In September and October 2010 Hill Cap Cloud Thuringia 2010 (HCCT-2010) campaign took place within the Thüringer Wald mountain range in Central Germany. The aim of the campaign was to evaluate the interaction trace gases and particulate matter within orographic clouds (i.e. clouds that have formed due to the forced lifting of air by local topography). The University of Leeds FAGE field instrument was deployed within the campaign to make sequential measurements of OH and HO$_2$ on top of a 22 m high tower to ensure measurements were made within the cloud. Measurements of ambient HO$_2$ along with a number of cloud measurements were used to obtain a value for the rate of heterogeneous loss HO$_2$ to clouds. Model-measurement comparison showed that up to 90% of HO$_2$ was depleted within the cloud and revealed a strong dependence of HO$_2$ uptake to pH and droplet surface area. These measurements were the first observationally derived values of $\gamma$(HO$_2$) which were in good agreement with values derived from theory. The study then went onto undertake global model simulations to understand the impact clouds have on the oxidising capacity of the troposphere. These simulations showed that the impact of clouds on tropospheric levels of HO$_x$ was critically dependent on whether HO$_2$ uptake resulted in the production of H$_2$O$_2$ or H$_2$O.

1.7 Tropospheric HO$_x$ Cycle

The hydroxyl radical (OH) and the closely coupled hydroperoxyl radical (HO$_2$), collectively known as HO$_x$ (HO$_x$ = OH + HO$_2$), are key species for the chemical processes involved with...
climate change and air pollution. For example, the predominant sink for methane (CH₄), a greenhouse gas with a radiative efficiency around 26 times greater than carbon dioxide, is reaction with OH. In fact OH destroys around 3.7 Gt of trace gases in the atmosphere each year, which includes other greenhouse gases such as all hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Also, the reaction of HO₂ and organic peroxy radicals (RO₂) with nitric oxide (NO) initiates the only identified tropospheric in situ source of ozone (O₃), an important species when considering air quality.

The sources and sinks of OH and HO₂ radicals (known as the HOₓ cycle) follows a complex cycle of chemical reactions which are summarised in Figure 1.1 and described in further detail later. It is important to note the role of oxides of nitrogen (NOₓ) within the HOₓ cycle, which is more dominant in high NOₓ areas such as urban environments, and uptake of HO₂ to cloud droplets which is of direct relevance to this report.

Sunlight is the main driver of chemistry during the day within the troposphere and the primary pathway for the formation of OH via the photodissociation of O₃ (R1.1) followed by the reaction of the resulting excited oxygen atom with water (R1.2). In order for O₃ to photodissociate it must be excited above its dissociation energy (D₀), which corresponds to light with wavelengths lower than 340 nm.

\[
O₃ + h\nu (\lambda < 340 \text{ nm}) \rightarrow O(^1\Delta) + O_2 (^1\Delta) \quad \text{(R1.1)}
\]

\[
O(^1\Delta) + H_2O \rightarrow 2 OH \quad \text{(R1.2)}
\]

As H₂O vapour forms only a minor component of the atmosphere the majority of O(^1\Delta) formed is quenched to form ground state O(^3P) (R1.3) which sequentially reacts with diatomic oxygen to regenerate O₃ (R1.4), and therefore is a null cycle.26

\[
O(^1\Delta) + M \rightarrow O(^3P) + M \quad M = N_2, O_2 \quad \text{(R1.3)}
\]
O(\(^3\)P) + O\(_2\) + M → O\(_3\) + M \hspace{1cm} (R1.4)

The rate which OH is produced via this primary process is expressed in E1.3.

\[ P(\text{OH}) = 2f[O_3] \times j(O^1D) \hspace{1cm} (E1.3) \]

where \(P(\text{OH})\) is the rate of production of OH, \(j(O^1D)\) is the photolysis rate of ozone and \(f\) is the fraction of \(O^1D\) which reacts with \(H_2O\) (R1.2) as a proportion of the combined rates of R1.2 and other competing reactions of \(O^1D\) (R3) (see E1.4):

\[ f = \frac{k_{O^1D+H_2O-[H_2O]}}{k_{O^1D+H_2O-[H_2O]} + k_{O^1D+N_2-[N_2]} + k_{O^1D+O_2-[O_2]}} \hspace{1cm} (E1.4) \]

O\(_3\) within the troposphere can be stratospheric in origin, however another source of tropospheric ozone is the photolysis of NO\(_2\) (R1.5) which forms O(\(^3\)P) which is followed by R1.4.\(^5\)

\[ \text{NO}_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{O}(\^3\text{P}) + \text{NO} \hspace{1cm} (R1.5) \]

As shown in Figure 1.1 and R1.17 (below) NO can be oxidized by HO\(_2\) to regenerate NO\(_2\) so the formation of O\(_3\) via this process is not limited by the primary amount of NO\(_2\) present. This underlines how the HO\(_x\) and NO\(_x\) cycles are inextricably linked.

Another primary source of OH is the photolysis of nitrous acid (HONO, R1.6). HONO is formed via the heterogeneous, or to a lesser extent homogeneous, reaction between oxides of nitrogen (NO\(_x\)) and H\(_2\)O. HONO can undergo photolysis at relatively long wavelengths which can reach ground level \(^26\).

\[ \text{HONO} + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{OH} + \text{NO} \hspace{1cm} (R1.6) \]

Photolysis of hydrogen peroxide (H\(_2\)O\(_2\)) also results in production of OH in the atmosphere (R1.7) and can occur in both the gas and aqueous phases. Within the gas phase the quantum yield of R1.7 is close to unity whereas in the aqueous phase the reaction has a quantum yield of 0.5 \(^27\).

\[ \text{H}_2\text{O}_2 + h\nu (\lambda < 360 \text{ nm}) \rightarrow 2 \text{ OH} \hspace{1cm} (R1.7) \]

The key process for the formation of HO\(_2\) is via the reaction of OH with carbon monoxide (CO) in the presence of diatomic oxygen (R1.8). Around 70\% of OH formed will undergo this reaction in low NO\(_x\) and VOC environments \(^26\). OH can then be reformed from HO\(_2\) via the reaction with O\(_3\) (R1.9).

\[ \text{OH} + \text{CO} (+\text{O}_2) \rightarrow \text{HO}_2 + \text{CO}_2 \hspace{1cm} (R1.8) \]

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \hspace{1cm} (R1.9) \]
The other 30% will react with CH\textsubscript{4} in the unpolluted atmosphere or a combination of VOCs in high NO\textsubscript{x} and VOC environments (referred to as R) (R1.10) to form RO\textsubscript{2}:

\[
\text{OH} + \text{RH} (+\text{O}_2) \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad (\text{R1.10})
\]

RO\textsubscript{2} can then go on to undergo reaction with HO\textsubscript{2} (R1.11), self-reaction or cross reactions with other RO\textsubscript{2} radicals (R1.12) and eventually generate HO\textsubscript{2} (R1.13). For example, in the case of the methylperoxy radical (CH\textsubscript{3}O\textsubscript{2}):

\[
\begin{align*}
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \quad (\text{R1.11}) \\
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow 2\text{CH}_3\text{O} + \text{other products} \quad (\text{R1.12}) \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{HCHO} \quad (\text{R1.13})
\end{align*}
\]

We consider that the rate of change of OH in the atmosphere is governed by the rate of production (R1.2 and R1.8) of it minus the rate of destruction (R1.7 and R1.9). If it is assumed that the rate of production of OH is dominated by \(P(\text{OH})\) and the reciprocal of the rate of destruction of OH by reaction with CH\textsubscript{4}, CO and other VOCs (to a lesser extent) describes the atmospheric lifetime of OH then by applying the steady state approximation we can calculate its concentration (E1.5).

\[
[\text{OH}] = P(\text{OH}) \times \tau_{\text{OH}} \quad (\text{E1.5})
\]

where \(\tau\) is the atmospheric lifetime of OH and \(P\) is the total production. This is a general result that applies anywhere to OH as it is in steady state.

In highly vegetated areas, where levels of NO\textsubscript{x} are low and unsaturated VOCs (e.g. isoprene) are high, O\textsubscript{3} can attack the double bond on an unsaturated VOC (in this case propene) which can result in the formation of OH (R1.14a, R1.14b and R1.15). This reaction is referred to as ozonolysis. Ozonolysis results in the formation of a biradical known as a Criegee intermediate. These radicals are rich with energy and go on to decompose to form OH \textsuperscript{26}.

\[
\begin{align*}
\text{O}_3 + \text{CH}_2\equiv\text{CHCH}_3 & \rightarrow \text{CH}_3\text{CHO} + \text{HCHO} \quad (\text{R1.14a}) \\
\text{O}_3 + \text{CH}_2\equiv\text{CHCH}_3 & \rightarrow \text{CH}_2\text{OO} + \text{CH}_3\text{CHO} \quad (\text{R1.14b}) \\
\text{CH}_3\text{CHO}_2 & \rightarrow \text{CH}_3 + \text{CO} + \text{OH} \quad (\text{R1.15})
\end{align*}
\]

In remote environments where the levels of NO are very low, loss of HO\textsubscript{2} is governed by third-body self-reaction (R16) or with CH\textsubscript{3}O\textsubscript{2} (R1.11).

\[
\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M} \quad (\text{R1.16})
\]
In environments with higher concentrations of NO a different course of reactions are dominant, HO$_2$ regenerates OH (R1.17) while RO$_2$ forms alkoxy radicals (R1.18) which can then go and react with diatomic oxygen to form aldehydes as shown in R1.19 (e.g. methoxy radicals go on to form formaldehyde) $^5$. It should also be noted that NO$_2$ formed in R1.17 and R1.18 can undergo photolysis to produce NO and O($^3$P) (R1.5) which can go on to form O$_3$ upon reaction with O$_2$ which ultimately can go on to form more OH.

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R1.17)}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad \text{(R1.18)}
\]

\[
\text{RO} + \text{O}_2 \rightarrow \text{R'CHO} + \text{HO}_2 \quad \text{(R1.19)}
\]

Formaldehyde (HCHO) can then go on to photo-dissociate to produce two radicals (R1.20) $^{28}$ both of which re-enter the HO$_x$ cycle and regenerate HO$_2$ through R1.21 and R1.22.

\[
\text{HCHO} + \text{hv} (\lambda < 338 \text{ nm}) \rightarrow \text{H} + \text{HCO} \quad \text{(R1.20)}
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad \text{(R1.21)}
\]

\[
\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad \text{(R1.22)}
\]

It is also important to consider another process that involves the reaction of HO$_2$ with halogen oxides (XO, where X = Br or I) (R1.23). This process is important in the marine boundary layer. The HOX produced can then go on to regenerate OH and produce a halogen atom (X) via photolysis (R1.24) or can also be lost to heterogeneous uptake $^5$. The XO is then regenerated via reaction with X and O$_3$ (R1.25) $^{29}$.

\[
\text{HO}_2 + \text{XO} \rightarrow \text{HOX} + \text{O}_2 \quad \text{X = Br, I} \quad \text{(R1.23)}
\]

\[
\text{HOX} + \text{hv} \rightarrow \text{X} + \text{OH} \quad \text{(R1.24)}
\]

\[
\text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2 \quad \text{(R1.25)}
\]

Now that the dominant processes that govern the formation and loss of HO$_2$ have been introduced its kinetics are now discussed. The rate of production of tropospheric HO$_2$ in a low NO$_x$ environment is expressed in E1.6. Positive terms on the right-hand-side of the equation represent the sources of HO$_2$ and negative are sinks. The subscript next to the rate constant refers to the reaction referenced in this report.

\[
\frac{d[\text{HO}_2]}{dt} = k_8[\text{OH}][\text{CO}] - 2k_{16}[\text{HO}_2]^2 - k_9[\text{HO}_2][\text{O}_3] - k_{11}[\text{HO}_2][\text{CH}_3\text{O}_2] \quad \text{(E1.6)}
\]
As the rate of $R_{1.9}$ is slow in comparison with $R_{1.16}$ and $R_{1.11}$ it can be discounted from the equation. As the rate of loss of $\text{CH}_3\text{O}_2$ is slow compared to the rate of its formation, the steady state concentration of $\text{HO}_2$ can be expressed as in \( \text{E1.7} \): 

$$[\text{HO}_2] = \frac{k_9[\text{CO}][\text{OH}]}{2k_{16} + k_{11} \alpha} \quad \text{(E1.7)}$$

where $\alpha$ is $[\text{CH}_3\text{O}_2]/[\text{HO}_2]$.

The steady state equations for $\text{OH}$ and $\text{HO}_2$ are simplistic and often do not reflect the complex chemistry occurring in the atmosphere. Both $\text{OH}$ and $\text{HO}_2$ are highly reactive and therefore have relatively short atmospheric lifetimes; $\text{OH}$ typically has an atmospheric lifetime of less than a second \(^{30}\). This means that their concentrations are controlled by local in situ chemistry and not by transport processes. This makes them ideal species when testing our knowledge of atmospheric chemistry when using zero-dimensional box models. In recent years many observations of $\text{OH}$ and $\text{HO}_2$ have been routinely made in the field. These observations are then compared to predicted concentrations by box models that use a complex chemical mechanism that contains thousands of reactions and chemical species, such as the Master Chemical Mechanism (MCM). These box models are often constrained to observations of key longer-lived atmospheric species and photolysis rates, e.g. $j(\text{O}^1\text{D})$ \(^5\). A discrepancy between measured and modelled concentrations of $\text{OH}$ or $\text{HO}_2$ indicates a possible unidentified source or sink of these species.

The reactions above are purely gas phase chemical processes, however as previously mentioned and shown in Figure 1.1 $\text{HO}_2$ is also lost by heterogeneous uptake onto aerosols and cloud droplets.

### 1.8 Stratospheric $\text{HO}_2$ – A Sink for $\text{O}_3$

$\text{HO}_2$ is a key species within the stratosphere, being present at about 5 parts per trillion per unit volume (pptv) around the tropopause, and is involved in a $\text{HO}_4$ catalytic cycle responsible for $>40\%$ of O$_3$ depletion in the lower stratosphere via the following reactions \(^{31}\):

$$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R1.26)}$$

$$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(R1.9)}$$

$$2\text{O}_3 \rightarrow 3\text{O}_2 \quad \text{(Net: R1.26 + R1.9)}$$

However, this catalytic cycle is only important at altitudes below 30 km as atomic oxygen (O) is found in low concentrations at these altitudes \(^{26,31}\). Above 40 km O, formed by the photolysis of $\text{O}_2$ and $\text{O}_3$, is found in sufficient quantity so that the following catalytic cycle becomes important \(^{32}\):
OH + O₃ → HO₂ + O₂  \hspace{1cm} (R1.26)  
HO₂ + O → OH + O₂  \hspace{1cm} (R1.27)  
O + O₃ → 2O₂  \hspace{1cm} (Net: R1.26 + R1.27)

Moreover, HO₂ can also react with stratospheric ClO and BrO (products of the reaction between atomic chlorine and bromine with O₃) to produce HOCl and HOBr respectively, as seen in the marine environment (R1.23 – R1.25), which can be photolysed to produce further OH and atomic halogen species that contribute to further O₃ loss. A simplified chemical cycle for stratospheric HOₓ trace species is given in Figure 1.2.

![Figure 1.2: Chemical cycle for stratospheric HOₓ. Reproduced from reference 26.](image)

However, the presence of NO in the stratosphere can render these catalytic cycles null. NO is present in the stratosphere due to transportation of N₂O from the troposphere and subsequent reaction with excited O (R1.28) ²⁶.

N₂O + O(¹D) → 2NO  \hspace{1cm} (R1.28)

HO₂ is formed via the reaction between OH and O₃ (R1.26), however, rather than the resulting HO₂ reacting with O₃ (R1.27) or O (R1.28) it reacts rapidly with NO recycling OH and producing NO₂ (R1.17), which can then photolyse to produce NO and O atoms (R1.5). The cycle then results in no net change of odd oxygen species.

O₃ + hv → O₂ + O → O₃  \hspace{1cm} (Net: R1.26 + R1.5 + R1.17)

The presence of HOₓ in the stratosphere can be attributed to the transport of H₂O and CH₄ from the troposphere ³² or H₂O formed by oxidation of CH₄ ²⁶ (R1.10). OH is predominantly formed via O₃ photolysis (R1.1) that yields excited O atoms which go on to react with H₂O (R1.2) or CH₄ (R1.29), however, HO₂ is predominately formed via reaction with OH and O₃ (R1.26).
O(\(^{1}\)D) + CH\(_4\) \rightarrow OH + CH\(_3\) \quad (R1.29)

The partitioning of OH and HO\(_2\) at altitudes above 40 km is predominantly governed by R1.28, R1.30 and R1.31 (the products of which go on to form HO\(_2\)) \(^32\):

H + O\(_3\) \rightarrow O\(_2\) + OH \quad (R1.30)

OH + O \rightarrow O\(_2\) + H \quad (R1.31)

The reaction between OH and HO\(_2\) provides a loss process for HO\(_x\) in the stratosphere (R1.32) along with the self-reaction of HO\(_2\) (R1.16).

OH + HO\(_2\) \rightarrow H\(_2\)O + O\(_2\) \quad (R1.32)

Self-reaction of HO\(_2\) is the main source of H\(_2\)O in the stratosphere with some H\(_2\)O being formed from a third-body self-reaction of OH (R1.33).

OH + OH + M \rightarrow H\(_2\)O\(_2\) + M \quad (R1.33)

1.9 Mesospheric HO\(_2\) – The HO\(_x\) Dilemma

As with the stratosphere, the presence of HO\(_x\) in the mesosphere is due to transportation of H\(_2\)O from the troposphere. However, in the mesosphere (above 60 km) OH can be formed by photolysis of water by UV radiation (R1.34), particularly within the Lyman-alpha region (spectral emissions from hydrogen) and Schumann-Runge bands (molecular oxygen absorption bands) \(^32\).

H\(_2\)O + hv \rightarrow OH + H \quad (R1.34)

HO\(_2\) can then be formed by reaction of the resulting H with oxygen due to a three-body reaction (R1.35).

H + O\(_2\) + M \rightarrow HO\(_2\) + M (M = N\(_2\) or O\(_2\)) \quad (R1.35)

The removal of HO\(_x\) is primarily through R1.32 and the partitioning of OH and HO\(_2\) is as described above (R1.26 – R1.27).

Despite of the simplicity of the mechanisms that govern HO\(_x\) chemistry in this region, photochemical models cannot describe the HO\(_x\) densities observed. OH satellite observations by the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) found OH concentrations to be 30 to 40% lower than those predicted \(^33\). On the second MASHRSI mission OH concentrations were shown to increase rapidly below the mesopause reaching levels at 43 km that could not be explained by photochemical theory suggesting that the mechanism (R1.30 – R1.31) that was previously thought to dominate HO\(_x\) partitioning across the stratosphere and mesosphere may no longer be valid \(^34\). Moreover, ground-based
microwave measurements of mesospheric HO$_2$ showed that HO$_2$ concentrations were 23 to 43% higher than photochemical model predictions at midday, agreed prior to 09:00 local time and 70 to 100% higher after sunset $^{35}$. The substantial disagreement between modelled and measured HO$_x$ concentrations in the mesosphere is known as the “HO$_x$ Dilemma”. Recently, a long-term record of stratospheric and mesospheric HO$_2$ concentrations during day and night has been retrieved from measurements made by the Microwave Limb Sounder (MLS) on board the Aura satellite. Comparison of this data set made with a number of other measurements and model predictions (Whole Atmosphere Community Climate Model, WACCM Version 4) have shown that the measurements are robust and that the limitations in current understanding of middle atmospheric chemistry and deficiencies in the model spectral irradiance are likely to be the cause of the discrepancy. WACCM predictions of HO$_2$ and MLS records agree qualitatively, however quantitatively the model under predicts HO$_2$ concentrations by 100% in the day and 40% during the night in the mesosphere and by 20 to 30% between 1 and 0.1 hPa $^{32}$.

1.10 Properties and Sources of Atmospheric Aerosols

The atmosphere is predominantly composed of gases, however a significant component is liquid and solid particles that are suspended within it, referred to as aerosols. Aerosols can be defined in atmospheric science as a colloidal dispersion of solid particles or liquid droplets in a gas phase dispersing medium. Due to their high surface area to volume ratio they are thermodynamically unstable but are kinetically stable. They have a significant effect to the chemistry within the atmosphere and have a great influence on both climate change and air quality. Most aerosols (excluding absorbing aerosols such as soot and black carbon), unlike Greenhouse Gases (GHGs), cool the atmosphere and therefore have a negative radiative forcing value, i.e. the balance of energy between incoming solar energy and outgoing infrared radiation. Aerosols do this either directly through scattering or indirectly by the cloud albedo effect. Anthropogenic aerosols contribute an estimated $-0.9$ ($-1.9$ to $-0.1$) W m$^{-2}$ to the total net radiative forcing ($\approx 2.9$ W m$^{-2}$) directly and by the cloud albedo effect in 2011 relative to 1750 $^{36}$. However, Figure 1.3 shows that the level of scientific understanding in this area is still relatively low meaning this value is subject to a large error.
Figure 1.3: The radiative forcing for each emitted component to climate change during the Industrial era. Reproduced from reference 36.

The inhalation of aerosols is harmful to human health and exposure to them is regulated both at European (Council Directive 2008/50/EC) and National (Air Quality Standards Regulations 2010) levels. The Committee on the Medical Effects of Air Pollution advises the relevant government departments that anthropogenic particulate air pollution in the UK had an effect on mortality in 2008 equivalent to nearly 29,000 deaths at typical ages and an associated loss of total population life of 340,000 years 2.

There are a number of categories in which aerosols can be placed based on their size; nucleation mode (<0.01 µm), Aitken mode (0.01-0.1 µm), accumulation mode (0.1–1 µm) and coarse mode (>1 µm). Generally, particles with a diameter greater than 100 µm will not suspend within the atmosphere. Nucleation and Aitken mode particles are formed by gas-to-particle conversion. These ultrafine particles then grow either via coagulation or condensation of gases to accumulation mode aerosols. Course mode aerosols are generally formed from direct mechanical generation process (i.e. erosion) at the Earth’s surface. Within urban environments there are three distinct groups of particles; those with a diameter greater than 2.5 µm that dominant the volume distribution often referred to as coarse particles, those with a diameter less than 2.5 µm with dominant peaks in both the volume and surface area distributions often referred to as fine particles and those in largest number with a diameter of
Aerosols are affected by two physical forces; gravity and the kinetic energy of surrounding particles and molecules. Gravity pulls the particle downwards and causes sedimentation whereas the kinetic energy of surrounding molecules causes drag. The settling velocity (i.e. terminal velocity) is reached when the forces of drag and buoyancy on a particle is equal and opposite to the force of gravity. Stoke’s law states that the settling velocity of a spherical particle is proportional to the square of its radius (see E1.8). Particles with radii of 0.1µm have a settling velocity of around 0.2 m day\(^{-1}\) and are therefore essentially suspended whereas particles with radii of 100 µm have a settling velocity of around 0.5 m s\(^{-1}\) and therefore sediment out rapidly.

\[
\omega = \frac{2(\rho_p-\rho_f)gr^2}{9\mu}
\]  

(E1.8)

where \(\omega\) is the settling velocity, \(\rho_p\) is the density of particle, \(\rho_f\) is the density of fluid, \(g\) is the acceleration due to gravity, \(r\) is the radius of particle and \(\mu\) is the dynamic viscosity of fluid.

The atmosphere can be categorised into five layers based on changes in the mean temperature profile; the troposphere (\(~0-15\) km), the stratosphere (\(~15-50\) km), the mesosphere (\(~50-90\) km) and the thermosphere and exosphere (\(>\) ~90 km). Natural sources of tropospheric aerosols include sea-spray, wind-blown dust from erosion, forest fires and volcanoes. Mineral dust particles contribute the greatest fraction to tropospheric aerosol loading in terms of mass \(^{37,38}\). Anthropogenic emissions of aerosols are predominantly produced through combustion of fuel and account for approximately 20% of all solid particles in atmosphere \(^{39}\). Many aerosols in the troposphere are described as secondary aerosols. These aerosols are products of a gaseous phase reaction with lower vapour pressures that have condensed into particles fine enough to remain suspended. Gas-to-particle conversion occurring from natural sources are comparable to those produced by primary sources described above, however for anthropogenic sources secondary aerosols far outweigh primary aerosols. Examples of such a process are the oxidation of VOCs, where the vapour pressures of the products are lower than the reactants and hence form a secondary organic aerosol (SOA), or reactions of gas-phase ammonia with acid vapours to form inorganic ammonium salt aerosols. Theses inorganic salt aerosols tend to contain solid aggregates of salt which are in equilibrium with the dissolved salt in the aqueous medium that surrounds the aggregates and binds them together. Aqueous salts in the atmosphere cycle between liquid and crystalline phases depending on the amount of available gas-phase water in the atmosphere, controlled by the relative humidity (RH). RH dictates the amount of condensed aqueous salt aerosols in the atmosphere and also dictates their size. RH
is defined as the ratio between the partial pressure of water in the gas phase and the saturation vapour pressure of pure water at a fixed temperature. RH is given as a percentage with a fully saturated atmosphere having a RH of 100% and a dry desert atmosphere having a RH close to 0%. Depending on the chemical composition of an anhydrous solid particle, water vapour will condense on to it rapidly at a particular RH, increasing its size and forming a liquid. This is known as the deliquescence point. The deliquescence point of sodium chloride (NaCl) for example is at a RH of 75.3% at room temperature and atmospheric pressure. Past this point the size of the aerosol increases rapidly as RH is increased. However, hysteresis occurs as the solutes are dried meaning a solid particle is not formed from the liquid as the atmosphere dries (RH decreases) at the same RH at which deliquescence occurred. Regeneration of the solid particle from the condensed aerosol is known as efflorescence. At the efflorescence point a solid nucleus forms, however before this, due to the energy barriers of crystallization, the aerosol becomes super saturated forming a highly concentrated metastable solution.

Figure 1.4: Response of a solid particle of NaCl to changes in relative humidity at room temperature and atmospheric pressure. Reproduced from reference 40.

For aerosols that contain many different solid salt components it is important to know the composition and solubility of each salt component in order to determine the partitioning between solid, hydrated and the liquid phase. Depending on the RH, different components can become the dominant ion in the aerosol leading to significant changes to droplet pH.
The University of East Anglia have produced a publicly available model, the Atmospheric Inorganic Model (AIM) \(^{41}\), which predicts the change in volume of inorganic aerosols with relative humidity. Figure 1.5 presents the output from a model run for the theoretical change in the volume of 0.01 moles ammonium sulphate aerosols as the RH rises from 10\% (i.e. 0.1) to 99\% (0.99) at room temperature and atmospheric pressure. It shows that the deliquescence point for ammonium sulphate aerosols is \(\approx 80\%\).

![Figure 1.5: Response of solid particles of NaCl calculated by AIM to changes in relative humidity at room temperature and atmospheric pressure.](figure)

In the troposphere complex distributions of aerosol composition, size and morphology can be found, however, in the stratosphere the stratospheric sulphate aerosol is the main component of background aerosols \(^{42}\). These aerosols are composed of sulphuric acid and water and due to the thermal stability of the stratosphere they distribute into a thin layer, known as the Junge layer. These aerosols are formed by transport of precursors, such as sulphur dioxide (SO\(_2\)) emitted from volcanic eruptions or long lived sulphur compounds, e.g. carbonyl sulphide (COS), from the troposphere into the stratosphere \(^{26}\), which form sulphuric acid vapour that condenses onto particles. The heterogeneous chemistry of sulphate aerosols in the stratosphere is relatively well understood \(^{43}\), for instance the conversion of NO\(_3\) to nitric acid in the aerosol via N\(_2\)O\(_5\) adsorption and reaction, and also the activation of chlorine via the reaction of ClONO\(_2\) with HCl or water to form Cl\(_2\) and nitric acid within cold aerosols. It has been proposed that injection of aerosols into the stratosphere could be a possible solar radiation management scheme \(^{44}\). Such a scheme would have the effect of cooling the Earth’s surface as
the injected aerosols would scatter solar radiation back to space and serve as a measure to mitigate enhanced global warming. The obvious candidate for stratospheric injection is sulphuric acid aerosols, however injection of these particles could have important negative effects on the stratosphere through enhanced ozone depletion. After the eruption of Mt. Pinatubo in 1991, it was estimated that around 30 Tg of H$_2$SO$_4$ was injected in the stratosphere, resulting in a large increase of stratospheric aerosol loading and hence the available surface area for heterogeneous chemistry mentioned to occur. Following this volcanic event, the average global lower tropospheric temperature did decrease by 0.5 K $^{45}$, however, stratospheric ozone concentrations reached a record low in northern mid-latitudes $^{45}$, suggesting that sulphate aerosols are likely to be unsuitable for solar radiation management. TiO$_2$ particles have been proposed as a suitable alternative due to their large refractive indices $^{47}$, meaning that much less stratospheric aerosol loading would be required to achieve an equal level of cooling. The refractive index of TiO$_2$ particles at 550 nm is 2.5 compared to a value of 1.5 for naturally occurring stratospheric sulphate aerosols $^{48}$. If it is assumed that the size of TiO$_2$ particles can be optimised, it has been reported that to accomplish the same cooling effect that sulphate aerosols had during the Mt. Pinatubo event, approximately three times less in mass, and seven times less in volume of TiO$_2$ particles would be required compared with sulphate aerosols $^{47}$.

The kinetics of N$_2$O$_5$ $^{48}$ and ClONO$_2$ $^{49}$ uptake onto TiO$_2$ particles have been studied. Uptake of N$_2$O$_5$ results in the conversion to NO$_x$ (NO$_x$ = NO + NO$_2$) which is involved in a catalytic cycle that leads to significant O$_3$ depletion and production of non-reactive HNO$_3$.

The only known aerosols in the mesosphere are ice particles within noctilucent clouds $^{50}$ and meteoric smoke particles (MSP) that are formed by recondensation of the metallic vapours which are released by meteoric ablation $^{51}$. MSP are probably composed of Fe-Mg silicates known as Olivines $^{52}$.

### 1.11 Mechanism of Heterogeneous Uptake onto Aqueous Aerosols

#### 1.11.1 Resistance Model

Condensed water is the principal form of aerosol in the troposphere with clouds occupying approximately 7% of its volume $^{26}$. Aqueous phase aerosols are very important for heterogeneous uptake as they generally result in higher values of $\gamma$(HO$_2$) than dry aerosols. The overall volume of aerosols in the aqueous phase is small, however the collision rate of gas phase species with condensed phase aerosols is relatively rapid. Within typical polluted areas each gas phase molecule undergoes a collision with a condensed phase aerosol every few minutes $^4$. Figure 1.6 presents the steps involved in the reactive heterogeneous uptake of a molecule in the gaseous phase onto a liquid droplet.
The steps presented in Figure 1.6 are:

1. gas phase transport of the reactant to the surface of the droplet;
2. accommodation at the surface of the droplet;
3. diffusion into the droplet;
4. chemical reaction with a chemical species dissolved in the droplet;
5. diffusion of unreacted molecules or product to the surface of the droplet; and
6. desorption of species from the interface.

This process is often parameterised with the analogy of resistance in an electrical circuit, leading to what is known as the Resistance Model, whose essentials are described by E1.9.

Each step in the process is treated in terms of conductance ($\Gamma$) and normalised to the rate of gas-surface collisions $^3$.

\[
\frac{1}{\gamma(\text{HO}_2)} = \frac{1}{\Gamma_{\text{gas\ diff}}} + \frac{1}{\Gamma_{\text{sol}}} + \frac{1}{\Gamma_{\text{rxn}}} \tag{E1.9}
\]

where $\Gamma_{\text{gas\ diff}}$ is the conductance associated with gas-phase diffusion to the surface of the aerosol, $\Gamma_{\text{sol}}$ is the conductance associated with solubility, $\Gamma_{\text{rxn}}$ is the conductance associated with the reaction in the aqueous bulk, $\gamma(\text{HO}_2)$ is the uptake coefficient of HO$_2$ and $\alpha$ is the mass accommodation coefficient. Note the reciprocal of conductance is equal to resistance.

Step one of the process of heterogeneous uptake involves diffusion of the gas phase molecule to the surface of the aerosol which is dependent on the gas phase diffusion coefficient ($D_g$) and...
gas-surface collision frequency. This is process is characterised in the Resistance Model by $\Gamma_{\text{gas diff}}$. It can be assumed that the gas-surface collision frequency can be determined by the ambient pressure surrounding the droplet, however as gas-phase molecules are accommodated by the aerosol the concentration of the gas species around the surface depletes causing additional diffusion to the interface in accordance with Fick’s Law (i.e. diffusive flux goes from regions of high concentration to regions of low concentration). Gas-phase diffusion may provide significant resistance in the uptake process if transfer across the interface into the bulk is favourable, and therefore the rate of accommodation is limited by diffusive flux towards the aerosol alone. If this is slow, gas molecules around the surface are not sufficiently replenished. The conductance of gas-phase diffusion is calculated using E1.10.

$$\frac{1}{\Gamma_{\text{gas diff}}} = \frac{0.75 + 0.238Kn}{Kn(1 + Kn)}$$  \hspace{1cm} (E1.10)

where $Kn$ is the Knudsen number, defined as $\lambda/a$, $\lambda$ is the gas-phase mean path and $a$ is the radius of particle. The gas-phase mean free path is expressed in E1.11.

$$\lambda = \frac{3D_g}{\bar{c}}$$  \hspace{1cm} (E1.11)

where $\bar{c}$ is the average molecular speed (cm s$^{-1}$).

Once the gas phase molecule collides with the surface it will either “bounce” off the surface or be accommodated into the interface of aerosol. The fraction of gas phase molecules that are accommodated is a function of the viscosity of the aerosol. The interface of the aerosol is midway in its character between the gas and bulk liquid phases and is only a few monolayers in thickness. The fraction of gas phase molecules that are accommodated into the aerosol against the number of collisions with the aerosol surface is defined as the mass accommodation coefficient ($\alpha$). The flux of molecules into the droplet ($J$) in the absence of chemical reactions can be calculated using E1.12.

$$J = \frac{n_g c \alpha}{4}$$  \hspace{1cm} (E1.12)

where $n_g$ is the concentration of the gas (molecules cm$^{-3}$).

From here most molecules diffuse into the bulk of the aerosol however some molecules, known as surfactants, preferentially adsorb to the interface rather than undergo full solvation into the bulk. Surfactants have hydrophilic heads and hydrophobic tails and consequently it is less energetically favourable for these molecules to diffuse in the bulk where they would disrupt hydrogen bond networks. Diffusion in the liquid bulk of the aerosol is characterised in the Resistance Model by $\Gamma_{\text{sol}}$. Diffusion in the liquid is governed by the diffusion coefficient in the liquid ($D_l$) 53.
Uptake of the gas-phase molecule by the aerosol can either lead to desorption back into the atmosphere, i.e. non-reactive uptake, or a reaction within the bulk of the aerosol which leads to its destruction, i.e. reactive uptake. If there is non-reactive uptake or if the rate of reaction is slower than the rate of uptake and diffusion in the liquid equilibrium between the concentrations of the gas phase and liquid phase molecules occurs, the process can be expressed by E1.9 but without $\Gamma_{\text{rnx}}$. For volatile solutes (e.g. HO$_2$ and H$_2$O$_2$), the amount of gas that dissolves in the condensed phase aerosol is directly proportional to the partial pressure of the gas in equilibrium with the aerosol. This is known as Henry’s Law and is expressed in E1.13. Gases with high Henry’s law coefficients are very soluble whereas gases with low Henry’s law coefficients are not.

$$[A_{\text{aq}}] = H_A p_A$$  \hspace{1cm} (E1.13)

where $[A_{\text{aq}}]$ is the concentration of the gas A in water, $H_A$ is the Henry’s law coefficient for the gas (M atm$^{-1}$) and $p_A$ is the partial pressure of the gas.

Diffusion in the liquid is much slower than diffusion in a gas and is often the rate determining step. It often becomes a critical factor when the probability of the accommodation is great and gas-phase diffusion is not a limiting factor as the concentration of the gas rapidly increases within the interface preventing further accommodation. Over time the partitioning between gas and liquid phases will reach equilibrium. As the equilibrium point is approached the solubility, and therefore $\Gamma_{\text{solv}}$ decreases. The time taken for equilibrium to be reached is expressed in E1.14.

$$t = \frac{r \times H \sqrt{2\pi M R T}}{3\alpha}$$  \hspace{1cm} (E1.14)

where $r$ is the radius of the droplet (m), $H$ is the Henry’s law coefficient (M atm$^{-1}$), $T$ is the temperature (K) and $R$ is the molar gas constant (kg m$^2$ mol$^{-1}$ K$^{-1}$ s$^{-2}$).

Reactive uptake occurs when the rate of the reaction with accommodated species and an aqueous reagent within the deliquesced aerosol is greater than rate of uptake and diffusion. In some cases, the rate of reaction is so quick that reaction can occur within the interface of the aerosol or if slower and following diffusion in the bulk of the aerosol. The conversion of the accommodated species to a product may serve to offset saturation of the accommodated species, allowing continual uptake beyond that calculated by Henry’s law. The thickness of the layer where a reaction in the aqueous layer occurs can be calculated using E1.15 and the conductance of reaction in the bulk, $\Gamma_{\text{rnx}}$, is expressed in E1.16. Both E1.15 and E1.16 demonstrate the link with liquid diffusivity and reaction rate and therefore $\Gamma_{\text{rnx}}$ and $\Gamma_{\text{solv}}$. 

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\[ l = \sqrt{\frac{D_l}{k_{rxn}}} \]  
\[ \frac{1}{l_{rxn}} = \frac{\varepsilon}{4HRT} \sqrt{\frac{D_l}{k_{rxn}}} \]  
\[ \text{where} \ \bar{\varepsilon} \text{ is the average molecular speed, } D_l \text{ is the diffusion coefficient in liquid and } k_{rxn} = \text{rate constant for reaction.} \]

For smaller particles, \( l \) can be larger than the diameter of the aerosol and therefore there is no concentration gradient driving diffusion, which results in lower uptake than expected. A complication occurs when the reaction occurs within the interfacial region. When chemical reactions occur in this region reactive loss at the surface competes with \( \alpha \) and successive reactions in the liquid phase. Significant effects to the uptake coefficient can occur when there is potential for the formation of surface complexes, an increase of reactant concentration at the interface due to surface excess or electric double layer formation and the reaction rate is so fast that the reacto-diffusive length is only a few molecular diameters. In order to account for surface reactions another term (\( \Gamma_{surf} \), E1.17) can be added to the Resistor Model as presented in E1.18.

\[ \frac{1}{\Gamma_{surf}} = \frac{\bar{\varepsilon}}{4k_{surf}b'} \]  
\[ \text{where } b' \text{ is the surface adsorption equilibrium constant and } k_{surf} \text{ is the rate constant for surface reaction.} \]

\[ \frac{1}{\gamma} = \frac{1}{\Gamma_{diff}} + \frac{1}{s} + \frac{1}{s_{des}} + \frac{1}{s_{surf}} \]  
\[ \text{(E1.18)} \]

1.11.2 Self-Reaction

As HO₂ enters the aqueous phase within a condensed aerosol, it is most likely to react with another HO₂ molecule or with its conjugate base as shown in R1.36 – R1.38.

\[ \text{HO}_2(aq) + \text{HO}_2(aq) \rightarrow \text{H}_2\text{O}_2(aq) + \text{O}_2(aq) \]  
\[ \text{(R1.36, } k = 8.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}) \]

\[ \text{HO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{O}_2^- (aq) \]  
\[ \text{(R1.37)} \]

\[ \text{HO}_2(aq) + \text{O}_2^- (aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}_2(aq) + \text{OH}^- (aq) + \text{O}_2(aq) \]  
\[ \text{(R1.38, } k = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}) \]

Thornton and Abbatt \(^{54}\) conducted experiments of HO₂ uptake by sulphuric and ammonium sulphate aerosols. The results of the study suggest that the reaction is second-order with respect to aqueous HO₂ concentrations and is strongly temperature, pH and aerosol volume dependent (discussed in more detail later in section 1.13). The literature values for the rate
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constants of HO₂ loss via R1.36 and R1.38 shows that R1.38 occurs around 100 times faster. The rate of loss of HO₂ to R1.38 can be defined as:

\[-\frac{d[\text{HO}_2]}{dt} = 2k[\text{O}_2(\text{l})]^2\]  \hspace{1cm} (E1.19)

where \([\text{O}_2(\text{l})] = [\text{HO}_2(\text{aq})] + [\text{O}_2^-(\text{aq})]

Thornton et al. \(^*\) derived E1.20 from the resistor model to calculate \(\gamma(\text{HO}_2)\) due to the self-reaction of HO₂. It shows that \(\gamma(\text{HO}_2)\) is proportional to the concentration of HO₂ in the gas-phase, \([\text{HO}_2(\text{g})]\), the radius of the aerosol \(r_p\) and the square of the effective Henry’s Law constant \(H_{\text{eff}}\) which itself is inversely proportional to temperature.

\[\frac{1}{\gamma} = \frac{1}{a} + \frac{3cN_A}{8000H_{\text{eff}}RT^2k_{\text{eff}}[\text{HO}_2(\text{g})]^2r_p}\]  \hspace{1cm} (E1.20)

where \(c\) is the mean molecular speed \((\text{cm s}^{-1})\), \(k_{\text{eff}}\) is the effective rate constant and \(N_A\) is Avogadro’s number.

1.11.3 Reaction with Transition Metal Ions

HO₂ reacts rapidly with aqueous transition metal ions (TMI), such as Cu(II) and to a lesser extent Fe(II) due to its lower solubility and reactivity. O₂ reacts around 10-100 times quicker than HO₂ with TMI \(^\dagger\). Cu(II) catalyses the conversion of HO₂ to H₂O₂ and O₂ in the aqueous phase deliquesced aerosols, as shown in the reaction mechanism below (R1.39 – R1.42):

\[
\begin{align*}
\text{HO}_2(\text{aq}) + \text{Cu}(\text{II})(\text{aq}) &\rightarrow \text{Cu}(\text{I})(\text{aq}) + \text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) \quad \text{R1.39, } k = 1.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \\
\text{O}_2(\text{aq}) + \text{Cu}(\text{II})(\text{aq}) &\rightarrow \text{Cu}(\text{I})(\text{aq}) + \text{O}_2(\text{aq}) \quad \text{R1.40, } k = 9.4 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \\
\text{HO}_2(\text{aq}) + \text{Cu}(\text{I})(\text{aq}) + \text{H}_2\text{O}(\text{l}) &\rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{Cu}(\text{II})(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{R1.41, } k = 1.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \\
\text{O}_2(\text{aq}) + \text{Cu}(\text{I})(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) &\rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{Cu}(\text{II})(\text{aq}) + 2\text{OH}^-(\text{aq}) \quad \text{R1.42, } k = 8.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}
\end{align*}
\]

R1.39 can be the rate limiting step in acidic solutions as R1.40 and R1.42 are rapid. The catalytic conversion of HO₂ to H₂O₂ and O₂ by Fe is thought to be as follows (R1.43 – 1.46) \(^?\):

\[
\begin{align*}
\text{Fe}(\text{II})(\text{aq}) + \text{HO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) &\rightarrow \text{Fe}(\text{III})(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{R1.43, } k = 1.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \\
\text{Fe}(\text{OH})^{2+}(\text{aq}) + \text{HO}_2(\text{aq}) &\rightarrow \text{Fe}(\text{II})(\text{aq}) + \text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \quad \text{R1.44, } k = 2.0 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \\
\text{Fe}(\text{II})(\text{aq}) + \text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) &\rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{Fe}(\text{III})(\text{aq}) + 2\text{OH}^-(\text{aq}) \quad \text{R1.45, } k = 1.0 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \\
\text{Fe}(\text{OH})^{2+}(\text{aq}) + \text{O}_2(\text{aq}) &\rightarrow \text{Fe}(\text{II})(\text{aq}) + \text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{R1.46, } k = 8.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}
\end{align*}
\]

The decay of HO₂ in the presence of Cu(II) and Fe(II) doped aerosols follows first order reaction kinetics \(^5\). E1.21 demonstrates the relationship between the first-order rate constant \((k_{\text{300}})\) and \(\gamma\).
where $A$ is the total aerosol surface area, $\bar{c}$ is the mean molecular velocity and $\gamma$ is the uptake coefficient.

If gas-phase diffusion limits uptake, such as for larger aerosols or high $\alpha$, then the Fuchs and Sutugin correction needs to be applied (E1.22).

$$k_{\text{true}} = \gamma \frac{\bar{c} S_a}{4} (1 + \gamma \lambda(r))^{-1}$$  \hspace{1cm} (E1.22)

where $\bar{c}$ is the mean molecular speed, $\gamma$ is the true reactive uptake coefficient, $S_a$ is the total surface area and $\lambda$ is related to the Kn number (see E1.23 and E1.24)

$$\lambda(r) = \frac{0.75 + 0.283 Kn}{Kn(1 + Kn)}$$  \hspace{1cm} (E1.23)

$$Kn = \frac{3D_g}{\bar{c} r}$$  \hspace{1cm} (E1.24)

where $D_g$ is the gas diffusion coefficient (cm$^2$ s$^{-1}$) and $r$ is the radius of aerosol (cm).

Mozurkewich et al. performed the first pioneering experiments to measure the $\gamma$(HO$_2$) onto deliquesced Cu(II)-doped inorganic aerosols. As the reaction between Cu(II) for HO$_2$ in the aqueous phase is rapid and irreversible and the Henry’s Law constants for H$_2$O and O$_2$ show that these products will evaporate quickly from the aerosol, these measurements were considered to be kinetic upper limit values of $\gamma$(HO$_2$) and therefore estimates of $\alpha$. They found that in order to get significant HO$_2$ uptake the molality of Cu(II) had to be around $10^{-3}$ moles kg$^{-1}$. At concentrations of Cu(II) in the aerosol $> 0.05$ moles kg$^{-1}$ the most efficient scavenging was observed, although much higher concentrations were not used in order to minimize the effects to the deliquescence of the aerosol. A molality of $10^{-3}$ moles kg$^{-1}$ at a RH of around 74% corresponds to a solute mass fraction in the experiments of $1.5 \times 10^{-4}$. Usually free aqueous Cu(II) concentrations are around $10^{-9} - 10^{-6}$ moles kg$^{-1}$ in cloud and rainwater and around $10^{-4} - 10^{-1}$ moles kg$^{-1}$ in aerosols due to the differences in cloud droplet and aerosol volumes. In order to calculate $\gamma$(HO$_2$) for aerosols doped with TMI the follow equation (E1.25) was derived.

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{c}{H_{eff} RT \sqrt{k^1 D_{aq} Q}}$$  \hspace{1cm} (E1.25)

where $k^1$ is the pseudo-first-order rate constant equal to $k_{ITMI}[TMI]$ where $k_{ITMI}$ is the second order rate constant for aqueous phase reaction with HO$_2$/O$_2$ and TMI, $H_{eff}$ is the effective Henry’s Law coefficient, $\bar{c}$ is the mean molecular speed and $Q$ accounts for aqueous-phase diffusion limitations and is expressed below in E1.26.
\[ Q = \left[ \coth(q) - \frac{1}{q} \right]; q = r_p \sqrt{\frac{k_I}{D_{aq}}} \] (E1.26)

Mozurkewich et al. and George et al. both show that concentrations of Cu(II) in the aerosol need to be > 1x10^{-2} moles kg^{-1} for values of \(\gamma(\text{HO}_2)\) to be approximately equal to \(\alpha\). The implications for this result are that it is unlikely concentrations of Cu(II) would reach this level in cloud and rain water and for more than 50% of free aqueous Cu(II) aerosols in the atmosphere. Other issues such as Cu(II) in aerosols becoming part of a tightly bound, highly ionic and organic rich complexes could also reduce the Cu(II) available in the atmosphere for catalysis of \(\text{HO}_2\). Work undertaken by Taketani et al. measured relatively high \(\gamma(\text{HO}_2)\) (0.09 - 0.4) for aerosols produced by water extracts in China. The concentrations of Cu and Fe in the aerosols were 10 – 80 ng m^{-3} and 1.7 - 11.6 µg m^{-3} respectively. They calculated that only a small percentage of the Cu and Fe are in the free aqueous ion form. Lakey et al. have also shown that the addition of an organic compound to Cu(II) doped aerosols, such as oxalic acid which forms oxalate ions (C\(_2\)O\(_4\))\(^2-\) in the aerosol, results in lower \(\gamma(\text{HO}_2)\) as such ions forms a complex with the TMI.

There have been a number of studies showing that aerosols containing TMI result in much higher \(\gamma(\text{HO}_2)\) values than those without. Thornton and Abbatt showed that the decay of \(\text{HO}_2\) within aerosol flow tube experiments does not differ significantly with or without deliquesced \(\text{H}_2\text{SO}_4\) aerosols present, however upon addition of Cu(II)-doped \(\text{H}_2\text{SO}_4\) aerosols \(\text{HO}_2\) decays rapidly.

Mao et al. proposed a different catalytic mechanism when Cu(II) and Fe(II) ions are both present within the bulk of a deliquesced aerosol. They propose that the Cu(II) and Fe(II) couple together and act as a catalyst to convert \(\text{HO}_2\) to H\(_2\)O rather than H\(_2\)O\(_2\). The proposed reaction mechanism initiates with Cu(II) reacting with \(\text{HO}_2\) as presented in R1.39, a redox reaction with Cu(I) and Fe(III) occurs (R1.47) and Fe(II) will terminate the cycle with reactions R1.49 or R1.50.

\[
\begin{align*}
\text{Cu(I)}_{(aq)} + \text{Fe(III)}_{(aq)} &\rightarrow \text{Cu(II)}_{(aq)} + \text{Fe(II)}_{(aq)} \quad \text{(R1.47)} \\
\text{Fe(II)}_{(aq)} + \text{HO}_2_{(aq)} + \text{H}^+_{(aq)} &\rightarrow \text{Fe(III)}_{(aq)} + \text{H}_2\text{O}_2_{(aq)} \quad \text{(R1.48)} \\
\text{Fe(II)}_{(aq)} + \text{H}_2\text{O}_2_{(aq)} \quad \text{(}+ \text{H}^+\text{)} &\rightarrow \text{Fe(III)}_{(aq)} + \text{OH}_{(aq)} + \text{H}_2\text{O}_{(l)} \quad \text{(R1.49)} \\
\text{Fe(II)}_{(aq)} + \text{OH}_{(aq)} \quad \text{(}+ \text{H}^+\text{)} &\rightarrow \text{Fe(III)}_{(aq)} + \text{H}_2\text{O}_{(l)} \quad \text{(R1.50)}
\end{align*}
\]

Conversion of \(\text{HO}_2\) to \(\text{H}_2\text{O}_2\) limits how effective heterogeneous uptake is as a potential atmospheric sink of \(\text{HO}_2\). \(\text{H}_2\text{O}_2\) can readily photolyse to OH and therefore go on to recycle \(\text{HO}_2\). There are a number of field and modelling studies that support Mao’s hypothesis.
that HO$_2$ is indeed converted to H$_2$O upon reactive uptake. Predictions by a GEOS-Chem modelling study overestimated measurements of both HO$_2$ and H$_2$O$_2$ taken on the DC-8 aircraft during the ARCTAS spring field campaign in 2008. Mao et al. made his own interpretation of this data using GEOS-Chem in order to gain a better understanding of HO$_x$ and HO$_y$ (HO$_x$ + peroxides) chemistry. HO$_2$ uptake in the model was parameterized by using values of $\gamma$(HO$_2$) from 0.02 at 275 K to 0.5 at 220 K, reflecting the negative temperature dependence of the mass accommodation coefficient ($\alpha$) (see section 1.13.2). It also found that the standard gas-phase models over-predicted concentrations of HO$_2$ (by a factor of 2) and H$_2$O$_2$ if reactive uptake resulted in the conversion of HO$_2$ to H$_2$O$_2$. Mao et al. went onto alter the chemistry within the model so that reactive uptake of HO$_2$ resulted in the production of H$_2$O, resulting in better correlation between modelled and measured vertical distributions of both HO$_x$ and HO$_y$. As the Arctic spring is characterized by very low temperatures along with relatively high aerosol loading, conditions are favourable to HO$_2$ uptake. The model showed that heterogeneous uptake by aerosols account for around 30% loss of OH and HO$_2$ in the arctic troposphere and is the dominant sink of HO$_2$ at altitudes greater than 5 km.

Liang et al. took measurements of H$_2$O$_2$ using a wet-scrubber technique (phosphoric acid eluent) in Beijing, an urban environment. They found that a gas-phase chemistry box model (NCAR Master Mechanism) gave good agreement with measured data during non-hazy days, however during hazy days, where there was greatly enhanced aerosol loading and aerosol liquid water content, the model significantly over-predicted concentrations of H$_2$O$_2$. By adding a mechanism for HO$_2$ uptake that did not result in the conversion of HO$_2$ to H$_2$O$_2$ within the model, agreement between measured and modelled H$_2$O$_2$ concentrations was reached.

1.12 Mechanism of Heterogeneous Uptake onto Solid Aerosols

Experimental determination of $\gamma$(HO$_2$) for a variety of aerosols have shown that dry solid aerosols usually exhibit lower values of $\gamma$(HO$_2$) than those that have wet condensed surfaces. Taketani et al. experimentally determined that $\gamma$(HO$_2$) for deliquesced NaCl aerosols was 0.1, however $\gamma$(HO$_2$) onto effloresced NaCl aerosols reduced by an order of magnitude (0.01). Values of $\gamma$(HO$_2$) measured onto mineral dusts such as Arizona Test Dust (ATD) are also lower (0.031) than values onto deliquesced aerosols. Although $\gamma$(HO$_2$) onto dry solid aerosols tend to be lower than onto wet deliquesced aerosols, HO$_2$ uptake onto such aerosols can still be a significant sink of HO$_2$ during episodes of high aerosol loading, such as Saharan dust storms. Matthews et al. evaluated the impact HO$_2$ uptake would have during such events to ambient levels of HO$_2$. They applied the measured value of $\gamma$(HO$_2$) onto ATD (0.031), a proxy for all mineral dusts, to calculations for HO$_2$ uptake into a box model (MCM v3.1) constrained to conditions that were measured at the Cape Verde Atmospheric Observatory during the Radical
Halogens in the Marine Boundary Layer (RHaMBLe) field campaign in 2007. This area experiences periods of high aerosol loading due to seasonal Saharan dust events during the winter. During days of high aerosol loading uptake of HO₂ by Saharan dust accounted for around 10% loss of ambient HO₂.

There are two mechanisms possible for the heterogeneous reactions of HO₂ by solid dry aerosols; the Eley-Rideal and Langmuir-Hinshelwood. The Eley-Rideal (ER) mechanism involves one gas-phase molecule adsorbing onto the surface of the aerosol and a second molecule still in the gas-phase reacts with it, whereas the Langmuir-Hinshelwood (LH) mechanism involves both molecules adsorbing on to the surface of the aerosol and diffusing across the surface until they undergo a bimolecular reaction. Although reaction of HO₂ and a solid aerosol may occur it is likely that aerosol merely provides a surface for HO₂ to undergo self-reaction upon. The ER and LH mechanisms for HO₂ self-reaction are presented in R1.51 to R1.54.

Eley-Rideal Mechanism:

\[
\text{HO}_2(g) + S(s) \rightleftharpoons \text{HO}_2\cdot S(s) \quad (R1.51)
\]

\[
\text{HO}_2\cdot S(s) + \text{HO}_2(g) \rightarrow \text{H}_2\text{O}_2(g) + S-O_2(s) \quad (R1.52)
\]

Langmuir-Hinshelwood Mechanism:

\[
2\text{HO}_2(g) + 2S(s) \rightleftharpoons 2\text{HO}_2\cdot S(s) \quad (R1.53)
\]

\[
2\text{HO}_2\cdot S(s) \rightarrow S\cdot\text{H}_2\text{O}_2(s) + S-O_2(s) \quad (R1.54)
\]

Loukhovitskaya et al.⁶⁸ provided evidence of the self-reaction mechanism when they observed H₂O₂ as a product of the interaction between HO₂ and dry salt surfaces. They determined that the ratio of H₂O₂ being formed to HO₂ being lost was 0.48 ± 0.12 (i.e. for every two molecules of HO₂ lost one molecule of H₂O₂ is formed, overall 2HO₂ → H₂O₂) strongly indicating that the reactive loss of HO₂ occurs via self-reaction.

Remorov et al.⁶⁹ conducted experiments studying the heterogeneous uptake of HO₂ onto a dry NaCl coated rod within a temperature controlled flow tube. The results of the experiments showed γ(HO₂) was strongly negative temperature dependent (see section 1.12.2). They modelled the experiments dependence to temperature based purely on the ER mechanism and found good correlation with experimental data, however the rate constants for the reaction between the adsorbed molecule and gaseous molecule required were larger than those for the purely gas-phase reaction and therefore were judged to not be correct. Instead a mixture of both ER and LH mechanisms gave the best correlation with kinetic data. The theoretical value of γ(HO₂) can be calculated using E1.27. E1.27 can be simplified when only considering the
ER mechanism as \( \theta \) (surface coverage) is equal to 0 as the mechanism does not involve the reaction of two adsorbed species.

\[
\gamma = \frac{2f_{\text{LH}}k(\theta Z)^2}{k_{\text{ads}}[\text{HO}_2]} + \frac{2f_{\text{ER}}k(1-\theta)Z}{k_{\text{ads}}} \times d
\]

(E1.27)

where \( f \) is the average fractions of the salt sites that favour either the ER or LH mechanism, \( k \) is the rate coefficient of reaction, \( k_{\text{ads}} \) is the rate coefficient of adsorption, \( k_{\text{des}} \) is the rate coefficient for desorption, \( \theta \) is the surface coverage, \( Z \) is the surface density of the ionic salt species and \( d \) is a kinetic parameter defined in E1.28 below:

\[
d = \frac{k_{\text{ads}}[\text{HO}_2]}{k_{\text{ads}}[\text{HO}_2] + kZ[\text{HO}_2] + k_{\text{des}}Z}
\]

(E1.28)

1.13 Parameters that Influence Heterogeneous Uptake

The parameterisation of \( \gamma(\text{HO}_2) \) experimentally allows the derivation of expressions for its dependence on environmental and chemical parameters that can then be inputted into numerical models in order to give a more detailed interpretation of the heterogeneous processes within them. This will allow for better comparison of model predictions with field measurements. It should also be noted that a number of parameters are inextricably linked with each other. An example of this is that as the size of the deliquesced aerosol increases as RH is increased resulting in the dilution of \( \text{H}^+ \) reducing the pH of the sea salt aerosol. Both RH and the pH of an aerosol strongly affects \( \gamma(\text{HO}_2) \). Previous studies have used an equilibrium model (EQUISOLV II) to investigate the pH of sea salt aerosol as RH increases using measurements taken during the Aerosol Characterisation Experiment (ACE 1) campaign.

1.13.1 Aerosol pH

Aqueous \( \text{HO}_2 \) is a weak acid at room temperature \( (pK_a \sim 4.7) \), therefore making its solubility and reactivity in the aerosol dependent on pH. Both the rate of the self-reaction and the reaction with TMI are strongly dependent on the pH of the deliquesced aerosol, as pH strongly effects equilibrium of \( \text{HO}_2 \) dissociation to its conjugate base, \( \text{O}_2^- \). The solubility of aqueous \( \text{HO}_2 \) is enhanced within aerosols with a pH > 4 due to its dissociation and thereby decreasing the evaporative flux out of gaseous \( \text{HO}_2 \) out of the aerosol. This effect on the solubility, i.e. the Henry’s Law constant, of aqueous \( \text{HO}_2 \) can be calculation using E1.29.

\[
H^\text{eff} = H^\text{HO}_2 \left( 1 + \frac{K_{\text{eq}}}{[\text{H}^+]} \right)
\]

(E1.29)

For cloud water with a pH \( \leq 5 \) the self-reaction mechanism (see section 1.11.2) is the most important loss pathway for \( \text{HO}_2 \). Although the reaction is slow, the dominant \( \text{HO}_2 \) loss reaction in cloud chemistry modelling at pH < 3 is \( \text{HO}_2 + \text{HO}_2 \), whereas, the dominant reaction
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at pH ~ 5 is HO$_2$ + O$_2^-$ which reacts over two orders of magnitude faster. The effect of the pH on the rate constant for the self-reaction mechanism is expressed in E1.30.

\[
 k_{\text{eff}} = \frac{k_{36} + \left( \frac{k_{36}}{[H^+][aq]} \right) k_{38}}{1 + \left( \frac{k_{36}}{[H^+][aq]} \right)^2}
\]  

(E1.30)

\( \gamma(\text{HO}_2) \) has been measured on aqueous H$_2$SO$_4$ and aqueous (NH$_4$)$_2$SO$_4$ aerosols buffered to pH 5.1 \(^{54}\), although due to the hygroscopic properties of inorganic salt aerosols it is doubtful that the pH of aerosols can be controlled in this way. For aqueous H$_2$SO$_4$ aerosols, the rate of HO$_2$ uptake was too small to be detected under the experimental conditions and it was estimated that an upper limit value for \( \gamma(\text{HO}_2) < 0.01 \), however at the optimized pH of 5.1 the buffered ammonium sulphate aerosols resulted in clear HO$_2$ decay yielding a value for \( \gamma(\text{HO}_2) \sim 0.1 \).

The effect of deliquesced aerosol pH on the value of \( \gamma(\text{HO}_2) \) has previously been modelled using E1.20 in section 1.11.2 and E1.29 and E1.30 given above \(^{24}\). This study shows a dramatic linear increase of \( \gamma(\text{HO}_2) \) as pH was increased from 2 to 8. Below a pH of 2 and above a pH of 8 \( \gamma(\text{HO}_2) \) is predicted to be independent of pH. Indeed, above a pH of 8 \( \gamma(\text{HO}_2) \) is predicted to reach its theoretical maximum value of one \(^{24}\).

1.13.2 Temperature

Both theoretical \(^{24}\) and experimental \(^{8}\) studies show that \( \gamma(\text{HO}_2) \) has a negative dependence to temperature. This dependency occurs for heterogeneous uptake by both deliquesced and effloresced aerosols and can be explained by both the negative temperature dependence of the solubility of a gas in liquid (i.e. Henry’s Law constant) and of the mass accommodation coefficient, \( \alpha \). As a gas has higher entropy than a liquid, the entropy of the system decreases as a gas dissolves in a liquid, which is unfavourable. However, when a gas dissolves in a liquid heat is released as this process is exothermic (\( \Delta H < 0 \)), which is also true for adsorption of a gas onto a solid. As discussed, the concentration of a species in the aqueous phase is in dynamic equilibrium with the concentration of the species in the gas phase. Therefore, increasing the temperature favours higher entropy, i.e. \( [A_{\text{aq}}] \rightarrow [A_{\text{g}}] \), and Le Chatelier’s principle dictates that the system counteracts the increase of temperature by favouring the endothermic effect of desorption of the species from the aqueous phase to the gaseous \(^{71}\).

These effects therefore reduce the solubility of HO$_2$ and the likelihood that it will be accommodated upon collision with the aerosol surface. As with pH, the same methodology has been used to model dependence of \( \gamma(\text{HO}_2) \) to temperature \(^{24}\). The study shows a strong negative linear relationship between \( \gamma(\text{HO}_2) \) and temperature until \( \gamma(\text{HO}_2) \) reaches its maximum value of one. An experimental study of \( \gamma(\text{HO}_2) \) and temperature onto dry NaCl surfaces also show a strong negative temperature dependence \(^{69}\).
1.13.3 Relative Humidity

There have been a number of studies that report the effect that RH has on $\gamma$(HO$_2$). Deliquesced salt aerosols consistently show higher $\gamma$(HO$_2$) values than effloresced salt aerosols as fast aqueous phase chemistry can occur. As RH is increased beyond the deliquescence point of the aerosol, it rapidly takes up water and grows in size. This results in an increase of $\gamma$(HO$_2$) due to a reduction in aerosol pH and an increase of the aerosol surface area, which in turn increases the rate of uptake, although aerosol growth also leads to gas-diffusion limitations.

Studies of $\gamma$(HO$_2$) onto solid surfaces and aerosols give contradictory results as water can either act as a promoter or inhibitor of HO$_2$ uptake depending on the chemistry at play. One study showed that increasing the RH within their apparatus resulted in a decrease of $\gamma$(HO$_2$) on dry NaCl surfaces, whilst another study contradicted this result and showed no change of $\gamma$(HO$_2$) at all between RH 0 – 28%. A study of $\gamma$(HO$_2$) onto MgCl$_2$.6H$_2$O aerosols showed a significant drop in $\gamma$(HO$_2$) as RH was increased, suggesting that water rapidly adsorbs on to the surface having an inhibiting effect on HO$_2$ uptake, whereas, a study of $\gamma$(HO$_2$) on Arizona Test Dust (ATD) shows that $\gamma$(HO$_2$) shows a general increasing trend as RH was increased.

A study was conducted which sought to measure $\gamma$(HO$_2$) for polystyrene latex (PSL) particles, which do not change size with RH and therefore any change of $\gamma$(HO$_2$) is unlikely to be associated with the presence of water on the particle, and levoglucosan particles (a product of biomass burning) which do but not in the typical stepwise hygroscopic growth typical of inorganic salt aerosols. The surfaces of levoglucosan particles are never dry, even at 4% RH. The results of their experiment show a clear positive dependence of $\gamma$(HO$_2$) with RH for both types of aerosols. Values of $\gamma$(HO$_2$) onto levoglucosan particles correlate well with hygroscopic growth of the particles, however, as PSL particles do not undergo such growth its positive dependence on RH must be associated with something other than the water content of the particle. The HO$_2$.H$_2$O complex has been observed in the gas phase. The study speculates that under humid conditions more HO$_2$.H$_2$O will form, and if uptake of HO$_2$.H$_2$O is more efficient than HO$_2$ uptake then a positive dependence of $\gamma$(HO$_2$) with RH would be detected.

Another way a change in RH could affect $\gamma$(HO$_2$) onto some aerosols is by altering the aerosol viscosity. A study of the dependence of $\gamma$(HO$_2$) onto copper-doped sucrose aerosols with RH using experimental measurements along with the KM-SUB model has previously been conducted. The change of the aerosols viscosity and small molecule diffusion coefficients within them as a function of RH is well characterised. At low RH the surface and interfacial layer becomes very viscous, almost glass-like, allowing only limited HO$_2$ uptake to occur and causing HO$_2$ concentration gradients. As RH was increased a critical point was reached and
the viscosity of the aerosols was suddenly reduced and accommodation can proceed at a much faster rate. Below a RH of around 43% there was little change in $\gamma(\text{HO}_2)$ as $\gamma(\text{HO}_2)$ is diffusion limited meaning the diffusion coefficient of HO2 is low leading to slow diffusion within the aerosol. However, a critical point at around 43% RH was reached and $\gamma(\text{HO}_2)$ increases linearly with RH until around 65 - 70% RH where $\gamma(\text{HO}_2)$ becomes independent of RH as $\gamma(\text{HO}_2)$ is limited kinetically and by mass accommodation. At the highest RH, the HO2 reacto-diffusive length (defined as the distance a molecule of HO2 can diffuse before reacting) varied from between 4 and 7 nm which decreases to around 0.006–0.05 nm at the lowest RH.

1.13.4 Concentration of HO2 and Exposure Time

As previously stated in section 1.11.2, $\gamma(\text{HO}_2)$ is theoretically proportional to the concentration of HO2, stressing the importance of using atmospherically relevant concentrations of HO2 and the need for sensitive detection techniques within laboratory experiments to determine values for $\gamma(\text{HO}_2)$. However, this relationship has not been observed in laboratory experiments \[9, 66\] which show that $\gamma(\text{HO}_2)$ is inversely proportional to [HO2], possibly due to surface saturation effects. Such surface saturation effects are also likely to explain observed $\gamma(\text{HO}_2)$ dependence to exposure time, where $\gamma(\text{HO}_2)$ is initially high but then decreases until concentrations of reactants and products equilibrate between the gas and condensed phases. At higher concentrations of [HO2] the interfacial layer may become saturated with HO2, therefore reducing the flux of HO2 into the aerosol. The effect seems to be more apparent at higher RH which could be associated with the difference in size of the aerosols. Saturation of active sites on the surfaces of dry aerosols has also shown to reduce measured values of $\gamma(\text{HO}_2)$ \[69\]. Another explanation for the observed trend between $\gamma(\text{HO}_2)$ and [HO2] is the production of gas-phase H2O2 during generation of HO2 \[78\]. When generating higher [HO2] self-reaction is more prevalent creating more H2O2, which could recycle HO2 once accommodated into the aerosol resulting in reduced values of $\gamma(\text{HO}_2)$ being observed. The time dependence of $\gamma(\text{HO}_2)$ also could be explained by a negative concentration gradient of HO2 along the aerosol flow tube caused by wall loss and uptake by HO2 resulting in decreasing values of $\gamma(\text{HO}_2)$ as a function of residence time within the aerosol flow tube. Discrepancies of measured $\gamma(\text{HO}_2)$ between various studies maybe explained in some part by differences in the initial [HO2] used.

1.14 Global Distribution of Heterogeneous Uptake of HO2

By determining the dependence of $\gamma(\text{HO}_2)$ with such parameters as temperature, aerosol pH and RH it is possible to model the global spatial distribution of HO2 and $\gamma(\text{HO}_2)$. Such a study has been performed \[8\] using the GEOS-Chem global chemical-transport model \[63\]. A mean $\gamma(\text{HO}_2)$ value across all aerosol components was calculated for each grid box. Parameterisations determined previously \[24, 54, 61\] were used within the model, however TMI
catalysis was not considered within their model, suggesting their results would likely offer at best the lower range of $\gamma($HO$_2$). Despite this, the study can be qualitatively considered and will likely highlight global locations where heterogeneous uptake of HO$_2$ is of potential importance. The rate of heterogeneous HO$_2$ uptake ($k_{het}$) was calculated using the equation previously derived $^{79}$ (E1.31).

$$k_{het} = \left( \frac{r}{D_g} + \frac{1}{\gamma c} \right)^{-1} A$$

(E1.31)

where $r$ is the aerosol radius, $D_g$ is the gas-phase diffusion constant, $\bar{c}$ is the mean molecular speed and $A$ is the aerosol surface area concentration.

A global mean value for $\gamma($HO$_2$) of 0.028 was calculated, which is around an order of magnitude less than previously recommended values of 0.2 and 0.1 $^{7, 24}$. High values of $\gamma($HO$_2$) are predicted at high latitudes due to the negative temperature dependence and the positive RH dependence. Particularly high values of $\gamma($HO$_2$) are predicted in July around Antarctica as the temperature around this time is around 210 K and RH > 60% resulting in predicted values of $\gamma($HO$_2$) for sea salt aerosol to be around 0.1. Relatively high $\gamma($HO$_2$) was also predicted around the west of Sahara Desert due to high aerosol loading in this area, however $\gamma($HO$_2$) over the Sahara itself is low due to hot and dry conditions. Relatively large values of $\gamma($HO$_2$) was consistently predicted 15 km above ground level at the equator, however during July the highest values of $\gamma($HO$_2$) are predicted to be around 5 – 10 km above Antarctica.

The GEOS-Chem global chemical-transport model was also used to assess the likely effect that HO$_2$ uptake onto cloud droplets has on the global oxidising capacity of the atmosphere $^{80}$. Three simulations were run; with no cloud uptake of HO$_2$, with cloud uptake of HO$_2$ resulting in conversion to H$_2$O$_2$ and with cloud uptake of HO$_2$ resulting in conversion to H$_2$O. It was assumed in all simulations that the pH of cloud droplets was 5. The simulations showed that HO$_2$ uptake onto cloud droplets was most prevalent in areas where HO$_2$ lifetimes were long. These areas are usually associated with low atmospheric concentrations of HO$_2$ and NO$_x$, such as areas within the extra-tropics. A 25% and 10% reduction of surface and column HO$_2$ concentrations respectively was predicted in such areas. Uptake of HO$_2$ onto cloud droplets was predicted to have little effect on concentrations of O$_3$. The impact of HO$_2$ uptake onto cloud droplets to OH concentrations was predicted to be 10 – 20%, however impacts to column concentrations of OH vary depending on whether H$_2$O$_2$ or H$_2$O is the product of HO$_2$ uptake.
1.15 Radical Production by Aerosols

Direct detection of gas-phase HO$_2$ emissions from aerosols has never been observed, however emissions of HO$_2$ were indirectly observed (i.e. conversion of NO to NO$_2$ within the flow tube) by illuminating (NH$_4$)$_2$SO$_4$ aerosols containing imidazole-2-carboxaldehyde, a photosensitizer produced within aerosols by glyoxal chemistry, and citric acid, an organic proxy and H donor, in the presence of limonene $^{81}$. Emissions of HO$_2$ cannot be verified by this observation technique as it could be that RO$_2$ radicals or some other reactant generated by this process was converting NO to NO$_2$. The production rate of HO$_2$ from coated wall experiments was shown to be to be a linear function of the ratio of imidazole-2-carboxaldehyde to citric acid and the photon flux. The HO$_2$ radicals were thought to be generated within the condensed phase when excited imidazole-2-carboxaldehyde triplet states are reduced by citric acid which go onto react with O$_2$ to regenerate imidazole-2-carboxaldehyde resulting in a catalytic cycle.

The direct detection of OH emissions has been observed from illuminated TiO$_2$ surfaces $^{82}$. HO$_2$ emissions have also been observed from H$_2$O$_2$ decomposition upon illuminated TiO$_2$ surfaces $^{83,84}$. The photocatalytic properties of TiO$_2$ are widely known $^{85}$ and have been exploited in many applications such as water and air purification and self-cleaning materials $^{86}$. TiO$_2$ is a semiconductor material and when illuminated with UV light an electron ($e^-$) is promoted from its valance band into its conduction band, also creating a hole ($h^+$) (R1.55). The magnitude of the band gap for TiO$_2$ nanoparticles is ~ 3.2 eV, meaning light that has a wavelength < 388 nm can make TiO$_2$ electronically conductive $^{84}$. The $e^-$ and $h^+$ pair can migrate to the crystal surface and subsequently oxidise and reduce adsorbed donor and acceptor molecules respectively $^{87}$. One reaction of particular interest is the oxidation of water by $h^+$ to produce highly reactive hydroxyl radicals (OH, R1.56) on the TiO$_2$ surface $^{83}$. Other reactive oxygenated species (ROS), such as the HO$_2$, H$_2$O$_2$ and singlet oxygen (O$_2$(1$\Delta$), R1.57 – R1.64), can also be formed on the surface of TiO$_2$ materials. The detailed reaction mechanism for the formation of these ROS on the surface of TiO$_2$ is not well understood, however it is believed to be as follows $^{83}$:

\[
\text{TiO}_2 + h\nu (\lambda < 388 \text{ nm}) \rightarrow \text{TiO}_2 + h^+ + e^- \quad \text{(R1.55)}
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ \quad \text{(R1.56)}
\]

\[
\text{O}_2 + \text{H}^+ + e^- \rightarrow \text{HO}_2 \quad \text{(R1.57)}
\]

\[
2\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad \text{(R1.58)}
\]

\[
\text{HO}_2 + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad \text{(R1.59)}
\]

\[
2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R1.60)}
\]
ROS formed on the surface of the TiO$_2$ catalyst can react and degrade adsorbed organic compounds making it ideal for air and water purification applications. However, some laboratory studies have shown that some ROS can also desorb from the surface of TiO$_2$ materials into the gas phase. Lee and Choi 88 observed the degradation of soot particles that came within close proximity, but not into direct contact, with an illuminated substrate partially covered with TiO$_2$. Tatsuma et al. 89 saw the degradation of organic films separated with air by 50 µm up to 2.2 mm from a TiO$_2$ film in the presence of light. Both experiments indicate possible OH emissions. Murakami et al. 82 conducted the first study that directly observed gas phase OH radicals using low pressure Laser Induced Fluorescence up to 8 mm from illuminated TiO$_2$ powders. They demonstrated that OH was produced from photocatalytic activity on the surface of the TiO$_2$ powder through deuterated water vapour studies and observed a decrease in OH signal as calcination temperatures of TiO$_2$ powders were increased. HO$_2$ emissions from irradiated TiO$_2$ surfaces in the presence of gas phase H$_2$O$_2$ at low pressures (50 and 200 Torr) were first observed by Bahrini et al. 83 In that study HO$_2$ was detected up to 44 mm away from the TiO$_2$ surface using Cavity Ring Down Spectroscopy (cw-CDRS) which directly observed the decomposition H$_2$O$_2$ and production of HO$_2$ simultaneously. They showed that large concentrations of H$_2$O$_2$ ($1.2 \times 10^{14}$ molecule cm$^-3$) decomposed over 140 s until a steady state concentration was reached. In one example, it was demonstrated that large concentrations of HO$_2$ ($6.9 \times 10^{11}$ molecule cm$^-3$) were generated in this way. It was concluded that gas phase HO$_2$ was produced via the decomposition of H$_2$O$_2$ by irradiated TiO$_2$, however the mechanism for the formation of HO$_2$ was unclear. This study was taken further by Yi et al. 84 who showed that gas phase HO$_2$ was only produced if H$_2$O$_2$ was also present within their system and that using either N$_2$ or O$_2$ as carrier gas made little difference in gas phase HO$_2$ concentrations. This suggests that HO$_2$ was created via H$_2$O$_2$ decomposition and not from photocatalytic reduction of O$_2$ and that H$_2$O$_2$ serves as the electron acceptor as well as an electron donor (R1.65 – 1.66). They also showed that different polymorphs of TiO$_2$, such as anatase and rutile, perform very differently with some showing rapid degradation of H$_2$O$_2$ but little HO$_2$ emissions and others with slower degradation but with higher emissions of HO$_2$. Through studies with e$^-$ and h$^+$ scavengers it was shown H$_2$O$_2$ decomposition is initiated by reaction with h$^+$ (R1.66).

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- & (R1.61) \\
O_2^- + h^+ & \rightarrow O_2(\Delta) & (R1.62) \\
H_2O_2 + O_2^- & \rightarrow OH + OH^- + O_2 & (R1.63) \\
OH + HO_2 & \rightarrow H_2O_2 + \frac{1}{2}O_2 & (R1.64)
\end{align*}
\]
H₂O₂ + e⁻ → OH + OH \quad \text{(R1.65)}

H₂O₂ + h⁺/OH → HO₂ + H⁺/H₂O \quad \text{(R1.66)}

1.16 Summary

This chapter has outlined the fundamental gas-phase reactions that control atmospheric HO₂ concentrations. It has been shown that purely gas-phase models often over predict atmospheric concentrations of HO₂ eluding to a missing heterogeneous sink. The rate of heterogeneous loss of HO₂ has been demonstrated to be dependent on a number of parameters such as aerosol phase, aerosol composition with the presence of transition metals resulting in large values of \( γ(\text{HO}_2) \), aerosol pH, RH, temperature and [HO₂]. HO₂ can also react on the surfaces of solid dust aerosols via the Eley-Rideal and Langmuir-Hinshelwood mechanisms. Aerosols in the troposphere have been shown to have a number of sources resulting in a large variety of aerosol composition, whereas, aerosol loading of the stratosphere is dominated by sulphuric acid particles and in the mesosphere by MSP. Aerosols may also be a potential source of HO₂ via the photocatalytic activity of photosensitizers within aqueous phase aerosols or TiO₂ within mineral dust particles or particles which may be used within SRM schemes.
Chapter 2 – Experimental Methods

The chapter presents the apparatus and the experimental and data analysis procedures used within this study.
2.1 Apparatus Overview

The kinetics of HO₂ uptake by atmospheric aerosols were determined using an aerosol flow tube coupled with a sensitive HO₂ detector based on chemical conversion to OH followed by laser-induced fluorescence (LIF) detection of OH at low-pressure, known as Fluorescence Assay by Gas Expansion (FAGE), and a Scanning Mobility Particle Sizer (SMPS). The system worked by passing a flow of gas and aerosols along a length of a laminar flow reactor with the reagent, in this case HO₂, being added through a movable injector. The change in HO₂ concentrations was determined as a function of exposure time or aerosol concentration. When investigating radical production from aerosol surfaces the movable injector was pulled back to its furthest position away from the detector and only a small flow of dry nitrogen was passed through it effectively making it redundant within the system. Aerosol flow tubes are well characterised and understood and have not only been used to investigate the kinetics of heterogeneous uptake of HO₂ but also other atmospheric species such as N₂O, ClONO₃ and H₂O₂. A schematic of the experimental set-up used for the kinetic study of heterogeneous reactions with HO₂ and airborne TiO₂ nanoparticles and inorganic salt aerosols, typical for aerosols generated using a constant output atomizer, is presented in Figure 2.1.

![Figure 2.1: Schematic diagram of the aerosol flow tube experiment used to investigate the kinetics of heterogeneous reactions with HO₂ and airborne TiO₂ nanoparticles.](image)

Differences in the experimental set-up are primarily due to the method used for entrainment of particles into the bath gas. All flows, unless otherwise stated as some experiments require addition of air, within the experiment are composed from departmental nitrogen that has been passed through a gas purification system (TSI 3074B, shown in Figure 2.2), consisting of two coalescing filters which removes water, oil droplets and particles, a membrane dryer to remove moisture and a carbon-vapour filter which removes any oil vapour, before use. The
purification system removes 99.99995% of particles with a diameter of 100 nm at a velocity of 10 cm s$^{-1}$.  

![Diagram of the purification system]

**Figure 2.2**: Filtered Air Supply TSI 3074B.

### 2.2 Aerosol Generation and Characterisation

#### 2.2.1 Generation and Entrainment

Deliquesced inorganic and TiO$_2$ aerosols were generated by a commercial constant output atomizer (TSI 3076), shown in Figure 2.3. Polydisperse aerosols are generated by flowing nitrogen at high pressure (~ 2 - 3 atm) through a small orifice (0.0135 inch diameter), in order to create a high velocity jet, into a flow of the aqueous solution drawn from a reservoir within the liquid feed bottle. Solutions used within the liquid feed bottle to generate inorganic aerosols (e.g. (NH$_4$)$_2$SO$_4$, KI, NaCl, CuSO$_4$) were made up by dissolving 0.01 moles of the inorganic salt of interest into 500 ml of milli-Q water (18.2 MΩ), resulting in a 0.02 M solution. In order to investigate the affect the presence of transition metal ions within inorganic aerosols has to HO$_2$ uptake these solutions were doped with known quantities of either CuSO$_4$, FeSO$_4$, MnSO$_4$ or KI. Solutions used within the liquid feed bottle to generate TiO$_2$ aerosols were made up by suspending 5 g of TiO$_2$ nanoparticles (Aldrich Chemistry 718467, 99.5% Degussa i.e. 80% anatase and 20% rutile) in 500 ml of milli-Q water. The aerosols follow the flow of nitrogen and exit through the top of the atomizer and the exhaust. Any larger droplets formed hit the wall of the atomizer and the excess liquid falls back into the...
liquid feed bottle. By recirculating the liquid in the atomizer back into the liquid feed bottle the liquid is kept at a constant concentration and allows for a constant distribution of aerosols to be generated. In order to create effloresced inorganic aerosols or dry TiO$_2$ aerosols the aerosol flow from the atomizer was passed through a diffusion drier (TSI 3062) so that the relative humidity (RH) of the flow was reduced to below 15%. A schematic of the cross-section of atomizer used within the experiment is presented in Figure 2.3.

![Figure 2.3: Cross-section of a TSI 3076 atomizer assembly block.](image)

Particle samples that are inert in water, such as TiO$_2$, can be entrained into a nitrogen flow using the atomizer, however particles whose chemical properties may change once placed in solution (i.e. analogues of meteoric smoke particles, MSP, as discussed in Chapter 6) require a separate piece of apparatus to entrain them within the flow. During previous experiments, a sample of the particles was placed within a 500 ml high density polyethylene (HDPE) bottle which has a hole drilled into its lid and another around 5 cm from its base. A short ¼ inch Teflon tube was fixed into each hole. The tube located on the lid was connected to the rest of the experimental setup and nitrogen was flowed through the bottom tube. A magnetic stirrer bar was also placed in the bottle and the bottle placed on to a magnetic stirrer set to maximum stirring speed. The combination of stirring and the nitrogen flow causes dispersion of the particles in the bottle and particles are entrained into the N$_2$ flow. However, a more robust particle disperser was developed due to a number of problems with the HDPE bottle particle dispersers; namely it entrains a highly unstable distribution of aerosol concentrations and sizes.
into aerosol flow which can fluctuate quicker than the FAGE instrument can detect changes in [HO₂], unreliable entrainment of particles into the aerosol flow, particles can agglomerate and cause blockages and particles tended to stick to the walls of the HDPE bottle meaning a new disperser was required for each experiment and much of the sample was wasted. A new particle disperser was necessary and its design was based on a disperser which is similar to the HDPE bottle disperser in principal but uses a glass vessel and has two N₂ inlets. However, a piezoelectric transducer (Mylar speaker), rather than using a magnetic stirrer, was used to cause dispersion of the particle samples. A cross-sectional schematic of the particle disperser is presented in Figure 2.4.

![Cross-section of the Acoustic Particle Disperser (APD) used to entrain meteoric smoke particles within a flow of N₂. Not to scale.](image)

Figure 2.4: Cross-section of the Acoustic Particle Disperser (APD) used to entrain meteoric smoke particles within a flow of N₂. Not to scale.

Testing of the particle disperser, now referred to as the acoustic particle disperser (APD), showed that transmitting a sine wave with a frequency of around 600 kHz through the speaker resulted in the greatest dispersion of MSP. Measurement of the particle number concentration and size distribution of particles entrained in the flow showed a reasonably stable log-normal distribution, as shown in Figure 2.5. The distribution was an improvement on the previous technique, which had resulted in irregular particle size distribution and concentration entrained within the flow, meaning it was impossible to know with any accuracy the surface area density of aerosols within the aerosol flow tube during each measurement. Instead an assumption was made that the surface area density is a function of an averaged size distribution taken over a number of hours. However, this technique was still not stable enough (fluctuation of aerosol surface area density was up to 20% during a measurement) for moving injector experiments (defined in section 2.4.3) and the anti-correlation experimental methodology (defined in section 2.4.5) should still be employed.
2.2.2 Impactor and Neutraliser

Aerosols generated by the atomizer are highly charged due to a high number of aerosol-aerosol collisions and therefore are liable to wall losses throughout the experimental system due to Coulombic forces. Highly charged aerosols are also difficult to characterise within the Differential Mobility Analyser (TSI 3080, DMA described in section 2.2.5) which is dependent on the charge of the particle. After the aerosols exit the atomizer they enter a neutralizer (Grimm 5522) in order to reduce charge on generated aerosols. This reduced wall losses along with the application of a known electrical charge distribution, which allowed for a more accurate aerosol characterisation within the DMA. The neutralizer contains a radioactive source, Krypton-85, to ionise the aerosol flow into positive and negative ions. The aerosols collide with the ions and highly charged particles lose some of their charge and particles with low charge gains some charge. After a short period of time equilibrium is reached and a known bipolar charge Boltzmann distribution has been applied to the aerosols. In addition to this, anti-static tubing (TSI, Conductive Silicon Tubing 0.19 inch ID) was used for all aerosol flows throughout the experimental set-up to further reduce aerosol wall losses.

The aerosol flow then enters an impactor (TSI 1034900) with a 0.071 cm nozzle. An impactor was used to remove large particles well beyond the scanning range of detection of the SMPS do not enter the aerosol flow tube. It was also used to monitor the aerosol flow rate into the

Figure 2.5: Size distribution of an analogue of MSP (Mg$_2$SiO$_4$) aerosols entrained using the APD obtained with the SMPS.
experimental setup by detecting the pressure drop across the impactor, which is proportional to the square root of the flow rate. The impactor removes particles above a specified size by inertial impaction. The aerosol flow is accelerated through the nozzle and directed to a flat plate which deflects the flow by 90°. Larger particles with greater inertia impact onto the plate and are removed from the flow, where smaller particles with small inertia follow the flow as shown in Figure 2.6.

![Figure 2.6: Cross-section of an inertial impactor.](image)

The aerodynamic size of particles that are separated from the flow is referred to as the cut-point diameter ($D_{50}$). The impactor removes 50% of all particles with a diameter of $D_{50}$ (see Figure 2.7).

![Figure 2.7: Typical efficiency curve for a impactor.](image)

A plastic impactor (built in-house based on TSI 1034900) was used when experimenting on condensed aerosols to avoid potential contamination of aerosols with transition metal ions.
where a metal impactor was used when experimenting on dust. The impactor used in this study removes 50% of particles with a diameter of 685 nm (i.e. $D_{50} = 685$ nm) and has a curve similar in shape shown in Figure 2.7.

2.2.3 Control of Relative Humidity
The resulting flow from the atomiser was mixed with a humidified flow of nitrogen (3 L min$^{-1}$) to control the RH within the system. The RH of the humidified flow was altered by changing the ratio of dry nitrogen and nitrogen passed through a water bubbler. These two flows were controlled using two calibrated mass flow controllers (MKS 1179). This flow was then passed through a conditioning tube (residence time ~ 6 s) before entering the aerosol flow tube to allow time for water adsorption or absorption onto aerosols to equilibrate at the given RH. A range of RH from 10 – 70% can easily be achieved within the aerosol flow tube. The RH of the flow was measured using a probe (Rotronics HygroClip2, accuracy ± 0.8% RH) in the exhaust of the aerosol flow tube, which itself was calibrated against a dew point hygrometer (Buck Research Instruments CR-4).

2.2.4 Control of Aerosol Concentration
It is important to be able to alter the aerosol concentration within the aerosol flow tube to enable the accurate determination of the uptake coefficient, $\gamma$, and radical production rates. In order to control the aerosol concentration within the aerosol flow tube a fraction of the aerosol flow was passed through a high-efficiency particulate air (HEPA, PALL Life Sciences) filter which was situated within a by-pass loop. These filters are comprised of a mat of densely packed fibres which trap aerosol through impaction, interception or diffusion of aerosols onto the fibres. The filter was arranged with a by-pass loop in order to keep the overall flow rate constant.

2.2.5 Characterisation of Aerosols
As previously stated, aerosols generated by the atomiser, as in the atmosphere, are polydisperse i.e. particle sizes vary. The most applicable mathematical distribution function for fitting polydisperse aerosol data from a single source is a log-normal distribution, although there is no theoretical reason for this. A Scanning Mobility Particle Sizer (SMPS) was used to measure the particle size distribution and aerosol number concentration three times during each measurement and once for each radical production measurement. This data can then be used to calculate the total surface area density ($S_a$) assuming that the aerosols are spherical. The SMPS comprises of two stages; the first stage is the DMA which extracts a known size fraction of aerosols from the flow of polydisperse aerosols, essentially creating a flow of monodisperse aerosols, and the second stage is the Condensed Particle Counter (CPC, TSI 3775) which counts the number of particles within that fraction.
The SMPS samples the flow from the exhaust of the aerosol flow tube (0.3 L min⁻¹), as shown in Figure 2.1. Initially, this flow enters the SMPS and was directed through an additional impactor located within the SMPS instrument \((D_{50} = 1024 \text{ nm})\) and then a Kr-85 neutraliser (TSI 3077). This, as previously described, is necessary to apply a known Boltzmann charge distribution to the particles. Previously, experiments were conducted that showed the internal TSI Kr-85 neutraliser alone cannot effectivel\(^9\)y apply the Boltzmann charge distribution when the number of aerosols in the flow is relatively high \(^9\), hence why the external Grimm neutraliser described earlier is necessary.

A schematic diagram of the SMPS instrument is presented in Figure 2.8. The DMA consists of two concentric metal cylinders. Polydisperse aerosol and sheath flows enter the top of the DMA and flow between the two metal cylinders in a laminar regime, i.e. they do not mix. The inner cylinder, a high-voltage rod, is negatively charged while the outer cylinder is grounded creating an electric field between the two cylinders. Positively charged aerosols are attracted towards the high-voltage rod and move through the sheath air flow. The ability of a particle to move through the electric field is referred to as particle electrical mobility \((Z_p)\). E2.1 shows that \(Z_p\) is dependent on the mid-point diameter of the particle \((D_p)\) \(^{99}\).

\[
Z_p = \frac{neC}{3\pi\mu D_p} \quad \text{(E2.1)}
\]

where \(n\) is the number of elementary charges on the particle, \(e\) is the elementary charge \((1.6 \times 10^{-19} \text{ Coulomb})\), \(C\) is the Cunningham slip correction (accounts for non-continuum effects when calculating the drag on small particles) and \(\mu\) is the gas viscosity. Particles with a narrow bandwidth of \(Z_p\) flow out of the monodisperse aerosol outlet, the rest are flowed through the excess air outlet. The relationship between \(Z_p\) and the DMA parameters are presented in E2.2 \(^{99}\).

\[
Z_p = \frac{q_{sh}}{2\pi V L} \ln \left( \frac{r_2}{r_1} \right) \quad \text{(E2.2)}
\]

where \(q_{sh}\) is the sheath air flow rate, \(V\) is the average voltage on the inner collector rod, \(L\) is the length between exit slit and polydisperse aerosol inlet, \(r_2\) is the outer radius of the space between the cylinders and \(r_1\) is the inner radius of the space between the cylinders.

Equation 2.2 shows that by altering \(V\) it is possible to control \(Z_p\) and hence the diameter of the particles exiting through the monodisperse aerosol outlet. In order to calculate the diameter of the particle it is possible to combine E2.1 and E2.2 to give E2.3 \(^{99}\).

\[
\frac{D_p}{C} = \frac{2neVL}{3\mu q_{sh} \ln \left( \frac{r_2}{r_1} \right)} \quad \text{(E2.3)}
\]
The sheath flow is usually set to be ten times greater than the aerosol flow sampled by the instrument. In this study the sheath flow was set at a flow rate ten times that of the sampling rate (3.0 L min⁻¹).

Particles within the monodisperse aerosol flow enter into a CPC where they are counted. Aerosols flowed into the CPC firstly enters through a heated saturator where butanol is vaporised and diffuses into the aerosol flow. Then the butanol vapour and aerosol flow enters a cooled condenser causing the butanol to condense on to the aerosols to form larger droplets, which can be counted by an optical detector consisting of a laser-diode source and diode detector to collect scattered light from aerosols. At aerosol concentrations < $5 \times 10^4$ cm⁻³ (low mode), each aerosol is detected as an individual pulse totalling to the concentration of aerosols within the flow, however, at aerosol concentrations above this (high mode) the magnitude of the scattered light that has been directed through the flow is used to determine aerosol concentrations. The CPC was operated in the low mode during all experiments.

![Figure 2.8: Schematic of the SMPS instrument](image)

Depending on the sampling time, the SMPS measures aerosols with mid-point diameters ranging from 14-725 nm. Particles with diameters < 14 nm contribute an insignificant amount to the total surface area and are discounted from the distribution. Particles with a diameter >700 nm are removed by the impactor. When set to sample over a period of three minutes, the SMPS produces an aerosol distribution and is accurate to within 7 nm. Data from the SMPS are collated by the Aerosol Instrument Manager software (AIM v8.1.0.0). It allows the user to watch real-time measurements of aerosol concentration, aerosol diameter and aerosol surface area concentration and to create data files from measurements made during the experiment.
The DMA is calibrated periodically by passing a flow of polystyrene latex beads with a known size through the instrument in accordance with the an accepted methodology \(^{100}\). Solutions of surfactant-free carboxylate-modified polystyrene latex beads (CML, Life Technologies, Grand Island, NY) were prepared by diluting 15 drops of the CML beads suspensions in 150 ml of milli-Q water. In total, four solutions were prepared each containing different size CML beads. CML beads with diameters of 100 nm, 300 nm, 400 nm and 500 nm were used to calibrate the SMPS against as they cover most of the range to which SMPS is commonly applied. The CML beads are spherical polymers, terminated by carboxylic acid groups. Conventionally, beads are surrounded by a surfactant to stop agglomeration of the beads, however, the surfactant has been shown to add peaks to the size distribution taken by the SMPS which could overlap and hide the desired peaks created by the PSL beads themselves \(^{100}\). A surfactant with the CML beads is not necessary, as when a base is added (in this case a NaOH solution) the carboxylic acid termini are all negatively charged causing the CML beads to repel each other. The solutions were made up to a pH of 10 to ensure all carboxylic groups were converted to anions. The solutions were placed within the atomizer and entrained in a flow of nitrogen. The resulting flow was dried using a diffusion drier (TSI 3062) and flowed through the aerosol flow tube experiment apparatus. Three size distributions were measured with the SMPS using standard operating parameters (scan time 150 s, retrace time 30 s every 240 s) in order assess the SMPS sizing accuracy under typical operating conditions. Figure 2.9 presents the SMPS particle number size distributions taken within a calibration experiment. A log-normal function was fitted to the number size distributions in order to calculate their peak values.

![Figure 2.9: Average particle number size distributions fitted to a log-normal function measured by SMPS in normal experimental scan mode for carboxylate-modified polystyrene latex beads (CML) beads at pH 10.](image-url)

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\(^{100}\) References are not included in the natural text representation.
These values were then plotted against the actual size of the beads reported by the manufacturer (Figure 2.10) in order to make a judgement on the agreement. Figure 2.10 shows that SMPS sizing gives good agreement with the actual size of the CML beads reported by the manufacturer and gives consistent precision with the exception of the 300 nm CML beads, which was later known to be associated with a manufacturing error.

![Graph showing comparison between SMPS sizing and actual CML beads diameter](image)

**Figure 2.10**: Comparison with measurements of CML beads diameter made with the SMPS to actual CML beads diameter.

When measuring the size distribution of some mineral dusts, mainly MSP, a significant proportion of the size distribution was beyond the scanning range of the SMPS (see Figure 2.5, 4.1 and 5.1). As the impactor cut-off characteristics are unknown, a significant proportion of larger aerosols may enter the aerosol flow tube without being directly accounted for in the SMPS output. In such cases, a lognormal function was fitted to the raw SMPS data in order to estimate the aerosol surface area concentration outside the SMPS scanning range, which was then considered in subsequent calculation of the $\gamma$(HO$_2$).

### 2.3 HO$_2$ Generation and Detection

#### 2.3.1 HO$_2$ Generation and Movable Injector

HO$_2$ radicals were produced within the movable injector (110 cm length, 1.9 cm O.D., 1.6 cm I.D.) by passing a 1.3 L min$^{-1}$ humidified flow of nitrogen (mixture of 0.9 + 0.4 L min$^{-1}$ of dry
N\textsubscript{2} and N\textsubscript{2} passed through a water bubbler respectively) containing trace amounts of oxygen (~40 ppm, manufacturer specification) over a mercury lamp (L.O.T.-Oriel 6035) via the following reactions:

\[ \text{H}_2\text{O} + h\nu (\lambda = 185 \text{ nm}) \rightarrow \text{OH} + \text{H} \]  
(R2.1)

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  
(R2.2)

As the flows through the movable injector and mercury lamp current (usually 20 mA) were kept constant, it is assumed that the initial HO\textsubscript{2} concentration, [HO\textsubscript{2}]\textsubscript{0} (defined in this investigation as [HO\textsubscript{2}] at the first injector position, i.e. 30 cm downstream of the injector) was the same for the duration of the experiment. OH is also created by the photolysis of water vapour in R2.1, but no OH was observed exiting the injector, presumably owing to rapid losses at the walls of the injector.

By housing the mercury lamp in the end of the moveable injector away from the aerosol flow tube it was possible to dissipate heat from the lamp and cool it using either an external fan or by pumping cold water around an external metal housing. Typically, initial concentrations of HO\textsubscript{2} were in the range of ~10\textsuperscript{8} - 10\textsuperscript{9} molecule cm\textsuperscript{-3} at the first injector position of 30 cm.

A Teflon tube (1.5 cm O.D. and 0.8 cm I.D.) was placed within the injector to reduce HO\textsubscript{2} radical losses to the walls. The injector flow was injected into the aerosol flow tube via a Teflon tip which has 20 × 1 mm holes drilled equally around its circumference 0.5 cm from the end of the tip, meaning the injector flow enters the aerosol flow tube perpendicular to the aerosol flow in order to create some local turbulence to aid mixing. Figure 2.11 presents a photograph of the aerosol flow tube injector used within the experiment.

\[ \text{Figure 2.11: HO}_2 \text{ injector used in the experiment.} \]

Nitrogen is preferred to synthetic air within the injector flow as significant quantities of O\textsubscript{2} in the synthetic air may also photolyse to produce O\textsubscript{3} that could result in significant losses of HO\textsubscript{2} or aerosol modification. With N\textsubscript{2} and trace O\textsubscript{2} impurities only a few ppb of O\textsubscript{3} is produced \textsuperscript{9}.  

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Other generation methods have been used in previous experiments by other groups. In similar apparatus, HO$_2$ has been produced by adding a small amount of H$_2$ (0.3%) to humidified air at 20°C and passing over a coil of hot Nichrome wire. However, there are a number of problems with this method, such as having to cool the flow of air via a heat exchange prior to it entering the aerosol flow tube, a number of substantial small particles were produced by the hot wire and the potential to produce organic peroxy radicals (RO$_2$) which can interfere with the HO$_2$ signal. Other groups have produced HO$_2$ radicals via R2.2, however, they generated hydrogen radicals by passing Ar containing a trace amount of H$_2$ through microwave discharge plasma operated at atmospheric pressure. The discharge was then passed through a 2 m Teflon tube (3 mm O.D.), the final 1 m served as the injector into the aerosol flow tube, which was contained within a second tube (6 mm O.D.) with a flow of O$_2$ through it. The two gases were allowed to mix 1 cm prior to injection into the aerosol flow tube.

2.3.2 HO$_2$ Detection

HO$_2$ was sampled by a 0.7 mm diameter pinhole at the end of the flow tube (see Figure 2.1) at a rate of ~ 4 L min$^{-1}$, and after chemical conversion to OH by addition of excess NO (50 sccm, BOC, 99.5 %) just inside the pinhole, LIF at low-pressure (the fluorescence assay by gas expansion technique, FAGE) \(^{101}\) was used to measure OH. This technique has been successfully deployed in many field and laboratory studies\(^5\) with current detection limits of 6×10$^5$ molecule cm$^{-3}$ and 1×10$^6$ molecule cm$^{-3}$ for OH and HO$_2$ respectively, taken with 30 second integration time.

The Q$_1$(2) line of the OH (A$^2\Sigma^+$ $v'$ = 0 $\leftarrow$ X$^2\Pi_i$ $v'' = 0$) transition at ~ 308 nm was used to detect OH. The energy level diagram of excitation and fluorescence of OH is presented in Figure 2.12.

![Figure 2.12: Energy level diagram of the excitation and fluorescence of OH in FAGE technique. R represents changes in rotational energy levels and Q represents quenching. Figure taken from the https://www.chem.leeds.ac.uk/fage/the-fage-technique.html.](https://www.chem.leeds.ac.uk/fage/the-fage-technique.html)
A Nd:YAG pumped dye laser (JDSU Q201-HD Q-series, Sirah Cobra Stretch) was used to produce the required 308 nm radiation (line width ~ 0.1 cm$^{-1}$) at a pulse repetition rate of 5 kHz. The dye used within the laser was made up by dissolving 0.3 g of Rhodamine B and 0.075 g of Rhodamine 640 into 2 L of methanol. A reference fluorescence cell, in which a large concentration of OH was generated and detected by LIF, was used to facilitate the identification of OH lines and tune the laser wavelength. Light from the laser was passed through a beam splitter, which directs 5% of the light into the reference cell. High concentrations of OH were produced in the reference cell by flowing humidified air over a heated filament Nichrome wire that has 5.3 amps of electrical current at ~ 4 V running through it resulting in the thermal decomposition of the water vapour to OH. The pressure in the reference cell was kept at ~ 2 Torr. The resulting fluorescence was detected by an un-gated Channel Photomultiplier (CPM, Perkin Elmer 993P). Before each measurement the OH LIF signal was measured as a function of wavelength in order to tune the wavelength of the laser light to the OH Q$_1$(2) rotational line ($\lambda = 307.9951$ nm) $^{102}$.

The 308 nm light from laser was delivered into the FAGE cell via a fibre launcher (Oz Optics), a 5 m optical fibre (Oz Optics), a fibre collimator (Oz Optics) and a sidearm fitted with optical baffles to reduce laser scatter. Opposite this side arm is a second baffled sidearm. A photodiode (New Focus 2032) was located at its end in order to monitor laser power exiting the FAGE cell throughout the experiment (see Figure 2.13). The direction of the laser beam, the flow being drawn into the cell and fluorescence imaged from the resulting OH were perpendicular to each other.

The resulting fluorescence of the OH radical (also $\lambda \sim 308$ nm) upon relaxation back to the electronic ground state was passed through a 308 nm narrow bandpass filter (Barr Associates, 308 nm, FWHM = 8 nm), to ensure only light at this wavelength was detected to reduce background counts, then focused onto the active area of the photocathode of the detector by a number of lenses and detected using a gated CPM (Perkin Elmer 993P), or later on in the study, by a more sensitive Micro-Channel Plate (MCP, Photek). These devices, via the photo-electric effect, convert single photons that enter the device into electrical pulses (MCP pulses ~ -200 mV) which were counted by a gated photon counting card (Becker and Hickl GmbH, PMS-400). A back reflector was also housed within the FAGE cell (see Figure 2.13) below the fluorescence region in order to reflect any downwards travelling fluorescence up towards the detector and thereby increasing the sensitivity of the detector by ~ 40%. The photon count rate (i.e. FAGE signal) is proportional to the concentration of HO$_2$ in the cell. The software controlling the FAGE instrument recorded the HO$_2$ signal as counts every second. In order to calculate the absolute concentration of HO$_2$ in the cell it is necessary to undertake a calibration experiment. This experiment was also useful for determining the sensitivity of the cell and
indicating any deficiencies within the FAGE instrument. FAGE calibration is discussed later in this section 2.2.3. Figure 2.13 presents photographs from the side and inside the FAGE Cell and a line drawing of the FAGE cell.

![Figure 2.13: Photographs and line drawing of the FAGE cell used within the University of Leeds Aerosol Flow Tube Experiment.](image)

The FAGE cell was continuously evacuated using a combination of a rotary pump (Edwards, model E1M80) and a roots blower (EH1200), and was kept at a pressure of 0.8–0.9 Torr, which was monitored using a capacitance monitor (Tylan General, CDC 11) and controlled using a gate valve. It is necessary to operate the FAGE cell at such low pressures as expansion of the gas to low pressures lengthens the fluorescence lifetime of OH enabling fluorescence to be distinguished from scattered laser light at the same wavelength (on-resonance detection, i.e. the light used to excite OH is the same wavelength at which it fluoresces) by gating the CPM or MCP and photon counting card. The gating timings used within this FAGE setup are shown in Figure 2.14. An internal triggering system within the laser was used to set the start of the gating cycle, \( t_0 \), and triggers both the laser and a delay
The gating cycle was set to repeat every 200 μs i.e. 5000 Hz. The laser Nd:YAG pumped dye laser fires a pulse of light, with a pulse width of 18 ± 10 ns, 150 ns after the trigger (t₀ + 200 ns). At this time the CPM/MCP detector and photon counting card were switched off. The delay generator sends a pulse to switch on the photon counting card 50 ns prior to the laser pulse (t₀ + 150 ns) to account for a variable 50 ns delay within the internal clock of the photon counting card before counting. The delay generator then sends a pulse to a gating system at t₀ + 280 ns. The gating system then rapidly switches on the CPM/MCP detector for 50 μs then it is switched off. The photon counting card remains on for the rest of the gating cycle. The signal from the CPM/MCP detector was passed through a discriminator of -40 mV before reaching the photon counting card filtering noise from switching the CPM/MCP detector on and interference from connecting wires. The photon counting card counts the number of photons detected within a 1 μs bin after it switches on (“A” gate signal, Aₙₐₚ). This signal consists of OH LIF, scattered light from either the laser or room light entering through the pin hole and CPM/MCP detector dark counts (usually around 1 - 3 counts). After 10 μs the photon counting card counts photons again for a 20 μs bin (“B” gate signal, Bₙₐₚ) consisting of room light entering through the pin hole and CPM/MCP detector dark count. To determine the signal from OH LIF and scattered laser light Bₙₐₚ is subtracted from Aₙₐₚ as shown in E2.4.

\[
\text{Signal} = A_{\text{sig}} - \frac{B_{\text{sig}}}{20} \quad \text{(E2.4)}
\]

**Figure 2.14:** Diagram showing the trigger cycle of the laser, CPM and photon counting card.\(^8\)
Nitric oxide (NO, BOC 99.5%) was used to chemically convert HO$_2$ radicals to OH radicals within the FAGE cell via R2.3.

$$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R2.3)}$$

NO was delivered into the FAGE cell via four injection ports centred symmetrically around the gas flow sampled from the aerosol flow tube and ~ 5 cm downstream from the pinhole as shown in Figure 2.13. The flow of NO was controlled at 50 sccm using a calibrated mass flow controller (Brooks 5850S). FAGE calibration experiments showed that ~ 70% of HO$_2$ was converted to OH within the cell. It is not possible to convert all HO$_2$ to OH owing to a competing reaction (R2.4).

$$\text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \quad \text{(R2.4)}$$

An experiment was conducted to determine the relationship between the flow of NO entering the cell and the FAGE signal. From this it was possible to determine the optimum flow of NO into the FAGE cell. Ten measurements were taken at ten different flow rates between 5 – 50 sccm of NO into the FAGE cell in a random order. The average HO$_2$ signal over an averaging period of ten seconds was measured at each flow rate of NO. The error is defined as 1σ of the measurements made within the ten second averaging period. The tip of the injector was placed 22.5 cm away from the FAGE inlet to ensure low wall losses. The results of the experiment are presented in Figure 2.15. A box-lucus fit was applied to the measurements. It showed that NO flow rates > 50 sccm are likely to give little gain in FAGE signal. It was concluded that 50 sccm of NO will ensure optimum conversion of HO$_2$ to OH within the FAGE cell.

![Figure 2.15: Relationship between NO flow in to the FAGE cell and FAGE signal. Pressure = 0.8 Torr.](image-url)
2.3.3 FAGE Calibration

The relative LIF signal from converted HO\textsubscript{2} was calibrated using an established method developed for field measurements of OH and HO\textsubscript{2} radicals. Hence, it was possible to measure the absolute concentration of HO\textsubscript{2} during passage from the injector to the sampling inlet. The calibration experiment yields a calibration constant (C\textsubscript{HO2}) for the FAGE instrument which can be used to convert the signal produced by FAGE to an absolute HO\textsubscript{2} concentration as shown in E2.5.

\[ S_{\text{HO2}} = C_{\text{HO2}}[\text{HO2}] \]  \hspace{1cm} (E2.5)

where \( S_{\text{HO2}} \) is the signal generated by FAGE.

The value of \( C_{\text{HO2}} \) also serves as the sensitivity factor for the FAGE instrument, i.e. high values of \( C_{\text{HO2}} \) indicate a high degree of sensitivity the FAGE instrument has to measure changes in concentrations of HO\textsubscript{2} and a lower limit of detection. E2.6 shows the relationship between \( C_{\text{HO2}} \) and a number of instrumental parameters.

\[ C_{\text{HO2}} = D \times B \times P \times \phi_f \times f_{\text{Boltz}} \times f_{\text{gate}} \]  \hspace{1cm} (E2.6)

where \( D \) is the instrumental parameters, such as focal volume of laser beam, collection efficiency, detector response and filter transmission, \( B \) is the OH absorption coefficient, \( P \) is the laser power, \( \phi_f \) is the OH fluorescence quantum yield (pressure dependent), \( f_{\text{Boltz}} \) is the Boltzmann fraction of the OH molecules in the quantum state probed by the laser (temperature dependent) and \( f_{\text{gate}} \) is the fraction of OH fluorescence within the gate of the photon counter.

As \( D \) can change over a period of time, the FAGE instrument was calibrated periodically over the duration of this study. It is difficult to measure all these parameters individually, therefore in order to measure \( C_{\text{HO2}} \) the HO\textsubscript{2} signal was recorded when different known concentration of HO\textsubscript{2} was introduced into the FAGE cell. To produce a known concentration of HO\textsubscript{2} vacuum-ultraviolet photolysis of water vapour using a mercury lamp in the presence of O\textsubscript{2} (i.e. synthetic air, BOC 055) was used. Photolysis of water vapour results in the production of OH and HO\textsubscript{2} in a 1:1 ratio (R2.1 and R2.2).

The rate at which OH and HO\textsubscript{2} was produced is presented in E2.7:\n
\[ \frac{d[\text{HO2}]}{dt} = \frac{d[\text{OH}]}{dt} = [\text{H}_2\text{O}] \sigma_{\text{H}_2\text{O}} \varphi_{\text{OH}} F \]  \hspace{1cm} (E2.7)

where \( \sigma_{\text{H}_2\text{O}} \) is the absorption cross section of water at 184.9 nm, \( \varphi_{\text{OH}} \) is the photolysis quantum yield of water to form OH (\( \varphi_{\text{OH}} = 1 \)) and \( F \) is the photon flux of the mercury lamp.

Upon integration of E2.7 it is possible to obtain an expression for the concentration of HO\textsubscript{2} (E2.8).
\[ [\text{HO}_2]_t = [\text{OH}]_t = [\text{H}_2\text{O}] \sigma_{\text{H}_2\text{O}} \phi_{\text{OH}} F t \]  

(E2.8)

Parameters such as absorption cross section and photolysis quantum yield of water vapour are well established, however, \( F t \) has to be measured by chemical actinometry. This was performed periodically and involves photolysis of \( \text{N}_2\text{O} \) in a flow of air to form NO which can be detected using a commercial chemiluminescent analyser.\cite{103}

The FAGE calibration experimental apparatus consists of a ‘wand’, through which a turbulent humidified flow was passed. An Hg penray lamp, located on the other end of the wand in order to minimise loss of OH to impurities in the flow and internal walls of the wand, provided the photons at 184.9 nm necessary for photolysis of the water vapour. The outlet of the wand is placed directly adjacent to the FAGE inlet at a 45° angle. A humidified flow of air was produced (30 L min\(^{-1}\)) by flowing air controlled using a MFC through a water bubbler. In order to control the concentration of HO\(_x\) produced by the wand the current supplied to the Hg penray lamp was altered. The concentration of water within the flow was measured with a dew-point hygrometer (CR4, Buck Research Instruments). A schematic of the FAGE calibration experimental setup is presented in Figure 2.16.

![Schematic of aircraft FAGE calibration experimental setup](image)

**Figure 2.16:** Schematic of aircraft FAGE calibration experimental setup.\cite{105} Note that the FAGE inlet here is designed for use on an atmospheric chamber and is not used within the apparatus within this work.

The HO\(_2\) signal was recorded and averaged over a 20 s period at a suitable number of different known HO\(_2\) concentrations. The FAGE signal was normalised to the initial laser power, which
was recorded throughout the calibration experiment, and plotted against the concentration of HO$_x$ entering the FAGE cell. From E2.5, the gradient of such a plot yields $C_{HO2}$. Figure 2.17 presents a calibration plot of the FAGE instrument used within this study with a CPM detector installed within it, resulting in a value of $C_{HO2}$ of $1.97 \times 10^{-8}$ mW$^{-1}$ s$^{-1}$ molecule$^{-1}$ cm$^3$ being measured. With a MCP detector installed within the FAGE instrument, the same experiment yielded a value of $C_{HO2}$ of $2.63 \times 10^{-7}$ mW$^{-1}$ s$^{-1}$ molecule$^{-1}$ cm$^3$, therefore increasing the sensitivity of the instrument by over an order of magnitude.

![Figure 2.17: Example of the FAGE signal at different [OH] (red line, $C_{OH} = (3.36 \pm 0.05) \times 10^4$ mW$^{-1}$ s$^{-1}$ molecule$^{-1}$ cm$^3$) and [HO$_2$] (blue line, $C_{HO2} = (1.97 \pm 0.06) \times 10^4$ mW$^{-1}$ s$^{-1}$ molecule$^{-1}$ cm$^3$) used to obtain a calibration constant ($C$).](Image)

### 2.4 Aerosol Flow Tube

The aerosol flow tubes used within the experiment are cylindrical, made of glass and roughly have the same dimensions (approximately 100 cm length and 5.9 cm O.D.). Glass is a suitable material due to the sensitivity of the experiment to transition metal contamination and it is possible to see the alignment of the injector within the aerosol flow tube. To reduce wall losses of HO$_2$ the inner walls are coated with a halocarbon wax (Halocarbon Wax Corporation, 600). The halocarbon wax was applied by dissolving it in chlorinated solvent, such as chloroform, which was poured into the tube until the entire inner wall has been coated. It was then left to dry leaving behind a halocarbon wax film. The halocarbon wax essentially provides an inert surface along the inner wall of the tube with little capacity to form any inter-
molecular bonds, therefore reducing losses of $\text{HO}_2$ to the aerosol flow tube walls. The aerosol flow tube was encased within a glass jacket capable of flowing heated or cooled liquid through it if temperature dependent experiments were required. The temperature within the aerosol flow tube was monitored using a calibrated probe (Rotronics HygroClip2, accuracy $\pm 0.1 \text{ K}$). The aerosol flow was introduced into the upstream end of the aerosol flow tube via two ports located adjacent to the injector port. The downstream end of the aerosol flow tube was connected to the FAGE cell with a compression fitting containing a Viton O-ring seal. Figure 2.18 presents a photograph of the aerosol flow tube set up within the experiment.

![Aerosol flow tube within experimental setup.](image)

**Figure 2.18**: Aerosol flow tube within experimental setup.

The total flow rate within the aerosol flow tube ($\sim 5.3 \text{ L min}^{-1}$) was the sum of the injector flow ($\sim 1.3 \text{ L min}^{-1}$) and aerosol flow ($\sim 4 \text{ L min}^{-1}$). It is important that the flow within the aerosol flow tube was laminar i.e. a stable concentration and known radial velocity profile. The concentration and velocity profile within the flow tube is parabolic as some $\text{HO}_2$ is lost on the aerosol flow tube wall surface and friction with the walls of the aerosol flow tube slows the flow at the boundary between the gas and the tube walls, meaning the flow in the middle of the tube is unaffected and flows faster. In order to determine whether the flow within the aerosol flow tube was laminar or turbulent, the Reynolds number ($Re$) must be calculated using E2.9.

If $Re$ is less than 2100 in a cylindrical pipe, then the flow is considered laminar. If $Re$ is less than 2100 in a cylindrical pipe, then the flow is considered laminar.

$$Re = \frac{2rv\rho}{\eta}$$  \hspace{1cm} (E2.9)

where $r$ is the radius of the aerosol flow tube (2.95 cm), $v$ is the velocity of the flow within the aerosol flow tube (3.23 cm s$^{-1}$), $\rho$ is the density of air (1.195 kg m$^{-3}$) and $\eta$ is the viscosity of air ($18.2 \times 10^{-6}$ kg m$^{-1}$ s at atmospheric pressure and 20$^\circ \text{C}$). This calculation results in a $Re$ of 125.2 meaning that the flow within the flow tube was in the laminar regime. Initially, as the aerosol flow enters the aerosol flow tube, the flow in the aerosol flow tube will not be laminar. However, the flow will become laminar after the flow has travelled a certain length along the
aerosol flow tube. This distance is referred to as the entrance distance (Le) and can be calculated using E2.10.  

\[ Le = 0.035 \times D \times Re \]  

(E2.10)

where \( D \) is the diameter of the aerosol flow tube (5.9 cm). This calculation results in a \( Le \) of 25.8 cm.

If mixing of the injector flow with the aerosol flow was purely characterised by diffusion, the time it takes for the two gases to mix (\( t_d \)) in a cylindrical tube under laminar conditions can be calculated using E2.11.

\[ t_d = \frac{r^2}{5D_g} \]  

(E2.11)

where \( r \) is the radius of the flow tube (2.95 cm) and \( D_g \) is the diffusion gas constant for HO\(_2\) (0.25 cm\(^2\) s\(^{-1}\), measured in oxygen and has been assumed to be the same as in nitrogen for the purposes of this calculation). This calculation results in a \( t_d \) of ~7 s which corresponds to a length of ~25 cm along the aerosol flow tube. However, this value is likely to be an overestimate as the design of the injector tip, which injects the HO\(_2\) flow perpendicular to the flow along the aerosol flow tube, should make the flow in this region of the aerosol flow tube turbulent and aid mixing reducing this time. Previously, experiments were undertaken to determine mixing time within the aerosol flow tube. These experiments showed that analyte concentrations stabilise at around 30 cm downstream of the injector. They also showed that initially the FAGE signal increases as a function of distance away from the FAGE cell inlet due to the time it takes HO\(_2\) to mix/diffuse to the centre of the flow tube. At an injector distance of ~12.5 cm the FAGE signal begins to decrease as a function of distance away from the FAGE cell inlet, as the reduction of HO\(_2\) due to wall losses and uptake by aerosols outweighs the increase of FAGE signal due to mixing and diffusion to the centre of the flow tube. At distances >25 cm HO\(_2\) appears to be well mixed as the decay in FAGE signal follows expected kinetics due to wall losses and uptake by aerosols.

During radical production experiments it was necessary to illuminate the flow tube in order to irradiate aerosols and initiate radical production. The aerosol flow tube was illuminated with a UVA lamp located adjacent to the FAGE cell and approximately 5 cm above the aerosol flow tube. Two UV lamps were used in this study; a 15 W UVA bench lamp (2 × 15 W 420 mm fluorescent tubes, UVP, XX-15) and an 8 W UVA lamp (1 × 8 W 300 mm fluorescent tube, Eterna, LFT58WH). The 15 W UVA lamp was used in all studies unless otherwise stated. The spectral output along with the lamp flux of the lamps were measured using a spectral radiometer (Ocean Optics QE500) and are presented in Figure 2.19. The spectral output of
light emissions from the lamps shown in Figure 2.19 was measured outside the aerosol flow tube since it was not possible to fit the spectral radiometer inside of the flow tube. The aerosol flow tube and the halocarbon wax film attenuates light entering the aerosol flow tube. An experiment was conducted where the spectral output of the 8 W lamp whilst placed inside the aerosol flow tube was measured outside the aerosol flow tube where the UV lamps are usually placed. It showed that the total flux of UVA photons from the lamp inside the aerosol flow tube was 16 times lower than that measured outside the aerosol flow tube (see Figure 2.19), in consequence the light flux inside of the aerosol flow tube is expected to be 16 times smaller than that measured outside the aerosol flow tube. However, this experiment is only indicative as lensing effects due to the curvature of the aerosol flow tube could affect the measurement.

Figure 2.19 compares the spectral flux of the lamps to the actinic flux measured at Weybourne (UK) during a typical summer’s day. It shows that the amount of light entering the flow tube from the 8W was likely to be less than typical actinic fluxes experienced within the troposphere.

**Figure 2.19:** UVA emission spectra for the 8 W UVA lamp inside (green line) and outside (black line) the aerosol flow tube and the 15 W UVA lamp outside the aerosol flow tube (red line) used within this investigation. The actinic flux (blue line) measured at Weybourne (UK) on the 1st July 2015.
2.5 Experimental Procedure & Data Analysis

2.5.1 Overview

There are three different experimental procedures used to measure the kinetics of heterogeneous uptake of HO$_2$ by aerosols using the aerosol flow tube apparatus; the sliding injector procedure, the fixed injector procedure and the anti-correlation procedure. The experimental procedures and methodologies for data analysis are based on those used within previous studies.$^9$, $^{66}$, $^{91}$ The sliding injector procedure was used to determine $\gamma$(HO$_2$), defined as $\gamma_{obs}$ after correction, for aerosols that can be easily generated by the constant output atomiser (i.e. deliquesced inorganic aerosols and TiO$_2$), where a stable concentration and size distribution of the aerosols can be produced within the aerosol flow. The anti-correlation procedure allows for the determination of $\gamma$(HO$_2$) for aerosols where a stable concentration and size distribution of aerosols cannot be achieved within the aerosol flow (e.g. MSP). The fixed injector procedure allows for the time-dependency of $\gamma$(HO$_2$) to be determined and was not too dissimilar to the anti-correlation procedure. During both these procedures, the injector was held at a fixed position corresponding to a fixed residence time of HO$_2$ within the aerosol flow tube and the change in HO$_2$ signal with aerosol concentration was measured. Whereas, during sliding injector experiments the change in HO$_2$ signal as the injector was pulled and pushed in and out of the aerosol flow tube (i.e. different HO$_2$ residence times within the aerosol flow tube) at a fixed aerosol concentration was measured.

Production of HO$_2$ by irradiated aerosols was investigated by measuring the absolute concentration of HO$_2$ at the end of the illuminated region of the aerosol flow tube. The length of this region corresponds to the exposure time of aerosols to UVA light. Loss of HO$_2$ produced by irradiated aerosols to the aerosol flow tube walls was determined by conducting sliding injector experiments in the absence of aerosols. The flow rate passed through the aerosol flow tube equalled 5.3 L min$^{-1}$ for all experimental procedures to ensure known mixing and laminar conditions occurred within the aerosol flow tube. The laser power was recorded during all experiments and used to normalise the HO$_2$ signal to correct for any fluctuations in laser power (typically < 5%).

2.5.2 Background Signal Measurement

Before any measurements were carried out the background signal (i.e. zero) of the FAGE instrument was determined. The injector was placed 30 cm away from the pinhole on the FAGE cell and the signal for the following experimental conditions were recorded:

1. Injector lamp turned off, NO flow to FAGE cell turned off;
2. Injector lamp turned on, NO flow to FAGE cell turned off; and
3. Injector lamp turned off, NO flow to FAGE cell turned on.
The first condition allows the measurement of dark counts and laser scatter to be determined and was averaged over ten seconds (average of ten 1 s measurement points, each corresponding to 5000 laser shots). The second condition allows for the amount of OH produced by the HO₂ generation setup, in addition to dark counts and laser scatter, to be determined and was averaged for 20 s (usually comparable to the first condition, suggesting all OH produced by the photolysis of water vapour was lost to the injector walls). The third condition, resulting in the highest counts of the three, allows the determination of total reactive nitrogen, \( \text{NO}_y \) \( (\text{NO}_y = \text{NO}_x + \text{NO}_z, \text{NO}_x = \text{NO} + \text{NO}_2, \text{NO}_z = \text{NO}_3 + \text{HONO} + \text{HO}_2\text{NO}_2 + \text{N}_2\text{O}_5 + \text{PAN} + \text{organic nitrates}) \), contamination (i.e. HONO photolysed by the 308 nm probe laser light producing OH in the cell) within the cell from the NO used to convert HO₂ to OH and was averaged for 45 seconds. This third condition determines the background signal for the FAGE instrument and was subtracted from all data taken during the experiment.

2.5.3 Moving Injector Experiment

The HO₂ signal was measured at eight positions as the moveable injector was pulled back from 30 to 70 cm (i.e. 30 cm, 40 cm, 45 cm, 50 cm, 55 cm, 60 cm, 65 cm and 70 cm) away from the FAGE cell inlet using a linear stepper drive under computer control (BSL Engineering 15 KR4610A, to an accuracy of 0.25 mm) and again as the moveable injector was pushed forwards back to its initial position (30 cm). The HO₂ signal was averaged over 20 s (average of twenty 1 s measurement points, each corresponding to 5000 laser shots), the same length of time as measurements during the calibration experiment, at each injector position with a 22 s delay between measurements at each injector position in order to ensure a full flush of the aerosol flow tube so that the LIF signal corresponds to HO₂ emitted from the injector position being measured and to allow time for mechanical vibrations to subside. The HO₂ signals with the injector moving forwards and backwards were then averaged, and this procedure repeated six times with varying concentrations of aerosols present in the aerosol flow tube. The aerosol concentration and size distribution was measured three times during each decay using the SMPS. The wall loss rate of HO₂ \( (k_{wall}) \) was determined by recording the HO₂ decay in the absence of aerosols, but at the same RH, and was repeated three times for each experiment.

The HO₂ concentration as a function of time along the flow tube can be expressed as:

\[
\ln[\text{HO}_2]_t = \ln[\text{HO}_2]_0 - k_{obs} t
\]

(E2.12)

where \([\text{HO}_2]_t \) and \([\text{HO}_2]_0 \) are concentrations of HO₂ at time \( t \) and \( t = 0 \) (in this case defined as when the injector was at its initial position, i.e. 30 cm from FAGE inlet to injector tip) respectively, and \( k_{obs} \) is the observed pseudo-first-order rate coefficient for HO₂ uptake. As the HO₂ signal is directly proportional to the concentration of HO₂ and this is a first-order process,
the gradient of a plot of ln(FAGE HO Signal) against residence time, \( t \), (calculated from the injector position and measured flow rate) also yields \( k_{\text{obs}} \).

An average of \( k_{\text{wall}} \) was subtracted from \( k_{\text{obs}} \), which was subsequently corrected (typically from 10% to 40% depending on \( k_{\text{wall}} \)) to account for non-plug flow conditions in the aerosol flow tube (i.e. flow is faster in the centre of the aerosol flow tube than at the walls due to friction and there is a radial gradient of \([\text{HO}_2]\) due to losses from wall losses) following the procedure outlined by Brown \(^{108}\) to yield, \( k \)' , the pseudo-first-order loss of HO\(_2\) by heterogeneous reaction with aerosols. If the flow within the aerosol flow tube could be characterised by plug flow conditions E2.13 could be used to calculate the concentration of HO\(_2\) at any given point along the aerosol flow tube, however as this is not the case and there is a parabolic radial \([\text{HO}_2]\) and flow velocity gradient due to HO\(_2\) reactions and friction with the walls of the aerosol flow tube respectively E2.13 needs modifying accounting for molecular gas-phase diffusion and wall loss rates giving E2.14. In order to provide the solution to E2.14 Brown \(^{108}\) developed a Fortran code, which was used in this work.

\[
[\text{HO}_2] = [\text{HO}_2]_0 e^{-\frac{k_{\text{obs}} z}{\langle u \rangle}} \quad (\text{E2.13})
\]

\[
[\text{HO}_2](r) = [\text{HO}_2]_0(r) e^{-\frac{k' z}{\langle u \rangle}} \quad (\text{E2.14})
\]

where \( k_{\text{obs}} \) is the observed first-order rate coefficient, \( z \) is the distance along the flow tube, \([\text{HO}_2]_0 \) is the concentration of HO\(_2\) when \( z = 0 \), \( \langle u \rangle \) is the average carrier flow velocity, \( k' \) is the true rate coefficient which is a function of \( \langle u \rangle \), the diffusion coefficient of HO\(_2\) in the gas-phase (0.25 cm\(^2\) s\(^{-1}\)), \( k_{\text{obs}} \) and the wall loss rate coefficient (\( k_{\text{wall}} \)) and \( r \) is the distance from the centre of the flow tube.

The relationship between \( k' \) and total surface area of aerosols (\( S_a \)) can be expressed as \(^9\):

\[
k' = \frac{\gamma_{\text{obs}} \omega_{\text{HO}_2} S_a}{4} \quad (\text{E2.15})
\]

where \( \omega_{\text{HO}_2} \) is the mean velocity of HO\(_2\) (~ 435 m s\(^{-1}\) at 293 K) and \( \gamma_{\text{obs}} \) is the observed reactive uptake coefficient, obtained from a plot of \( k' \) versus \( S_a \).

Gas-phase diffusion of HO\(_2\) to the aerosols surface limits heterogeneous uptake leading to an under-prediction of the reactive uptake coefficient, therefore, \( \gamma_{\text{obs}} \) was corrected (typically ~1%) to account for the gas diffusion limitation using the following formulae \(^{109}\):

\[
\gamma = \frac{\gamma_{\text{obs}}}{(1 - \gamma_{\text{obs}} \lambda(r))} \quad (\text{E2.16})
\]

where \( \lambda(r) \) is a function of the Knudsen number:
\[ \lambda (r) = \frac{0.75 + 0.283 Kn}{Kn(1+Kn)} \]  
(E2.17)

The Knudsen number, \( Kn \), is defined as:

\[ Kn = \frac{3Dg}{\omega_{HO_2} r_s} \]  
(E2.18)

where \( r_s \) is the geometric mean of the radius of the aerosols.

Compared to surface-film and Knudsen apparatus, diffusion limitations are much less for the size of aerosols used in this work, however, the effect maybe significant when measuring uptake onto relatively large aerosols or where the \( \gamma_{obs} \) is large.

### 2.5.4 Fixed Injector Experiment

The \( HO_2 \) signal was measured at various stable aerosol concentrations for fixed injector positions. The injector was fixed at five positions in a random order along the aerosol flow tube from 30 cm to 70 cm (i.e. 30 cm, 40 cm, 50 cm, 60 cm and 70 cm) during each experiment. The \( HO_2 \) signal when no aerosols were present in the aerosol flow tube was measured for ten seconds (average of ten 1 s measurement points, each corresponding to 5000 laser shots) at the beginning and end of each decay. Subsequently, aerosols were introduced within the aerosol flow tube and the \( HO_2 \) signal was measured for ten seconds and the aerosol concentrations and size distribution was measured by the SMPS. The aerosol concentration was altered using a HEPA filter situated within a by-pass loop and the procedure was repeated in total seven times.

As the residence time, \( t \), is constant \( k_{wall} \) and \( k_{obs} \) can be expressed as:

\[ \ln[HO_2]_{t, aerosol=0} - \ln[HO_2]_0 = -k_{wall} \]  
(E2.20)

\[ \ln[HO_2]_{t, aerosol} - \ln[HO_2]_0 = -k_{wall+aerosols} \]  
(E2.21)

\[ \ln[HO_2]_{t, aerosol=0} - \ln[HO_2]_{t, aerosol=0} = -k_{obs} \]  
(E2.20 – E2.21)

It was necessary to conduct a sliding injector experiment in the absence of aerosols to correct \( k_{obs} \) for non-plug flow conditions within the aerosol flow tube using the procedure described by Brown \(^{108}\) to yield \( k' \).

As with the sliding injector experiment, a plot of \( k' \) against \( S_a \) for each fixed injector position, and hence \( t \), yields the time dependent values of \( \gamma_{obs} \) which are subsequently corrected for the gas diffusion limitation \(^{109}\) to give \( \gamma(HO_2) \).
2.5.5 Anti-Correlation Experiment

During an anti-correlation experiment, as with fixed injector experiments, the injector position was fixed at five positions in a random order along the aerosol flow tube from 30 cm to 70 cm (i.e. 30 cm, 40 cm, 50 cm, 60 cm and 70 cm), corresponding to a fixed \( t \), during each experiment. The \( \text{HO}_2 \) signal was then measured every second for 70 s in tandem with the unstable aerosol concentration using the CPC. As the unstable aerosol concentration fluctuated the \( \text{HO}_2 \) signal anti-correlated with the aerosol concentration (i.e. as the aerosol concentration increased the \( \text{HO}_2 \) signal decreased). The Acoustic Particle Disperser (APD) was used to stabilise the aerosol concentration fluctuation somewhat allowing time for the \( \text{HO}_2 \) signal to respond yielding better results. The \( \text{HO}_2 \) signal and aerosol concentration measurements were averaged every three measurements with the error being 1\( \sigma \) of the three measurements. The natural log of the \( \text{HO}_2 \) signal was plotted against the aerosol concentration, the gradient of which yields a value equal to 0.25\( \gamma_{obs} \omega A_d \), where \( A_d \) is the geometric mean surface area of a single aerosol. A plot of 0.25\( \gamma_{obs} \omega A_d \) against \( t \) was then produced, the gradient of which yields a value for 0.25\( \gamma_{obs} \omega A_d \). As \( \omega \) can be easily calculated and \( A_d \) can be experimentally determined (see below) \( \gamma_{obs} \) can be obtained. \( A_d \) was determined by taking an average of around thirty size distributions of the aerosol flow with the SMPS. Assuming that the particles are spherical, then it is possible to use the fit of the average size distribution to calculate the average radius of a particle (\( r_{av} \)) by utilising E2.22.

\[
A_{total} = 4\pi r_{av}^2 N_{total}
\]  
\hspace{1cm} (E2.22)

where \( A_{total} \) is the total surface area of the distribution and \( N_{total} \) is the total number of particles in the distribution. It is then possible to calculate the average surface area of a particle (\( A_d \)) using E2.23.

\[
A_d = 4\pi r_{av}^2
\]  
\hspace{1cm} (E2.23)

As with all other experiments, corrections were made for non-plug flow conditions within the flow tube\(^{[41]} \) and the gas diffusion limitation\(^{[109]} \).

2.5.6 \( \text{HO}_2 \) Production Experiment

At the beginning of all experiments the FAGE background measurements were taken without and with NO injected into the FAGE cell and subtracted from the OH and \( \text{HO}_2 \) signals respectively. The FAGE signal was averaged over 20 s (average of twenty 1 s data points, each corresponding to 5000 laser shots) for each measurement. Eight 20 s measurements were taken during each run. Measurements were made in the absence of aerosols and in the presence of aerosols. Measurements of \( \text{HO}_4 \) concentration under varying conditions were made; at different total surface area density of TiO\(_2\) aerosols, RH, light flux and oxygen
concentration. The laser power was recorded for each measurement and used to normalise the \( \text{HO}_2 \) signal to correct for any fluctuations in laser power (< 5%). Within the aerosol flow tube a number of radical production and loss processes occurred:

1. radical production from photocatalytic activity on airborne aerosol surfaces \( (k_{\text{prod}}) \);  
2. radical production from photocatalytic activity on the surfaces of a small number of aerosols that have deposited on the walls of the aerosol flow tube \( (k_{\text{prod\;wall}}) \);  
3. radical loss from homogeneous \( \text{HO}_2 \) self-reaction \( (k_{\text{self}}) \);  
4. radical loss from reactive heterogeneous uptake on aerosol surfaces \( (k_{\text{aerosol\;loss}}) \); and  
5. radical loss from reactive heterogeneous uptake on the walls of the aerosol flow tube \( (k_{\text{wall}}) \).

The concentration of \( \text{HO}_2 \) measured at the end of the aerosol flow tube will be a function of all these processes, therefore to obtain a value for the rate of production \( \text{HO}_2 \) from aerosols only these processes were then included in a model developed within a numerical integrator, Kintecus (Windows Version 2.80)\(^{110}\). The rate of radical production from aerosols was calculated by constraining the model to measurements of \( \text{HO}_2 \) made with \( (k_{\text{prod}} + k_{\text{prod\;wall}}) \) and without aerosols \( (k_{\text{prod\;wall}}) \) present within the aerosol flow tube and in the presence of light and to experimental determinations of \( k_{\text{wall}} \) and \( k_{\text{aerosol\;loss}} \). The reactions considered within the model are as follows:

\[
\begin{align*}
\text{HO}_2 & \xrightarrow{k_{\text{wall}}} \text{Wall loss} \quad \text{(R2.5)} \\
\text{HO}_2 & \xrightarrow{k_{\text{uptake}}} \text{Aerosol Uptake} \quad \text{(R2.6)} \\
2\text{HO}_2 & \xrightarrow{k_{\text{self}}} \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R2.7)} \\
[\text{Wall}] + h\nu & \xrightarrow{k_{\text{prod\;wall}}} \text{HO}_2 \quad \text{(R2.8)} \\
[\text{Aerosol}] + h\nu & \xrightarrow{k_{\text{prod}}} \text{HO}_2 \quad \text{(R2.9)}
\end{align*}
\]

where \([\text{Wall}]\) and \([\text{Aerosol}]\) are the surface area concentration (cm\(^2\) cm\(^{-3}\)) of the illuminated walls of the aerosol flow tube (i.e. surface area of the interior walls of the aerosol flow tube divided by the internal volume of aerosol flow tube) and TiO\(_2\) aerosols, respectively and \( t \) is the average residence time within the illuminated region of the flow tube. The concentration of aerosols and the walls were given as surface area density (cm\(^2\) cm\(^{-3}\)) in the model as these processes occurred on surfaces. The reaction time was calculated from the flow rate of the bath gas through the aerosol flow tube and the length of the UVA lamp.
2.5.7 Error Analysis

The error of the averaged HO$_2$ signal was defined as 1σ of the number of data points taken during the averaging period. Where a parameter was obtained by the gradient of a plot, the error was 1σ of the gradient and was obtained from plotting software, Origin Pro (v.9.0). The error given on all measurements of γ(HO$_2$) presented in this work represents 2σ of variability of measurements of either $k'$ for sliding injector and fixed injector experiments or $0.25\gamma_{\text{obs}}\omega A_{dt}$ for anti-correlation experiments. During all calculations errors were propagated using the standard laws of error propagation. The Brown correction calculation is complex and is performed by a FORTRAN subroutine called ROOT. When propagating error through Brown correction calculations the correction factor was determined by plotting the Brown corrected pseudo-first-order rate constant, $k'$, against the uncorrected observed rate constant minus the rate constant observed during the wall loss run (Figure 2.20) resulting in a linear plot. The gradient of such a plot was the correction factor calculated by ROOT. The values of $k_{\text{obs}}$ determined by anti-correlation and fixed injector experiments along with the error of $k_{\text{obs}}$ for all experimental procedures were multiplied by this factor. The Brown correction methodology typically increases uncorrected values by 10 - 40% depending on temperature, flow rate and $k_{\text{wall}}$.

![Figure 2.20](image_url)
2.6 Summary

This chapter has described the apparatus used to investigate heterogeneous reactions involving HO₂ radicals and atmospherically relevant submicron aerosols. In order to measure the reactive uptake coefficient, $\gamma$(HO₂), HO₂ was injected co-axially at different positions along a laminar aerosol flow tube which alters the HO₂ exposure time to a known size distribution and concentration of aerosols. Changes in HO₂ concentrations were detected using the sensitive FAGE technique and the aerosol size distribution was measured using a SMPS. HO₂ was produced in the back of the injector by the photolysis of water vapour in the presence of trace amounts of O₂. Inorganic and TiO₂ aerosols were generated by a constant output atomiser, where MSP were entrained into a flow of N₂ using a stirrer plate or a piece of apparatus specially designed known as an APD. The FAGE detector was calibrated periodically using a turbulent flow tube known as a wand, a technique developed and regularly used within field campaign measurements. The SMPS was also calibrated a number of times using CML beads of a known size. The chapter also presents four different measurement methodologies; the moving injector methodology was used to measure $\gamma$(HO₂) onto aerosols where a constant and steady aerosol concentration could be generated, the fixed injector methodology allowed for the determination of the time dependence of $\gamma$(HO₂), the anti-correlation methodology was used to measure $\gamma$(HO₂) onto aerosols where only a unstable aerosol concentration could be generated within the flow and the HO₂ production methodology which allows for the determination of the rate of production of HO₂ from aerosol surfaces, $k_{prod}$. 
Chapter 3 – HO₂ Uptake on Aerosols relevant to the Troposphere

The chapter presents the results and interpretation of experiments conducted on deliquesced inorganic salt aerosols doped with transition metal and iodide ions.
3.1 Introduction

The presence of copper (Cu) or iron (Fe) ions within deliquesced aerosols is known to catalyse reactive uptake of HO₂, playing an important role in the variability of the oxidative capacity of the atmosphere (see section 1.11.3). Cu is the most effective known transition metal ion (TMI) at catalysing HO₂ uptake, so much so it has been used in previous studies to dope deliquesced inorganic aerosols in order to measure the mass accommodation coefficient for HO₂, α(HO₂)⁹⁴,⁵⁷,⁶¹. These studies were all carried out using a similar experimental setup as this work, i.e. a kinetic experiment involving an aerosol flow tube coupled to some type of HO₂ detector. However, measured values of reactive uptake coefficient, γ(HO₂), (see Table 3.1) are inconsistent between studies, probably due to differences in certain conditions such as RH and the initial concentration of HO₂, [HO₂]₀. Iron is not as effective at catalysing HO₂ uptake, however it is much more abundant in atmospheric aerosols⁵³ and therefore the reaction of HO₂ with Fe ions within aerosols are important, although the only published values of γ(HO₂) onto Fe-doped inorganic aerosols are within Dr Lakey’s thesis⁷⁸. Manganese (Mn) is another TMI present in significant quantities within deliquesced inorganic aerosols from polluted regions, although no known measurements of HO₂ onto such aerosols are reported. The presence of Cu or Fe has been thought to catalyse the conversion of HO₂ to H₂O₂, which if desorbed out of the aerosol can undergo photo-dissociation producing OH radicals, limiting the effectiveness of aerosol uptake as a potential sink of HOₓ (see section 1.11.3). Also, H₂O₂ can undergo Fenton reactions with Fe ions in the aqueous phase also resulting in the recycling HOₓ. However, more recent studies⁶² have suggested that HO₂ uptake results in conversion to H₂O rather than H₂O₂. It is postulated that HO₂ aerosol uptake is driven via a different mechanism in the presence of both Cu and Fe ions involving a fast electron transfer reaction between Cu(I) and Fe (III) (see section 1.11.3). Aquoeous-phase photochemistry is known to be enhanced within aerosols partly due to increased light intensity within aerosols due to Morphology-Dependent Resonances and increased path lengths within aerosols caused by refraction as light crosses the air–liquid interface, but predominantly due to a decreased solvent-cage effect and/or enhanced concentrations within the interfacial layer¹¹¹. To our knowledge, HO₂ uptake onto irradiated TMI-doped deliquesced inorganic aerosols has never been studied, although it is known that Fenton reactions occur at an accelerated rate in the presence of light and organic-Fe complexes within aerosols produce significant quantities of HO₂ when irradiated.

Iodide (I⁻) ions can be found within surface seawater, typically reaching concentrations of 1 – 20 × 10⁻⁸ M¹¹², therefore they are often present in fresh sea salt aerosols within the marine boundary layer. It was once thought that I⁻ is not present in significant properties within aged sea salt aerosols as it undergoes a series of reactions that result in its conversion to volatile species that desorbed into the gas-phase. However, modelling studies have shown that this
process was not as significant as previously thought\textsuperscript{113} and concentrations of iodide within aerosols measured during extended ship cruises in the Atlantic Ocean were often similar or exceeded concentrations of iodate (IO\textsubscript{3})\textsuperscript{114}, present due to uptake of gas-phase HIO\textsubscript{3} often thought to be inert within sea salt aerosols and accumulates within them. I\textsuperscript{-} undergoes some interesting chemistry at the sea surface. Reaction between aqueous phase I\textsuperscript{-} and accommodated O\textsubscript{3} is rapid (1 – 2 \times 10^9 \text{ M s}^{-1}) and results in the production of I\textsubscript{2}. The reaction between I\textsuperscript{-} and O\textsubscript{3} at the sea surface is the dominant source of I\textsubscript{2} emissions in the atmosphere\textsuperscript{112}. In order to understand whether similar chemistry could occur between I\textsuperscript{-} and HO\textsubscript{2} within the condensed phase, a study measuring the kinetics of heterogeneous reactions between HO\textsubscript{2} and KI and KI doped NaCl aerosols was conducted.

This study presents measurements of \(\gamma(\text{HO}_2)\) using the moving injector experimental methodology (see section 2.4.3) onto deliquesced inorganic aerosols doped with TMI and I\textsuperscript{-}. The first study investigates HO\textsubscript{2} uptake onto aerosols doped with Cu(II), Fe(II) or Mn(II) ions showing the importance of aerosol composition, RH and pH to this process. The range of aerosol TMI concentrations used within this study (\(\sim 10^0 – 10^{-4} \text{ moles kg}^{-1}\)) was comparable to concentrations of TMI found in atmospheric aerosols (see section 1.11.3). The study provides a comprehensive dataset of \(\gamma(\text{HO}_2)\) measurements onto Cu-doped aerosols and the first measurements of \(\gamma(\text{HO}_2)\) onto Mn-doped aerosols. In order to test whether transition metal ion coupling is significant, HO\textsubscript{2} uptake onto aerosols doped with Cu(II) and Fe(II) ions was investigated. Experimental data sets are compared to calculated data using expressions derived by Thornton et al.\textsuperscript{24} and to other measurements within the literature. In addition to this, the effects of irradiation of aerosols doped with TMI with actinically relevant wavelengths and flux has been investigated. These measurements offer atmospherically relevant measurements of HO\textsubscript{2} uptake by aerosols during the daytime. Measurements of \(\gamma(\text{HO}_2)\) onto KI aerosols and NaCl aerosols doped with I\textsuperscript{-}, typical to the composition of sea salt aerosols within the marine boundary layer, are also present. All experiments were conducted at atmospheric pressure and at room temperature (\(\sim 293 \text{ K}\)).

3.2 Measurements of the Reactive HO\textsubscript{2} Uptake Coefficient onto Deliquesced Inorganic Salt Aerosols Doped with Cu(II) ions

In a number of studies the mass accommodation coefficient, i.e. the probability of a gas-phase molecule being absorbed or adsorbed upon collision with an aerosol surface (\(\alpha\)), for deliquesced inorganic aerosols relevant to the atmosphere has been experimentally determined by doping the aerosols with Cu(II) ions. The reaction of HO\textsubscript{2} or its conjugate base, O\textsubscript{2}^{-}, with Cu ions is rapid, therefore the lifetime of HO\textsubscript{2} within aerosols doped with large quantities of Cu ions will be short (\(\sim 1 \text{ ns}\)). So much so that all HO\textsubscript{2} accommodated within the aerosol will
have reacted with Cu ions before desorbing out of the aerosols and hence $\gamma$(HO$_2$) will be equal to $\alpha$. In order to make this measurement it is important to dope the aerosols with a sufficient concentration of Cu(II) ions, however as seen in Figure 3.1, adding too much Cu(II), in the form of CuSO$_4$, to the aerosols can depress values of $\gamma$(HO$_2$). Figure 3.1 shows measurements of $\gamma$(HO$_2$) onto deliquesced ammonium sulphate ((NH$_4$)$_2$SO$_4$) aerosols at a RH of 43% and 65%, LiNO$_3$ at a RH of 43% and NaCl aerosols at a RH of 63% doped with different concentrations of Cu(II).

![Figure 3.1: Measurements of $\gamma$(HO$_2$) onto (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% (red filled squares) and 65% (black filled circles and black empty circles), NaCl aerosols at a RH of 63% (blue filled triangles) and LiNO$_3$ aerosols at a RH of 43% (green diamonds) at different estimated Cu(II) concentrations within the aerosols. Note measurements of $\gamma$(HO$_2$) onto Cu-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 65%, represented by empty black circles, were provided by Dr Pascale Lakey (PL) 78.

The concentration of Cu(II) in the aerosols was estimated using E3.1.

$$[\text{Cu(II)}]_{\text{aerosol}} = \frac{\text{moles of Cu(II) in the atomiser}}{\text{AWC for moles of inorganic salt in the atomiser}}$$  \hspace{1cm} (E3.1)

where AWC is the aerosol water content at a given RH provided by the Aerosol Inorganic Model (AIM) $^{115}$ (http://www.aim.env.uea.ac.uk/aim/aim.php) for (NH$_4$)$_2$SO$_4$ and NaCl aerosols and the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients model (AIOMFAC) $^{116}$ for LiNO$_3$ aerosols.
The AIM and AIOMFAC are online thermodynamic phase equilibrium models for use within aerosol science. They can calculate the distribution of water in the liquid, solid and vapour phases. The models require the number of moles the salt, RH and temperature as their inputs. The models outputs the concentration of ionic species in the liquid phase as well as the volume of water in the liquid phase (i.e. the AWC). This enables the determination of the aerosol pH and concentration of species in the aerosol phase using E3.1.

Table 3.1 compares measurements of $\gamma$(HO$_2$) onto deliquesced Cu-doped NaCl and (NH$_4$)$_2$SO$_4$ aerosols made in this work and other studies 54, 61, 78. It shows that there is broad agreement between measurements across all studies. Measurements of $\gamma$(HO$_2$) by Taketani et al. 61 are the most suitable measurements to compare with measurements in this work and the work of Dr Lakey 78 as the initial concentration of gas-phase HO$_2$, [HO$_2$]$_0$, and the apparatus used are comparable. Taketani et al. 61 measurement of $\gamma$(HO$_2$) on Cu-doped (NH$_4$)$_2$SO$_4$ aerosols was higher than in this work due to a slightly higher [Cu(II)]$_{aerosol}$. Taketani et al. 61 measurements of $\gamma$(HO$_2$) onto Cu-doped NaCl are much higher than in this work, however inspection of the dataset in this work shows that a was not reached at the highest [Cu(II)]$_{aerosol}$ (0.369 M) and $\gamma$(HO$_2$) increases dramatically within this range of [Cu(II)]$_{aerosol}$. Projection of $\gamma$(HO$_2$), assuming $\gamma$(HO$_2$) increases at the same rate between [Cu(II)]$_{aerosol}$ = 0.29 M – 0.37 M, to [Cu(II)]$_{aerosol}$ = 0.5 M using the dataset from this work results in a value of $\gamma$(HO$_2$) = 0.613 which is in agreement with their measurement.

**Table 3.1:** Comparison of measured values of $\gamma$(HO$_2$) onto Cu-doped deliquesced inorganic aerosols with this work and other studies.

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>RH / %</th>
<th>[HO$_2$]$_0$ / molecule cm$^{-3}$</th>
<th>[Cu(II)]$_{aerosol}$ / M</th>
<th>$\gamma$(HO$_2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>45 - 55</td>
<td>~ 10$^8$</td>
<td>~ 0.5</td>
<td>0.53 ± 0.12</td>
<td>Taketani et al. (2008)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>42</td>
<td>(2.5 - 5) × 10$^{10}$</td>
<td>0.16</td>
<td>0.5 ± 0.1</td>
<td>Thornton &amp; Abbott (2005)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>43</td>
<td>(0.6 - 1.5) × 10$^9$</td>
<td>0.38</td>
<td>0.36 ± 0.02</td>
<td>This work</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>65</td>
<td>(0.6 - 1.5) × 10$^9$</td>
<td>0.29</td>
<td>0.39 ± 0.04</td>
<td>This work</td>
</tr>
<tr>
<td>NaCl</td>
<td>45 - 55</td>
<td>~ 10$^8$</td>
<td>~ 0.5</td>
<td>0.65 ± 0.17</td>
<td>Taketani et al. (2008)</td>
</tr>
<tr>
<td>NaCl</td>
<td>63</td>
<td>(0.6 - 1.5) × 10$^9$</td>
<td>0.37</td>
<td>0.34 ± 0.01</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 3.1 also presents measurements of $\gamma$(HO$_2$) onto LiNO$_3$ aerosols doped with Cu(II). Although LiNO$_3$ aerosols are not atmospherically relevant, previous measurements 57 of $\gamma$(HO$_2$) onto Cu-doped LiNO$_3$ showed high levels of uptake; $\gamma$(HO$_2$) ranging from 0.67 when [Cu(II)]$_{aerosol}$ = 5.9 × 10$^{-3}$ mol kg$^{-1}$ to 1.92 (theoretically impossible) when [Cu(II)]$_{aerosol}$ = 6.2 × 10$^{-3}$ mol kg$^{-1}$. Measurements of $\gamma$(HO$_2$) onto Cu-doped LiNO$_3$ aerosols made in this work
(0.24 when \([\text{Cu(II)}]_{\text{aerosol}} = 5.4 \times 10^{-1} \text{ mol kg}^{-1}\) and 0.19 when \([\text{Cu(II)}]_{\text{aerosol}} = 5.4 \times 10^{-2} \text{ mol kg}^{-1}\) are significantly lower than those previous measurements, even though \([\text{Cu(II)}]_{\text{aerosol}}\) are around two orders of magnitude higher. A likely reason for the discrepancy between the two datasets are that the previous measurements were made on monodisperse aerosols with a larger diameter (108 nm) than the average diameter of the polydisperse LiNO\(_3\) aerosols used within this work (43 nm), which also suggests that the previous measurements could have been made at a greater RH.

The relationship between \(\gamma(\text{HO}_2)\) onto both (NH\(_4\))\(_2\)SO\(_4\) and NaCl aerosols and \([\text{Cu(II)}]_{\text{aerosol}}\) gives a sigmoidal relationship due to the opposing effects of diffusion and the rate of chemical reaction within the aerosol. The following discussion, with regards to this relationship, refers to data for Cu-doped (NH\(_4\))\(_2\)SO\(_4\) aerosols at a RH of 65\% as the dataset covers measurements of \(\gamma(\text{HO}_2)\) across the widest range of \([\text{Cu(II)}]_{\text{aerosol}}\). At low \([\text{Cu(II)}]_{\text{aerosol}}\) the kinetics of the heterogeneous reaction between HO\(_2\) in the gas-phase and the aerosols is diffusion limited, meaning diffusion of HO\(_2\) to a reactant within the aerosol is the rate determining step. The length HO\(_2\) travels from being accommodated within the aerosol before reacting with Cu(II) is referred to as the reacto-diffusive length \((l)\) and can be calculated using E3.2 (also see section 1.11).

\[
l = \frac{D_{\text{HO}_2}}{k_{\text{II}}[\text{Cu(II)}]_{\text{aerosol}}} \quad \text{(E3.2)}
\]

where \(D_{\text{HO}_2}\) is the diffusion coefficient for HO\(_2\) \((1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\) \(^{24}\) and \(k_{\text{II}}\) is the bi-molecular rate for the reaction of Cu(II) + HO\(_2\)/O\(_2\) \((1.5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1})\) \(^{117}\).

Figure 3.2 presents the calculated \(l\) against \([\text{Cu(II)}]_{\text{aerosol}}\). At \([\text{Cu(II)}]_{\text{aerosol}} < 10^{-5} \text{ M}\), \(\gamma(\text{HO}_2)\) was measured to be equal to \(\gamma(\text{HO}_2)\) for pure (NH\(_4\))\(_2\)SO\(_4\) aerosols \((0.007)\) as the reacto-diffusive length is much greater than the diameter of the aerosol. HO\(_2\) will have either desorbed or reacted with itself or its conjugate base (O\(_2\)) before diffusing to and reacting with a Cu(II) ion. The value of \(l\) decreases rapidly as \([\text{Cu(II)}]_{\text{aerosol}}\) increases resulting in small observed increases of \(\gamma(\text{HO}_2)\) within this range of \([\text{Cu(II)}]_{\text{aerosol}}\) \((10^{-5} - 10^{-3} \text{ M})\) as some longer-lived molecules of HO\(_2\) within the aerosols that have diffused into the bulk diffuses to and reacts with Cu(II), particularly within larger aerosols. At a critical \([\text{Cu(II)}]_{\text{aerosol}}\) \((\sim 10^{-3} \text{ M})\) the reaction is no longer fully diffusion limited as \(l\) approaches the average diameter of the aerosol and smaller aerosols begin to play a significant role in uptake. HO\(_2\) is more likely to react with Cu(II) than self-react or desorb out of the aerosol beyond this \([\text{Cu(II)}]_{\text{aerosol}}\), resulting in large observed increases of \(\gamma(\text{HO}_2)\) until the reaction between HO\(_2\) and the aerosol becomes kinetically limited \(([\text{Cu(II)}]_{\text{aerosol}} \sim 10^{-1} \text{ M})\). At high \([\text{Cu(II)}]_{\text{aerosol}}\) \(l\) is only a few nanometres meaning that the reaction was occurring within the interfacial layer with all HO\(_2\) that is accommodated, not only...
HO₂ that diffuses into the bulk, reacting with Cu(II). \( \gamma(\text{HO}_2) \) is now limited to how fast HO₂ reacts with Cu(II) within the aerosol and by \( \alpha \). As it is thought that Cu(II) reacts so quickly with HO₂, unlike Mn(II) and Fe(II), within the aerosol, \( \gamma(\text{HO}_2) \) is therefore only limited by \( \alpha \). However, Figure 3.1 also shows that \( \gamma(\text{HO}_2) \) decreases when \([\text{Cu(II)}]_{\text{aerosol}} > 2 \times 10^{-1} \text{ M}\) when \( \gamma(\text{HO}_2) \) should remain constant at a value equal to \( \alpha \). At this \([\text{Cu(II)}]_{\text{aerosol}} \) the aerosol is more likely taking on the physical and chemical characteristics of CuSO₄ aerosols rather than copper-doped (NH₄)₂SO₄ aerosols and therefore values of \( \gamma(\text{HO}_2) \) onto (NH₄)₂SO₄ aerosols doped with \([\text{Cu(II)}]_{\text{aerosol}} > 0.4 \text{ M}\) are discounted in any further analysis (i.e. Figure 3.3).

Indeed, when \([\text{Cu(II)}]_{\text{aerosol}} > 2 \times 10^{-1} \text{ M}\) \( \gamma(\text{HO}_2) \) begins to tend towards \( \gamma(\text{HO}_2) \) onto CuSO₄ aerosols, which was measured to be 0.223 ± 0.016 at RH 65%. It might be expected that \( \gamma(\text{HO}_2) \) onto CuSO₄ to be larger than (NH₄)₂SO₄ aerosols doped with a more dilute concentration of Cu(II), however it is likely that other factors such as differences in the solubility of HO₂ significantly affects \( \gamma(\text{HO}_2) \). These results show that \( \alpha \) can never be truly measured by this method due to the amount of \([\text{Cu(II)}]_{\text{aerosol}} \) required would in fact change the physical and chemical characteristics of the aerosol, although it does provide a good estimate.

![Figure 3.2](image-url): Calculated reacto-diffusive length as a function of the concentration of Cu(II) in the aerosols using E3.2.

Figure 3.1 shows that parameters such as RH and aerosol composition can significantly affect the relationship between \( \gamma(\text{HO}_2) \) and \([\text{Cu(II)}]_{\text{aerosol}} \). In order to understand what could be driving the differences observed between the datasets, measurements of \( \gamma(\text{HO}_2) \) presented in
Figure 3.1 are compared to calculated values of $\gamma$(HO$_2$) using E3.3, referred to as the Thornton expression $^{24}$ (also see section 1.11.3). This expression allows for the parameterisation of $\gamma$(HO$_2$) with changes of [Cu(II)]$_{aerosol}$ and has been derived from the resistor model (section 1.11.1) and so accounts for gas-phase diffusion, diffusion in the bulk of the aerosol phase, desorption from the aerosol, Langmuir adsorption and surface and bulk reactions. However, it assumes that the composition is homogeneous within the aerosol and does not account for any time dependences. Any deviation of measurements of $\gamma$(HO$_2$) away from what is predicted could be associated with a concentration gradient within the aerosol of certain species.

$$\frac{1}{\gamma} = \frac{1}{a} + \frac{\bar{c}}{H_{eff}RT \sqrt{k_{II}[Cu(II)]_{aerosol}D_{HO2}Q}} \quad (E3.3, \text{Thornton Expression})$$

where $\bar{c}$ is the mean molecular speed (435 cm s$^{-1}$ at 295 K), $H_{eff}$ is the effective Henry’s law coefficient (see below), $R$ is the universal gas constant (8.2057 × 10$^{-2}$ atm L mol$^{-1}$ K$^{-1}$) and $Q$ is defined in E3.4 (also see section 1.11.3).

$$Q = \l[\coth(q) - \frac{1}{q}\r] q = R_p \sqrt{\frac{k_{II}[Cu]_{aerosol}}{D_{HO2}}} \quad (E3.4)$$

where $R_p$ is the particle radius (measured, see below).

The value of $k_{II}$ used within this work was 1.5 × 10$^7$ M$^{-1}$ s$^{-1}$ $^{117}$ rather than the more frequently used value of 1.0 × 10$^9$ M$^{-1}$ s$^{-1}$ $^{24, 54}$. The value of $k_{II}$ used in this work reflects that more than half of the HO$_2$ accommodated within the aerosol will not dissociate to O$_2^-$ at the pH within (NH$_4$)$_2$SO$_4$ aerosols (4.1) as the other value of $k$ is a measurement for the reaction of solely O$_2^-$ and Cu(II) which would require more alkali conditions in order for this reaction to become significant. It also reflects a rate constant for a mixture of Cu(I) and Cu(II) ions. Values of $H_{eff}$ were calculated firstly by correcting the Henry’s law constant ($H$, 2000 M atm$^{-1}$) $^{62}$, which assumes solutions are ideal, to account for the salting out effects to HO$_2$ solubility using E3.5 $^{62}$. It was then further corrected again for aerosol pH due to the enhanced solubility of HO$_2$ upon dissociation (HO$_2$ pK$_a$ = 4.7) $^{7, 54}$ using E3.6 (also see section 1.13.1).

$$H_{corr.} = \frac{H}{A} \quad (E3.5)$$

$$Heff = H_{corr.} \left(1 + \frac{K_{eq}}{[H^+]}ight) \quad (E3.6)$$

where $A$ is the sum of the activity coefficients for the inorganic salt species (calculated from AIM $^{41}$), [H$^+$] is the concentration of protons in the aerosols (calculated from AIM $^{41}$) and $K_{eq}$ is the equilibrium constant for the dissociation of HO$_2$ to its conjugate base (2.1 × 10$^{-5}$ M) $^{24}$. 
$D_{\text{HO}_2}$ was corrected to account for viscosity ($9.56 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), however this resulted in only a negligible change (~5%). The value of $\gamma(\text{HO}_2)$ was calculated for each aerosol radius within the measured size distribution during the experiments and then weighted according to the number of particles of that size range. The weighted values of $\gamma(\text{HO}_2)$ each particle size was then added together to give the combined value of $\gamma(\text{HO}_2)$. E3.3 does not account for reactive loss of HO$_2$ due to self-reaction. The self-reaction of HO$_2$ is not important at relatively high [Cu(II)] aerosol when $l$ is short, however the calculations under-predict $\gamma(\text{HO}_2)$ at lower [Cu(II)] aerosol where the reaction of HO$_2$ and Cu(II) is diffusion limited. The measured values of $\gamma(\text{HO}_2)$ onto pure (NH$_4$)$_2$SO$_4$ and NaCl aerosols were added to calculated $\gamma(\text{HO}_2)$ at low [Cu(II)] aerosol (< $10^{-3}$ M) in order to account for reactive loss due to self-reaction. The values of parameters used within this investigation along with the geometric mean aerosol radii during experiments are provided in Table 3.2.

### Table 3.2: Values for parameters used within calculations of $\gamma(\text{HO}_2)$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(NH$_4$)SO$_4$ RH 43%</th>
<th>(NH$_4$)SO$_4$ RH 65%</th>
<th>NaCl RH 63%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total $A$ for inorganic salt species, e.g. NH$_4^+$, SO$_4^{2-}$, HSO$_4^-$, Na$^+$ and Cl$^-$</td>
<td>1.95</td>
<td>1.26</td>
<td>3.66</td>
</tr>
<tr>
<td>$H_{\text{corr.}}$ / M atm$^{-1}$</td>
<td>1023.15</td>
<td>1584.57</td>
<td>547.05</td>
</tr>
<tr>
<td>[H$^+$] / M</td>
<td>$7.47 \times 10^{-5}$</td>
<td>$7.87 \times 10^{-5}$</td>
<td>$1 \times 10^{-7}^*$</td>
</tr>
<tr>
<td>pH</td>
<td>4.1</td>
<td>4.1</td>
<td>7.0</td>
</tr>
<tr>
<td>$H_{\text{eff.}}$ / M atm$^{-1}$</td>
<td>1310.76</td>
<td>2007.63</td>
<td>164660.83</td>
</tr>
<tr>
<td>$\gamma(\text{HO}_2)$ for pure aerosol</td>
<td>0.007</td>
<td>0.010$^*$</td>
<td>0.052</td>
</tr>
<tr>
<td>Average aerosol radius / nm</td>
<td>21</td>
<td>23</td>
<td>31</td>
</tr>
</tbody>
</table>

* Assumed to be same as pure water. ** Previously measured$^9$

### 3.2.1 Dependence of $\gamma(\text{HO}_2)$ onto deliquesced Cu-doped inorganic aerosols upon RH

In order to investigate how changes in RH affects $\gamma(\text{HO}_2)$ onto deliquesced inorganic aerosols doped with Cu(II), and possibly deliquesced inorganic aerosols in general, measurements and calculations of $\gamma(\text{HO}_2)$ onto (NH$_4$)$_2$SO$_4$ aerosols doped with Cu(II)SO$_4$ at a RH of 43% and 65% are compared. Figure 3.3 compares measured and calculated $\gamma(\text{HO}_2)$ onto (NH$_4$)$_2$SO$_4$ RH 65% at different [Cu(II)] aerosol. Calculated $\gamma(\text{HO}_2)$ correlates well measured $\gamma(\text{HO}_2)$ across the entire range of [Cu(II)] aerosol suggesting that (NH$_4$)$_2$SO$_4$ aerosols can be characterised as a homogeneously mixed droplet with consistent properties throughout the aerosol. The high degree of correlation provides confidence in the parameterisation of $\gamma(\text{HO}_2)$ and the values of the parameters used within it. The value of $a$ used to calculate $\gamma(\text{HO}_2)$ that gives the best fit to measured data is 0.44. This shows that the upper limit of the measurement of $\gamma(\text{HO}_2)$ at
[Cu(II)]_{aerosol} (concentration of Cu(II) within the aerosol) = 0.268 M gives a good estimation of \( \alpha \).

Figure 3.3: Calculated (red line) using E3.3 and parameters in Table 3.2 and measured (black squares) \( \gamma(\text{HO}_2) \) onto (NH$_4$)$_2$SO$_4$ aerosols at a RH of 65\% at different [Cu(II)]$_{aerosol}$.

Figure 3.1 shows that values of \( \gamma(\text{HO}_2) \) onto (NH$_4$)$_2$SO$_4$ aerosols at a RH of 65\% are larger than at a RH of 43\% for a given [Cu(II)]$_{aerosol}$. Figure 3.4 compares measured and calculated \( \gamma(\text{HO}_2) \) onto (NH$_4$)$_2$SO$_4$ at a RH of 43\% for different [Cu(II)]$_{aerosol}$. The main difference between the input parameters used to calculate \( \gamma(\text{HO}_2) \) at RH of 43\% and a RH of 65\% was the value used for \( H_{eff} \). Higher concentrations of inorganic salt species in aerosols at a RH of 43\% reduces the solubility of HO$_2$ (i.e. lower \( H_{eff} \)) which results in lower values of \( \gamma(\text{HO}_2) \) observed. Certainly, (NH$_4$)$_2$SO$_4$ aerosols at RH of 65\% are bigger than at a RH of 43\% which will result in larger values of \( \gamma(\text{HO}_2) \), however it is unlikely that such a small increase (2 nm) in the aerosol radius would result in differences in \( \gamma(\text{HO}_2) \) observed. In order to get the best fit of calculated \( \gamma(\text{HO}_2) \) to measured values, \( \alpha \) was set to a value of 0.4 (red line in Figure 3.4). A lowering of \( \alpha \) could be imagined when the solubility of HO$_2$ into the condensed phase is reduced leading to less HO$_2$ being accommodated with a small contribution from the reduced likelihood of collisions of HO$_2$ with smaller aerosols, as described in collision theory. Figure 3.4 shows good agreement between measured and calculated \( \gamma(\text{HO}_2) \) at high [Cu(II)]$_{aerosol}$ (> \( 10^{-4} \) M) supporting the hypothesis that the main driver for the observed differences into the two
datasets is the salting out effects to HO₂ solubility. However, the level of agreement between measured and calculated \( \gamma(\text{HO}_2) \) worsens as \([\text{Cu(II)}]_{\text{aerosol}}\) was lowered.

![Figure 3.4](image)

**Figure 3.4:** Calculated (red line, \( \alpha = 0.4 \) and \( H_{\text{eff}} = 1310.76 \text{ M atm}^{-1} \)) using E3.3 and parameters in Table 3.2 and measured (black squares) \( \gamma(\text{HO}_2) \) onto (NH₄)₂SO₄ aerosols at a RH of 43% at different \([\text{Cu(II)}]_{\text{aerosol}}\).

The worsening of agreement between measured and calculated for \( \gamma(\text{HO}_2) \) onto (NH₄)₂SO₄ aerosols at a RH of 43% doped with \([\text{Cu(II)}]_{\text{aerosol}} < 10^{-1} \text{ M} \) could offer some insight into some interesting properties of inorganic aerosols at a RH within close proximity to their efflorescence point. In order to get agreement between measured and calculated \( \gamma(\text{HO}_2) \) either a parameterisation of \( k_{\text{II}} \) or \( H_{\text{eff}} \) is required. It seems inconceivable that the rate of the reaction between Cu(II) and HO₂ is not consistent throughout the entire aerosol, especially in light of the agreement between measured and calculated \( A \) for (NH₄)₂SO₄ aerosols at a RH of 65%, and that previous measurements of \( k_{\text{II}} \) cannot be applied to condensed aerosol chemistry.

Agreement of calculated and measured \( \gamma(\text{HO}_2) \) at \([\text{Cu(II)}]_{\text{aerosol}} > 10^{-1} \text{ M} \) gives confidence in the value of \( k_{\text{II}} \). A higher degree of partitioning between Cu(II) and Cu(I) at \([\text{Cu(II)}]_{\text{aerosol}} < 10^{-1} \text{ M} \) may change \( k_{\text{II}} \), however as Cu(I) reacts faster with HO₂ than Cu(II) (see section 1.11.3) this would result in an increase rather than a decrease of \( k_{\text{II}} \). Solvation effects within the aerosol (i.e. incomplete solvent cage) may also change \( k_{\text{II}} \), however this would likely decrease the activation barrier for the reaction resulting in an increase rather than a decrease of \( k_{\text{II}} \). The
only other parameter that could offer better agreement with measured and calculated $\gamma$(HO$_2$) would be a parameterisation of $H_{\text{eff}}$ with [Cu(II)]$_{\text{aerosol}}$.

The efflorescence point of (NH$_4$)$_2$SO$_4$ aerosols is a RH of 37.1% \textsuperscript{118}, close to the RH within these experiments (43%). It is clear that the aerosols within the experiments are deliquesced somewhat as other studies \textsuperscript{9, 61} have shown $\gamma$(HO$_2$) onto effloresced aerosols to be much lower than observed in this work. In order get agreement between calculated and measured $\gamma$(HO$_2$) across the entire dataset $H_{\text{eff}}$ needs to be parameterised as a function of [Cu(II)]$_{\text{aerosol}}$ and hence $l$. As $l$ is a measure of the length travelled of HO$_2$ upon accommodation until reaction with Cu(II), this reaction could be used to probe how the solubility of HO$_2$ changes as a function of the length HO$_2$ has travelled within the aerosol. $H_{\text{eff}}$ decreasing as a function of $l$ implies that the solubility of HO$_2$ decreases as HO$_2$ diffuses from the interfacial layer into the bulk. Figure 3.5 shows the values of $H_{\text{eff}}$ required to get agreement between calculated and measured $\gamma$(HO$_2$) as a function of [Cu(II)]$_{\text{aerosol}}$.

Figure 3.5: Parameterisation of $H_{\text{eff}}$ as a function of [Cu(II)]$_{\text{aerosol}}$ (black squares) to achieve agreement between calculated and measured $\gamma$(HO$_2$) at [Cu(II)]$_{\text{aerosol}}$ for (NH$_4$)$_2$SO$_4$ aerosols at RH 43%. The red line represents $H_{\text{eff}}$ as a best-fit function of [Cu(II)]$_{\text{aerosol}}$ where $H_{\text{eff}} = -2035.4 + 447.6 \times (1-e^{-(\text[Cu(II)]_{\text{aerosol}}/0.1123)}) + 2909.7 \times (1-e^{-(\text[Cu(II)]_{\text{aerosol}}/0.0120)})$.

Figure 3.5 shows that only a small change within error of the calculated $H_{\text{eff}}$ was required when [Cu(II)]$_{\text{aerosol}} > 5 \times 10^{-2}$ M (i.e. $l < 36$ nm) to reach agreement between measured and calculated $\gamma$(HO$_2$), however below this concentration the required value of $H_{\text{eff}}$ is strongly
dependent on \([\text{Cu(II)}]_{\text{aerosol}}\). This indicates that there are two layers within the aerosol, an inner and an outer layer. The outer layer is likely to be an aqueous phase layer with its composition well parameterised by AIM. Using Cu(II) as a probe, the value of \(l\) for HO\(_2\) at \([\text{Cu(II)}]_{\text{aerosol}} = 5 \times 10^{-2}\) M is 36 nm, meaning HO\(_2\) travels 36 nm in the outer layer before diffusing into the inner layer. The inner layer could be either a supersaturated metastable phase with higher concentrations of ionic species, possibly a crystalline core or a core with high concentrations of crystal nuclei, or the speciation of Cu(II) ions or inorganic salt species could change to species with a higher activity within the bulk than in the outer interfacial layer. Both of these conditions would lead to a decrease in HO\(_2\) solubility. The solubility of HO\(_2\) continually decreases the further HO\(_2\) travels within the inner bulk layer, suggesting that HO\(_2\) solubility within this layer is not homogeneous. As the aerosols are exposed to a RH (43%) close to their efflorescence point (37.1%) it could be that the aerosols are at the beginning of their transition into an effloresced crystalline phase. If the decrease of HO\(_2\) solubility in the inner layer is a consequence of a crystalline core or crystal nuclei forming and increased concentrations of inorganic species within it, then this suggests that as the RH is decreased within the apparatus deliquesced aerosols lose water initially from the bulk and crystallisation of the inorganic salt proceeds from the inside outwards. As RH is further decreased the bulk becomes metastable as more particle-phase water is lost, however the outer interfacial layer remains aqueous and fully deliquesced. If salt concentrations at this RH do increase the further into the bulk travelled, the conditions in the centre of the bulk could be right for homogeneous crystal nucleation to begin to occur. However, there is no direct evidence that partial crystallisation of the aerosol or the formation of crystal nuclei has occurred. If there is a crystalline phase within the aerosol this could aid crystallisation as particles internally mixed within (NH\(_4\))\(_2\)SO\(_4\) aerosols aid crystal nucleation, increasing the RH at which they effloresce\(^{119}\). Ionic species would adsorb and arrange themselves around the crystalline surface\(^{120}\) which could account for the increased ionic activity within the bulk described within this hypothesis. It is possible that the Cu(II) itself has precipitated out of the aqueous bulk phase, meaning that calculations of \([\text{Cu(II)}]_{\text{aerosol}}\) could be an over-estimate of actual Cu(II) available for reaction within the inner layer. This might explain the differences between calculated and measured \(\gamma(\text{HO}_2)\) at low \([\text{Cu(II)}]_{\text{aerosol}}\) at a RH of 43%. Figure 3.6 provides a diagram describing the heterogeneous reaction of gas-phase HO\(_2\) and (NH\(_4\))\(_2\)SO\(_4\) aerosols doped with \(3 \times 10^{-1}\) M and \(3 \times 10^{-2}\) M of Cu(II)\(_2\)SO\(_4\) at a RH of 43% according to the hypothesis described above.
Figure 3.6: Diagram of heterogeneous reaction between gas-phase HO₂ and a deliquesced (NH₄)₂SO₄ aerosol doped with 3 x 10⁻¹ M (top) and 3 x 10⁻² M (bottom) of Cu(II) at a RH of 43%. Dashed black lines represents HO₂ diffusion, dashed blue line represents inner and outer layer boundary, small dark blue circles represent Cu(II) complexes and blue colour gradient represents salt concentration/HO₂ solubility gradient.
3.2.2 Dependence of $\gamma$(HO$_2$) onto deliquesced Cu-doped inorganic aerosols with different chemical composition

To investigate how changes in aerosol composition affects $\gamma$(HO$_2$) onto deliquesced aerosols doped with Cu(II) and possibly to deliquesced inorganic aerosols in general, measurements and calculations of $\gamma$(HO$_2$) onto (NH$_4$)$_2$SO$_4$ and NaCl aerosols doped with Cu(II)SO$_4$ at a RH around 65% are compared. Figure 3.1 shows that measured $\gamma$(HO$_2$) onto NaCl aerosols doped with [Cu(II)]$_{aerosol}$ $\approx$ 3 x 10$^{-4}$ M at a RH of 65% was slightly lower than $\gamma$(HO$_2$) measured onto (NH$_4$)$_2$SO$_4$ aerosols doped with a similar concentration of Cu(II) ions at a RH of 65% and comparable to such aerosols at a RH of 43%. However, $\gamma$(HO$_2$) onto NaCl aerosols doped with [Cu(II)]$_{aerosol}$ $<$ 3 x 10$^{-4}$ M was measured to be much lower than $\gamma$(HO$_2$) onto Cu(II)-doped (NH$_4$)$_2$SO$_4$ aerosols at both RH. Also, $\gamma$(HO$_2$) onto Cu(II)-doped NaCl aerosols was still limited by diffusion processes at much higher [Cu(II)]$_{aerosol}$ than Cu(II)-doped (NH$_4$)$_2$SO$_4$ aerosols suggesting another process was prolonging diffusion to be a limiting factor to reactive uptake. The value of $\gamma$(HO$_2$) measured onto pure NaCl ($\gamma$(HO$_2$) = 0.052 $\pm$ 0.003) was found to be much higher than onto pure (NH$_4$)$_2$SO$_4$ ($\gamma$(HO$_2$) = 0.010 $\pm$ 0.002) which is evident in Figure 3.1. The pH of NaCl aerosols is likely to be higher (7, pH of water) than the pH of (NH$_4$)$_2$SO$_4$ aerosols (4.1). Ammonium ions (NH$_4^+$) are in equilibrium with ammonia (NH$_3$) (R3.1 and R3.2) within (NH$_4$)$_2$SO$_4$ aerosols, therefore HO$_2$ in NaCl aerosols will predominantly be in the form of O$_2^-$ whereas less than half of HO$_2$ will dissociate within (NH$_4$)$_2$SO$_4$ aerosols. O$_2^-$ reacts much quicker with accommodated HO$_2$ (see section 1.11.2) and dissociation of HO$_2$ to O$_2^-$ aids HO$_2$ solubility within the aerosol resulting in larger values of $\gamma$(HO$_2$) in pure NaCl aerosols. It is likely that once accommodated the dissociation of HO$_2$ to H$^+$ and O$_2^-$ will decrease the NaCl aerosol pH.

$$\text{NH}_3^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \quad (\text{R3.1, } pK_a = 9.25)$$

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad (\text{R3.2, } pK_b = 4.75)$$

Figure 3.7 shows a poor correlation between measured and calculated $\gamma$(HO$_2$) as a function of [Cu(II)]$_{aerosol}$ for NaCl aerosols. It is likely that some of the parameters used to calculate $\gamma$(HO$_2$) using E3.3 are not correct. The value of $k_{\text{II}}$ used was based on the reaction between [Cu(H$_2$O)$_6$]$^{2+}$ and HO$_2$/O$_2^-$. It is possible that Cu(II) could form different complexes within NaCl aerosols than in (NH$_4$)$_2$SO$_4$ aerosols and most HO$_2$ will have dissociated to O$_2^-$ in NaCl aerosols, therefore the value of $k_{\text{II}}$ is likely not to be appropriate in this case. As the reaction between Cu-doped NaCl aerosols does not reach its kinetic limit within the range of [Cu(II)]$_{aerosol}$ measured, a value of 0.65 was used for $\alpha$ which is an estimate based on values determined in other studies $^{61}$ and for (NH$_4$)$_2$SO$_4$, i.e. as $H_{\text{eff}}$ was calculated to be much larger.
for NaCl aerosols than for \((\text{NH}_4)_2\text{SO}_4\), this would lead to a larger value for \(\alpha\). A value of 7 for pH could also be an inappropriate value for the reasons mentioned above.

\[ \text{Figure 3.7: Calculated (red line) using E3.3 and parameters in Table 3.2 and measured (black squares) } \gamma(\text{HO}_2) \text{ onto NaCl aerosols at a RH of } 63\% \text{ at different } [\text{Cu(II)}]_{\text{aerosol}}. \]

As previously mentioned, aerosol composition could change the speciation of Cu(II) ions within the aerosols. Cu(II) ions in the presence of NH3 or Cl- can form a number of different complexes. Initially as Cu(II) ions solvate, Cu(II) is in the form of \([\text{Cu(H}_2\text{O})_6]^{2+}\) which is a weak acid. In the presence of small concentrations of NH3, a weak base, copper hydroxide complexes are formed which can precipitate out of the solution as a pale blue solid (R3.3). In the presence of excess NH3, ligand substitution occurs turning the initial solution from a pale blue to a dark blue due to the formation of copper ammonia complexes (R3.4).

\[ [\text{Cu(H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightleftharpoons \text{Cu(OH)}_2(\text{H}_2\text{O})_{4(\text{aq})} + 2\text{NH}_4^+ \]  
\[ \text{R3.3} \]

\[ [\text{Cu(H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]^{2+} \]  
\[ \text{R3.4} \]

In the presence of Cl- ions \([\text{Cu(H}_2\text{O})_6]^{2+}\) undergoes a ligand substitution reaction producing \([\text{Cu(Cl)}_4]^{2+}\) turning the solution pale green (mixture of blue \([\text{Cu(H}_2\text{O})_6]^{2+}\) and yellow \([\text{Cu(Cl)}_4]^{2+}\) ions).

\[ [\text{Cu(H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{Cu(Cl)}_4]^{2+} + 6\text{H}_2\text{O} \]  
\[ \text{R3.5} \]
In order to investigate the likely complexes of copper that could be present within (NH₄)₂SO₄ and NaCl aerosols, 10 ml solutions were prepared with the same concentrations of inorganic species within the aerosols given by AIM. Whilst it is appreciated that the chemistry within bulk solution can be different to that within an aerosol, these experiments are judged to give a good indication of likely complexes formed. Not all of the NaCl or (NH₄)₂SO₄ salt could be dissolved into the solution at room temperature, therefore the solutions were gently heated to 50°C until all the salt dissolved. Table 3.3 presents the concentration of inorganic salts within the aerosols which were calculated by AIM and the amount of each salt dissolved into 10 ml of milli-Q water.

Table 3.3: Concentration of salt within aerosols and mass of salt added to 10 ml of milli-Q water.

<table>
<thead>
<tr>
<th>Species</th>
<th>(NH₄)₂SO₄ aerosols at a RH of 65%</th>
<th>NaCl aerosols at a RH 63%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration / M</td>
<td>Amount dissolved into 10 ml of water / g</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>5.70</td>
<td>7.53</td>
</tr>
<tr>
<td>Cu(II)SO₄</td>
<td>0.285</td>
<td>0.711</td>
</tr>
</tbody>
</table>

Figure 3.8 shows a solution of Cu(II)SO₄ only, a solution of (NH₄)₂SO₄ and Cu(II)SO₄ and a solution of NaCl and Cu(II)SO₄. It shows that the initial CuSO₄ solution was blue. Upon addition of (NH₄)₂SO₄ there was a slight change in the colour of the solution to a paler blue. When allowed to cool, a blue crystalline residue formed in the bottom of the beaker, likely a mixture of (NH₄)₂SO₄ and CuSO₄ salting out of the solution but possibly evidence of copper hydroxide precipitate. The experiment suggests that within (NH₄)₂SO₄ aerosols most copper remains as [Cu(H₂O)₆]²⁺ with possibly some Cu(OH)₂(H₂O)₄ precipitate. Indeed, AIM predicts that only a very small concentration of NH₄⁺ will dissociate to NH₃ ([NH₃] aerosol = 2 × 10⁻⁴ M) within pure (NH₄)₂SO₄ aerosols. When NaCl was added to the CuSO₄ solution the solution turned green once cooled, suggesting the presence of both [Cu(H₂O)₆]²⁺ and [Cu(Cl)₄]²⁻ in the solution. Prior to cooling, all the NaCl had dissolved and the solution was yellow suggesting the [Cu(Cl)₄]²⁻ was in a much higher concentration than [Cu(H₂O)₆]²⁺ in the solution and in NaCl aerosols.
The stability constant ($K_{stab}$) of $[\text{Cu(Cl)}_4]^{2-}$ can be described by E3.7. Considering that the value of $K_{stab} = 4.17 \times 10^5$ mol$^{-4}$ dm$^{12}$ and $[\text{Cl}^-] = 7.27$ the ratio of $[\text{Cu(Cl)}_4]^{2-}$ to $[\text{Cu(H}_2\text{O)}_6]^{2+}$ = $1.16 \times 10^8$ meaning most of the copper will exist as $[\text{Cu(Cl)}_4]^{2-}$ at low $[\text{Cu(II)}]_{\text{aerosol}}$ within NaCl aerosols. At high $[\text{Cu(II)}]_{\text{aerosol}}$, much higher than concentrations in this work, approaching a concentration that equal to $[\text{Cl}^-]$, this ratio will likely to change somewhat with a higher proportion of Cu(II) will be as $[\text{Cu(H}_2\text{O)}_6]^{2+}$.

$$K_{stab} = \frac{[\text{Cu(Cl)}_4]^{2-}}{[\text{Cu(H}_2\text{O)}_6][\text{Cl}^-]^4} \quad (E3.7)$$

To our knowledge there has not been a study within the literature that provides a value of $k_{\text{II}}$ for the reaction of HO$_2$ or O$_2^-$ with $[\text{Cu(Cl)}_4]^{2-}$, however it is likely not to be much slower than $k_{\text{II}}$ for the reaction of HO$_2$/O$_2^-$ and $[\text{Cu(H}_2\text{O)}_6]^{2+}$ due to the high values of $\gamma(\text{HO}_2)$ at high $[\text{Cu(II)}]_{\text{aerosol}}$ measured in this work and other studies $^{61}$. However, simply altering the value of $k_{\text{II}}$ or $H_{\text{eff}}$ or a combination of both does not provide good agreement across the entire dataset, likely caused by a process within the aerosol that enhances diffusion limiting uptake. It is known that halide concentrations within bulk salt solution and deliquesced inorganic salt aerosols are enhanced within the interfacial layer due to anion polarizability and by more favourable water–water interaction energies when the halide ions are partially solvated compared to when fully solvated $^{112, 122, 123}$. A possible hypothesis could be that an enhanced concentration of negatively charged Cl$^-$ ions within the interfacial layer will polarise deliquesced NaCl aerosols repelling negatively charged $[\text{Cu(Cl)}_4]^{2-}$ ions into their bulk. HO$_2$ will have to diffuse longer distances to $[\text{Cu(Cl)}_4]^{2-}$ ions in order to react with them. This enhances diffusion limitations of HO$_2$ uptake within deliquesced Cu-doped halide salt aerosols. It is only until a critical concentration of $[\text{Cu(Cl)}_4]^{2-}$ (~ 0.15 M) has been reached that repulsive forces of $[\text{Cu(Cl)}_4]^{2-}$ against each other are strong enough to overcome those from the interfacial Cl$^-$ ions that $[\text{Cu(Cl)}_4]^{2-}$ begins to populate the interfacial layer and diffusion limitations are overcome resulting in sudden large gains in $\gamma(\text{HO}_2)$ when $[\text{Cu(II)}]_{\text{aerosol}} > 0.15$ M (see Figure 3.7).
Figure 3.9: Diagram of heterogeneous reaction between gas-phase HO₂ and a deliquesced NaCl aerosol doped with $1.5 \times 10^{-2} \text{ M}$ and $1.5 \times 10^{-1} \text{ M}$ of Cu(II) at a RH of 63%. Dashed black lines represent HO₂ diffusion, dashed blue line represents boundary between the interfacial layer and the bulk, small dark blue circles represents $[\text{Cu(Cl)}_4]^{2-}$, green circles represents enhanced interfacial Cl⁻ and thick blue arrows represent repulsive forces.
3.2.3 Measurements of $\gamma$(HO$_2$) onto irradiated deliquesced Cu-doped inorganic aerosols with different chemical composition

The effect of irradiating deliquesced Cu-doped (NH$_4$)$_2$SO$_4$ and NaCl aerosols to $\gamma$(HO$_2$) was investigated. Aerosols were irradiated by a 15 W UVA bench lamp (see section 2.4.6) located 5 cm above the aerosol flow tube. During each experiment the background signal (see section 2.4.2) was determined twice; once with the lamp on and once with the lamp off. The HO$_2$ wall loss rate ($k_{wall}$, see section 2.4.3) was determined four times; twice with the lamp on and twice with the lamp off. The pseudo-first order rate constant for reactive loss to the aerosols ($k'$, see section 2.4.3) was measured seven times; twice with the lamp off, then three times with the lamp on and a further two times with the lamp off. As the light flux from the 15 W lamp was shown to be around three time greater than the 8 W lamp and the light flux detected from the 8 W lamp whilst inside the aerosol flow tube was around three time less than the actinic flux within the UVA region the light flux experienced by aerosols within these experiments was likely comparable to typical tropospheric actinic flux during the summer in the UVA region of the spectrum (see Figure 2.18). The values of $\gamma$(HO$_2$) onto irradiated deliquesced Cu-doped (NH$_4$)$_2$SO$_4$ and NaCl aerosols measured in this work are provided in Table 3.4. Plots of the $k$ against $S_a$, used to obtain a $\gamma$(HO$_2$), for each experiment are provided in Figures 3.10 – 3.12. They show that irradiation of Cu-doped NaCl does not change $\gamma$(HO$_2$), however upon irradiation of Cu-doped (NH$_4$)$_2$SO$_4$ aerosols a significant decrease of $\gamma$(HO$_2$) was observed. The observed decrease of $\gamma$(HO$_2$) onto Cu-doped (NH$_4$)$_2$SO$_4$ aerosols was also dependent on [Cu(II)]$_{aerosol}$. In fact, $\gamma$(HO$_2$) onto irradiated (NH$_4$)$_2$SO$_4$ aerosols with [Cu(II)]$_{aerosol} = 0.038$ M was lower than aerosols with a [Cu(II)]$_{aerosol} = 0.029$ M. This equates to a 56% drop of $\gamma$(HO$_2$) onto irradiated (NH$_4$)$_2$SO$_4$ aerosols with a [Cu(II)]$_{aerosol} = 0.038$ M and a 32% drop of $\gamma$(HO$_2$) onto irradiated (NH$_4$)$_2$SO$_4$ aerosols with a [Cu(II)]$_{aerosol} = 0.029$ M. The measurements suggest that HO$_2$, Na$^+$ and Cl$^-$ within the aerosols were not affected by irradiation. H$_2$O$_2$, formed by reaction of Cu(I) with HO$_2$, can undergo photolysis by UV light within aerosols creating OH radicals$^{124,125}$ which could alter the chemistry within the aerosols, with aerosols containing more Cu(II) and hence more H$_2$O$_2$ being the most affected. The presence of Cu(II) has been shown to considerably increase the quantum yields of H$_2$O$_2$ photolysis in solution$^{126}$. It could be possible that OH could extract a hydrogen from water ligands complexed with Cu(II) and the resulting radical ligand then goes on to react with hydrated electrons ($e'_{(aq)}$) produced by H$_2$O$_2$ photolysis$^{127}$ or $e'_{(aq)}$ may react with OH producing OH$^-$ which would then go on to react with Cu(II) with both mechanisms forming Cu(OH)$_2$(H$_2$O)$_4$ precipitate. NH$_4^+$ does not undergo reaction with OH, however, NH$_3$ does forming NH$_2$ radicals$^{127}$ which may also go on to form Cu(OH)$_2$(H$_2$O)$_4$ precipitate. The formation of a precipitate would reduce the amount of Cu within the aqueous phase available for reaction with HO$_2$ and a lowering of $\gamma$(HO$_2$).
Within NaCl aerosols, \([\text{Cu(Cl)}_4]^2-\) complexes may remain unaffected by the presence of OH or \(\text{OH}^-\) and they may not enhance \(\text{H}_2\text{O}_2\) photolysis quantum yields.

**Table 3.4:** Measured \(\gamma(\text{HO}_2)\) onto dark and irradiated Cu(II)-doped (NH\(_4\))\(_2\)SO\(_4\) and NaCl aerosols.

<table>
<thead>
<tr>
<th>Aerosol Composition</th>
<th>RH / %</th>
<th>[Cu(II)](_{\text{aerosol}}) / M</th>
<th>(\gamma(\text{HO}_2)) not irradiated</th>
<th>(\gamma(\text{HO}_2)) irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>43</td>
<td>0.029</td>
<td>0.172 ± 0.004</td>
<td>0.117 ± 0.004</td>
</tr>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>43</td>
<td>0.038</td>
<td>0.219 ± 0.008</td>
<td>0.094 ± 0.005</td>
</tr>
<tr>
<td>NaCl</td>
<td>61</td>
<td>0.212</td>
<td>0.202 ± 0.003</td>
<td>0.208 ± 0.007</td>
</tr>
</tbody>
</table>

**Figure 3.10:** First order rate coefficient for loss of HO\(_2\) due to heterogeneous reaction with irradiated (purple circles) and non-irradiated (black squares) Cu-doped NaCl aerosols ([Cu(II)]\(_{\text{aerosol}}\) = 0.212 M) at different total surface areas at RH = 61%.

**Figure 3.11:** First order rate coefficient for loss of HO\(_2\) due to heterogeneous reaction with irradiated (purple circles) and non-irradiated (black squares) Cu-doped (NH\(_4\))\(_2\)SO\(_4\) aerosols ([Cu(II)]\(_{\text{aerosol}}\) = 0.038 M) at different total surface areas at RH = 43%.
3.3 Measurements of the Reactive HO\textsubscript{2} Uptake Coefficient onto Deliquesced Inorganic Salt Aerosols Doped with Fe(II) ions

3.3.1 Dependence of γ(HO\textsubscript{2}) onto deliquesced inorganic aerosols doped with different amounts of FeSO\textsubscript{4}

Measured and calculated γ(HO\textsubscript{2}) on (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} aerosols doped with Fe(II)SO\textsubscript{4} at a RH of 43% are presented in Figure 3.13. Within the calculations of γ(HO\textsubscript{2}) (E3.3) the parameter α was replaced with the value of γ(HO\textsubscript{2}) when HO\textsubscript{2} uptake is kinetically limited (0.085), i.e. limited by the kinetics of the reaction of Fe(II) + HO\textsubscript{2}/O\textsubscript{2}-. From inspection of the dataset, this value seems appropriate as the data shows small gains of γ(HO\textsubscript{2}) at [Fe(II)]\textsubscript{aerosol} (concentration of Fe(II) in the aerosol) > 0.2 M, demonstrating that the rate of uptake is near the kinetic limit. A value of \(1.2 \times 10^6\) M s\textsuperscript{-1} for \(k_{\text{II}}\) was used in the calculations, this represents the rate of reaction for HO\textsubscript{2} + Fe(II). Figure 3.13 shows, as with Cu-doped (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} aerosols at a RH of 43%, good agreement with measured and calculated γ(HO\textsubscript{2}) at high [Fe(II)]\textsubscript{aerosol}, however agreement at lower [Fe(II)]\textsubscript{aerosol} agreement was poor. This gives confidence that the value of \(k_{\text{II}}\) used was correct and at high [Fe(II)]\textsubscript{aerosol}, HO\textsubscript{2} + Fe(II) is the dominant reaction within the aerosol.
Simply changing the value of $k_{II}$ and/or $\alpha$ results in poorer agreement. To get agreement between measured and calculated $\gamma$(HO$_2$) across the entire dataset the value $H_{\text{eff}}$ was decreased as [Fe(II)]$_{aerosol}$ decreases < 0.2 M. As with the analysis for Cu-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43%, the values of $H_{\text{eff}}$ at different [Fe(II)]$_{aerosol}$ to get agreement with measured and calculated $\gamma$(HO$_2$) were determined (see Figure 3.14). The parameterisation of $\gamma$(HO$_2$) with [Fe(II)]$_{aerosol}$ was not as good as that with Cu-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% due to a lower number of data points, however Figure 3.14 shows a similar trend as Cu-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43%. Very little change of $H_{\text{eff}}$ with [Fe(II)]$_{aerosol}$ at concentrations > 0.18 M was required, however below this concentration values of $H_{\text{eff}}$ required for agreement decrease linearly as [Fe(II)]$_{aerosol}$ decreases. The value of $l$ when [Fe(II)]$_{aerosol}$ = 0.18 M is 66 nm. The thickness of the outer layer must therefore be larger in Fe-doped aerosols than in Cu-doped aerosols suggesting that the TMI themselves are responsible or can influence the change in HO$_2$ solubility within the inner layer.
Chapter 3 – HO2 Uptake on Aerosols relevant to the Troposphere

Figure 3.14: Parameterisation of $H_{\text{eff}}$ as a function of $[\text{TMI(II)}]_{\text{aerosol}}$ (black is Cu(II) and red is Fe(II)) to achieve agreement between calculated and measured $\gamma$(HO2) at different $[\text{TMI(II)}]_{\text{aerosol}}$ for (NH4)2SO4 aerosols at a RH of 43%. The red line represents $H_{\text{eff}}$ as a best-fit function of $[\text{Fe(II)}]_{\text{aerosol}}$ where $H_{\text{eff}} = 1340.4 - 2149 \times e^{(-15.1 \times [\text{Fe(II)}]_{\text{aerosol}})}$.

As a single value of $k_{\text{II}}$ for the reaction of Fe(II) + HO2 offers the best agreement across the entire dataset, it is likely that Fe(II) in deliquesced (NH4)2SO4 aerosols was in the form of $[\text{Fe(H}_2\text{O)}_6]^{2+}$ as there is not enough NH3 in the aerosol to act as a base to form Fe(OH)$_2$(H2O)$_4$ precipitate. It could be that $k_{\text{II}}$ could change as a function of $[\text{Fe(II)}]_{\text{aerosol}}$ as at low $[\text{Fe(II)}]_{\text{aerosol}}$ a higher proportion of Fe ions could be Fe(III), produced via oxidation of Fe(II) by HO2, which reacts slower with HO2. However, this is unlikely as we might expect to observe an under-prediction of $\gamma$(HO2) at low $[\text{Cu(II)}]_{\text{aerosol}}$ within Cu-doped (NH4)2SO4 aerosols as Cu(I) reacts quicker with HO2 than Cu(II).

3.3.2 Dependence of $\gamma$(HO2) onto deliquesced Fe-doped inorganic aerosols with different chemical composition

The effect of aerosol composition (i.e. (NH4)2SO4, NaCl and LiNO3 aerosols) upon $\gamma$(HO2) for deliquesced Fe-doped inorganic aerosols was investigated. It should be noted that some degree of caution should be taken during the course of the following discussion due to the lack of data points for deliquesced Fe-doped NaCl and LiNO3 aerosols. Figure 3.15 shows measured $\gamma$(HO2) onto deliquesced Fe-doped (NH4)2SO4 aerosols at a RH of 43%, Fe-doped LiNO3 aerosols at a RH of 43% and Fe-doped NaCl aerosols at a RH of 59%. It shows that $\gamma$(HO2) onto Fe-doped NaCl aerosols > Fe-doped (NH4)2SO4 aerosols > Fe-doped LiNO3 aerosols at equivalent $[\text{Fe(II)}]_{\text{aerosol}}$. The value of $\gamma$(HO2) onto Cu-doped NaCl when
[Cu(II)]_{aerosol} = 0.03 M was much lower than Cu-doped (NH₄)₂SO₄ aerosols at the equivalent [Cu(II)]_{aerosol}, whereas the opposite is true for Fe-doped aerosols. The measurement of γ(HO₂) onto Fe-doped NaCl is in good agreement with calculated γ(HO₂). NaCl aerosols are not acidic, unlike (NH₄)₂SO₄ aerosols, so HO₂ solubility is enhanced due to near total dissociation of HO₂ to O₂ within the aqueous phase and also O₂ is a much more reactive species with TMI with both effects contributing to an enhancement of γ(HO₂). Fe(II), from our knowledge, does not undergo ligand substitution with Cl⁻ forming negatively charged complexes which may be electrostatically repelled into the bulk. Fe is commonly found within sea-salt aerosols with the soluble fraction of aerosol Fe, predominantly Fe(II), is a significant source of nutrient iron to the open ocean. This work shows that sea-salt aerosols containing even small amounts of Fe(II) could offer a significant sink of HO₂ in marine environments. The value of γ(HO₂) onto pure LiNO₃ aerosols at a RH of 43% was measured to be 0.031 ± 0.004. Upon the addition of relatively high concentrations of Fe(II) to the aerosol ([Fe(II)]_{aerosol} = 0.5 M) γ(HO₂) increased by only a small amount (0.01). Saturated inorganic salt solutions containing Fe(II)SO₄ were prepared. The 0.3 M FeSO₄ solution was a very faint green colour. No colour change or precipitate was observed upon addition of an excess of (NH₄)₂SO₄ or NaCl salt. However, upon addition of an excess amount of LiNO₃ the solution turned yellow (see Figure 3.16) indicating that Fe(II) had been oxidised to Fe(III) which explains why small values of γ(HO₂) were measured onto Fe-doped LiNO₃ as Fe(III) reacts a hundred times slower than Fe(II) with HO₂.

![Figure 3.15](image-url)  
*Figure 3.15: Measured γ(HO₂) onto Fe(II)-doped (NH₄)₂SO₄ aerosols at a RH of 43% (black squares), Fe(II)-doped LiNO₃ aerosols at a RH of 43% (blue circles) and Fe(II) doped NaCl aerosols at a RH of 59% (red triangles) at different [Fe(II)]_{aerosol}.*
3.3.3 Measurements of $\gamma$(HO$_2$) onto irradiated deliquesced Fe-doped inorganic aerosols

The effect of irradiating deliquesced Fe-doped (NH$_4$)$_2$SO$_4$ aerosols to $\gamma$(HO$_2$) was investigated. Experiments were conducted as described in sections 2.4 and 3.2.3. Figures 3.17 and 3.18 show plots of $k'$ for the heterogeneous reaction between irradiated and non-irradiated deliquesced (NH$_4$)$_2$SO$_4$ aerosols doped with Fe(II) ([Fe(II)]$_{\text{aerosol}} = 0.379$ M and 0.037 M respectively) and HO$_2$ at different $S_a$. The figures show that between a range of $S_a$ of $0 - 3 \times 10^{-5}$ cm$^2$ cm$^{-3}$, $k'$ for irradiated Fe-doped (NH$_4$)$_2$SO$_4$ aerosols decreases and was negative, suggesting that either OH or HO$_2$ (both detected by FAGE detector) was being emitted from the aerosols. Above $S_a = 3 \times 10^{-5}$ cm$^2$ cm$^{-3}$, $k'$ begins to increase showing uptake of HO$_x$ or some other gas-phase HO$_2$ loss mechanism (possibly OH + HO$_2$, $k = 1.1 \times 10^{-10}$ M$^{-1}$ s$^{-1}$ or HO$_2$(aq) + HO$_2$(aq), $k = 1.88 \times 10^{-12}$ M$^{-1}$ s$^{-1}$) was beginning to dominate over emissions of HO$_x$.

At $S_a \approx 5.5 \times 10^{-5}$ cm$^2$ cm$^{-3}$ for [Fe(II)]$_{\text{aerosol}} = 0.037$ M and $\sim 7 \times 10^{-5}$ cm$^2$ cm$^{-3}$ for [Fe(II)]$_{\text{aerosol}} = 0.379$ M, $k'$ onto irradiated Fe-doped aerosols was equivalent to $k'$ onto dark Fe-doped aerosols. Experiments were conducted to investigate possible emissions of OH or HO$_2$ from Fe(II) and Fe(III) doped aerosols following the methodology described in section 2.4.6, i.e. with no HO$_2$ generated within the injector, just looking for emission of HO$_x$ from aerosols directly. No emissions of OH or HO$_2$ from such aerosols was detected. The movable injector was pulled back to its furthest position away from the FAGE inlet and a flow of HO$_2$ was generated from it. No increase of the FAGE signal was observed above that from HO$_2$ formed in the injector with irradiated Fe(II) or Fe(III)-doped aerosols in the aerosol flow tube. These experiments ruled out emissions of HO$_2$ from irradiated Fe(II) or Fe(III)-doped aerosols, however they do not rule out possible emissions of OH. Any OH emitted would likely be lost to the walls of the aerosol flow tube or undergo reactive uptake with the aerosols, observed in this work as $k'$ becomes positive again at high $S_a$, than reach the FAGE detector. It is unlikely that any emissions of OH would be caused by photolysis of H$_2$O$_2$ formed by self-reaction.
(R3.6) or reaction of HO₂ with Fe(II) (R3.7) within aerosols as these reactions are slow. However, Fenton chemistry within aerosols is enhanced under illuminated conditions and could be a source of gas-phase OH. Fenton chemistry involves redox reactions with Fe (Fe(II) and Fe(III)) and H₂O₂. H₂O₂ reacts with Fe(II) (R3.8) resulting in the oxidation of Fe(II) to Fe(III) and the production of OH. Under dark conditions the Fenton reaction of Fe(III), formed in this case by R3.8, + H₂O₂ is slow (R3.9) as it has a more stable electron configuration than Fe(II) and is in competition with the formation iron hydroxides (Fe(OH)₃⁻, n = 1 – 6) (R3.10) causing Fenton chemistry to be ineffective over a short period of time as Fe(II) is irreversibly lost due to a decrease in the pH of the aerosol. However, under illuminated conditions Fe(OH)²⁺ photodegrades regenerating Fe(II) and producing further OH (R3.11). Fenton chemistry could be responsible for the catalysed conversion of H₂O₂ to OH alluded to in this work, which could have implications for studies on the oxidation of organic compounds accommodated within aerosols, such as oxalic acid, and could be a possible source of atmospheric HOₓ.

\[
2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R3.6)}
\]

\[
\text{Fe(II)} + \text{HO}_2 (+ \text{H}_2\text{O}) \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2 + \text{OH}^- \quad \text{(R3.7)}
\]

\[
\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH} + \text{OH}^- \quad \text{(R3.8)}
\]

\[
\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \text{HO}_2 + \text{H}^+ \quad \text{(R3.9)}
\]

\[
\text{Fe(III)} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad \text{(R3.10)}
\]

\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe(II)} + \text{OH} \quad \text{(R3.11)}
\]

![Figure 3.17: First order rate coefficient for loss of HO₂ due to heterogeneous reaction with irradiated (purple circles) and non-irradiated (black squares) Fe-doped (NH₄)₂SO₄ aerosols ([Fe(II)]ₐerosol = 0.379 M) at different total surface areas at a RH of 43%.

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3.4 Measurements of the Reactive HO₂ Uptake Coefficient onto Deliquesced Inorganic Salt Aerosols Doped with Mn(II) ions

Manganese (Mn), like copper and iron, catalyses the conversion of accommodated HO₂ to H₂O₂ within deliquesced inorganic aerosols. Figure 3.19 presents measured and calculated values of γ(HO₂) for deliquesced Mn-doped (NH₄)₂SO₄ aerosols at a RH of 43% at different [Mn(II)]_{aerosol} (the concentration of Mn(II) within the aerosol). As [Mn(II)]_{aerosol} increases beyond 10⁻² M diffusion of HO₂ to the Mn ions becomes less significant to the rate of reactive uptake resulting in an observable increase in γ(HO₂). Figure 3.19 shows there is not enough Mn(II) within the aerosol across the range of [Mn(II)]_{aerosol} measured to reach the kinetic limit of uptake, where uptake is limited by how fast Mn(II) can react with accommodated HO₂. The kinetic limit of γ(HO₂) is projected by the Thornton expression to be a value of 0.1, which is likely reached when [Mn(II)]_{aerosol} = 10 M. The conversion of HO₂ to H₂O₂ by Mn(II) catalysis may proceed via the following reactions, although within (NH₄)₂SO₄ aerosols R3.12 and R3.14 are more relevant to this study as most accommodated HO₂ will not dissociate at a pH of 4.1:

Mn(II) + HO₂ + H₂O → Mn(III) + H₂O₂ + OH⁻  \hspace{1cm} (R3.12, k = 6 \times 10^6 M^{-1} s^{-1})

Mn(II) + O₂⁻ + 2H₂O → Mn(III) + H₂O₂ + 2OH⁻  \hspace{1cm} (R3.13, k = 1.1 \times 10^8 M^{-1} s^{-1})

Mn(III) + HO₂ → Mn(II) + O₂ + H⁺  \hspace{1cm} (R3.14, k = 2 \times 10^4 M^{-1} s^{-1})

Mn(III) + O₂⁻ → Mn(II) + O₂  \hspace{1cm} (R3.15, k = 1.5 \times 10^8 M^{-1} s^{-1})
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Figure 3.19: Calculated ($\alpha = 0.1$, red line $H_{\text{eff}} = 70 \text{ M atm}^{-1}$ or $k_{\text{II}} = 1.4 \times 10^5 \text{ M s}^{-1}$, blue line is calculated $H_{\text{eff}}$ and previously measured values of $k_{\text{II}}$) using E3.3 and measured (black squares) $\gamma$(HO₂) onto (NH₄)₂SO₄ aerosols at a RH of 43% at different $\text{[Mn(II)]}_{\text{aerosol}}$.

Mn(II), like Fe(II), is oxidised by HO₂, whereas Cu(II) is reduced by HO₂. R3.12 is the dominant reaction within the aerosols as the reduction of Mn(III) (R3.14) is much slower and initially all Mn will be as Mn(II) in the aerosol. Measured values of $\gamma$(HO₂) onto Mn-doped aerosols are lower than $\gamma$(HO₂) onto Fe-doped aerosols at equivalent $\text{[TMI]}_{\text{aerosol}}$ even though the value of $k$ for R3.12 is greater than R1.43 (see section 1.11.3, $k = 1.2 \times 10^6 \text{ M s}^{-1}$). The blue line on Figure 3.19 represents calculated values of $\gamma$(HO₂) using a calculated value of $H_{\text{eff}}$ using E3.5 and E3.6 (1310 M atm⁻¹) and a literature value of $k_{\text{II}}$ of $6 \times 10^6 \text{ M s}^{-1}$ for R3.12. This shows that calculated values of $\gamma$(HO₂) do not agree with measured values when using calculated or literature values for $k_{\text{II}}$ or $H_{\text{eff}}$. The red line represents calculated values of $\gamma$(HO₂) when the value of $H_{\text{eff}}$ is changed to 70 M atm⁻¹ or $k_{\text{II}}$ is changed to $1.4 \times 10^5 \text{ M s}^{-1}$. These changes give good agreement between measured and calculated $\gamma$(HO₂). A lower than calculated value of $H_{\text{eff}}$ within (NH₄)₂SO₄ aerosols at a RH of 43%, within close proximity to the efflorescence point, is consistent with the hypothesis presented in section 3.2.1 and 3.3.1 within this work. However, in this case the difference between the calculated $H_{\text{eff}}$ and the $H_{\text{eff}}$ required to achieve agreement between measured and calculated $\gamma$(HO₂) values is constant with $\text{[TMI(II)]}_{\text{aerosol}}$, whereas in the case of Fe(II) and Cu(II) doped (NH₄)₂SO₄ aerosols at a RH of 43% the $H_{\text{eff}}$ required to achieve agreement between measured and calculated $\gamma$(HO₂) values is a parameterisation of $\text{[TMI(II)]}_{\text{aerosol}}$ and hence $l$. This suggests that there is no HO₂.
solubility gradient showing two distinct layers, rather the solubility of \( \text{HO}_2 \) is low throughout the entire aerosol which may explain why measured \( \gamma(\text{HO}_2) \) onto Fe-doped aerosols was higher than that onto Mn-doped aerosols even though Mn(II) reacts five-times quicker with \( \text{HO}_2 \) than Fe(II). This hypothesis suggests the presence of Mn(II) within deliquesced aerosols has the largest effect to \( \text{HO}_2 \) solubility, followed by Cu(II) and then Fe(II). Mn(III) ions could form a significant fraction of Mn speciation within the aerosols if Mn(II) is oxidised by an inorganic species within the aerosol prior to reaction with \( \text{HO}_2 \), as in the case of Fe-doped LiNO\(_3\) aerosols. This would lower \( k_{II} \) to a value in between values of \( k \) for R3.12 and R3.14. However, Mn(III) is particularly unstable within aqueous solutions as it has a 3d\(^4\) electron configuration which is less favourable than the Mn(II) 3d\(^5\) configuration and is liable to disproportionation reactions (R3.16), although it is stabilised somewhat in the presence of Mn(II) and H\(^+\) \(^{121}\). If this reaction does occur in the aerosol, Mn(III) could form a precipitate and the increased pH of the aerosol which could account for a significant fall of \( H_{eff} \) for (NH\(_4\))\(_2\)SO\(_4\) aerosols doped with Mn.

\[
2\text{Mn(III)} + 2\text{H}_2\text{O} \rightarrow \text{Mn(II)} + \text{MnO}_2 + 4\text{H}^+ \quad \text{(R3.16)}
\]

Mn(II) will not undergo ligand substitution reactions in the presence of excess NH\(_3\), however NH\(_3\) can act as a base forming a white precipitate of Mn(OH)\(_2\)(H\(_2\)O)\(_4\). The formation of a precipitate would mean that the estimation of Mn(II) available for reaction was an over-estimate. From a comparison of measured \( \gamma(\text{HO}_2) \) and calculated \( \gamma(\text{HO}_2) \) (blue line) in Figure 3.19, [Mn(II)]\(_{\text{aerosol}}\) could be over-estimated by two orders of magnitude. To investigate the speciation of Mn(II) within the aerosol a 10 ml salt solution was prepared with the same composition and concentrations of inorganic species within the aerosols as calculated from AIM, as in sections 3.2.2 and 3.3.2. Upon the addition of 10 g of (NH\(_4\))\(_2\)SO\(_4\) into a 0.39 M solution of MnSO\(_4\), heated to 50°C to ensure all the salts dissolved, the formation of precipitate nor a change in the colour of the solution was observed suggesting that all Mn within aerosols is [Mn(H\(_2\)O)\(_6\)]\(^{2+}\).

### 3.5 Measurements of the Reactive \( \text{HO}_2 \) Uptake Coefficient onto Deliquesced Inorganic Salt Aerosols Doped with Cu(II) and Fe(II) ions

#### 3.5.1 Dependence of \( \gamma(\text{HO}_2) \) onto deliquesced mixed Cu and Fe-doped inorganic aerosols to Cu:Fe mole fraction

Measurements of \( \gamma(\text{HO}_2) \) onto (NH\(_4\))\(_2\)SO\(_4\) aerosols doped with different ratios of Fe(II)SO\(_4\) and Cu(II)SO\(_4\) at a RH of 43% are presented in Figure 3.20. It is hoped that such measurements may shed light on the Mao hypothesis \(^{62, 128}\) that speculates that Fe and Cu ions couple together
within a catalytic cycle that converts HO\textsubscript{2} to H\textsubscript{2}O within the condensed phase, rather than to H\textsubscript{2}O\textsubscript{2}. The total amount of TMI within the aerosols was kept constant; [TMI\textsubscript{aerosol}] = 0.38 M and 0.04 M, equating to atomiser concentrations ([TMI\textsubscript{atomiser}]) of 1 × 10\textsuperscript{-3} M and 1 × 10\textsuperscript{-4} M respectively. Figure 3.20 shows similar trends for both datasets. Initially, as the mole fraction of [Cu(II)]\textsubscript{aerosol} increases a large increase of γ(HO\textsubscript{2}) was observed. Between a [Cu(II)]\textsubscript{aerosol} mole fraction of 0.25 – 0.5 ([Fe(II)]\textsubscript{aerosol} mole fraction 0.75 – 0.5) the dependence plateaus and no increase of γ(HO\textsubscript{2}) was observed. Above a Cu mole fraction of 0.5 a steady increase of γ(HO\textsubscript{2}) was observed.

Figure 3.20: Measured (black squares is [TMI]\textsubscript{atomiser} = 1 × 10\textsuperscript{-3} M and red circles is [TMI]\textsubscript{atomiser} = 1 × 10\textsuperscript{-4} M) γ(HO\textsubscript{2}) onto Cu and Fe-doped (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} aerosols at a RH of 43% at Cu and Fe mole fractions. Dashed lines represent general trend.

Calculations of γ(HO\textsubscript{2}), based on the sum of the parameterisations of γ(HO\textsubscript{2}) for (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} aerosols doped with either Cu(II) or Fe(II) individually (i.e. γ(HO\textsubscript{2}) onto Cu(II) doped aerosols + γ(HO\textsubscript{2}) onto Fe(II) doped aerosols) which are a function [Cu(II)]\textsubscript{aerosol} and [Fe(II)]\textsubscript{aerosol} (E3.3) determined and verified against measurements in sections 3.2 and 3.3, are compared to measured γ(HO\textsubscript{2}) in Figure 3.21. Within these parameterisations \(H_{\text{eff}}\) is also a function of [Cu(II)]\textsubscript{aerosol} and [Fe(II)]\textsubscript{aerosol} (E3.7 and E3.8 respectively).

\[
H_{\text{eff}} = \begin{cases} 
-2035.4 + 447.6 \times (1 - e^{(-1\,(Cu(II)_{aerosol}/0.1123)}) + 2909.7 \times (1 - e^{(-1\,(Cu(II)_{aerosol}/0.0120)}) & (E3.7) \\
1340.4 - 2149 \times e^{(-15.1\,(Fe(II)_{aerosol})} & (E3.8) 
\end{cases}
\]
Figure 3.21 shows that for $[\text{TMI}]_{\text{atomiser}} = 1 \times 10^{-4}$ M, calculating $\gamma(\text{HO}_2)$ in this way underestimates measured values of $\gamma(\text{HO}_2)$ up to a $[\text{Cu(II)}]_{\text{aerosol}}$ mole fraction of around 0.6, beyond which calculated values of $\gamma(\text{HO}_2)$ show good agreement as Cu(II) dominates the reactivity within the aerosol. On this basis, it could be postulated that the presence of a small amount of Cu(II) within Fe-doped deliquesced inorganic aerosols with a $[\text{Fe(II)}]_{\text{aerosol}} \leq 1 \times 10^{-4}$ M enhances $\gamma(\text{HO}_2)$ due to coupling between Cu(I) and Fe(III). As Fe(II) is oxidised and Cu(II) is reduced by reaction with HO$_2$, these two ions undergo a rapid electron transfer reaction converting them back to their more reactive forms and hence an enhancement of $\gamma(\text{HO}_2)$. However, it might be expected that $\gamma(\text{HO}_2)$ across the entire range of mole fraction ratios to be enhanced if this reaction mechanism was significant. As calculated and measured $\gamma(\text{HO}_2)$ agree above a $[\text{Cu(II)}]_{\text{aerosol}}$ mole fraction of around 0.6, it could be that diffusion of the transition metal ions for the reaction to occur is a limiting factor or effects to HO$_2$ solubility could be at play. At this concentration of TMI in the aerosol and at a RH just above the efflorescence point it has been shown that $\gamma(\text{HO}_2)$ dependent on $l$ and a parameterisation of $H_{\text{eff}}$, both these parameters are dependent on the type of TMI the aerosols are doped with and $[\text{TMI}]_{\text{aerosol}}$. It is could be that a mixture of TMI within an aerosol would have a very different effect to $H_{\text{eff}}$ compared to if the aerosols were doped with only Fe(II) or Cu(II) and it should also be noted that the values of $H_{\text{eff}}$ used to calculate $\gamma(\text{HO}_2)$ for Fe-doped and Cu-doped aerosols are not consistent. Figure 3.21 shows that at a $[\text{TMI}]_{\text{atomiser}} = 1 \times 10^{-3}$ M the sum of parameterisations of $\gamma(\text{HO}_2)$ as a function of $[\text{Cu(II)}]_{\text{aerosol}}$ and $[\text{Fe(II)}]_{\text{aerosol}}$ over predicts measurements of $\gamma(\text{HO}_2)$ onto mixed Cu(II) and Fe(II) doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% across the entire mole fraction range. It may be speculated that this is evidence that the reaction between HO$_2$ and TMI is competing with an enhancement of Fenton reactions (Fe(II) + H$_2$O$_2$ and Fe(II) + OH) caused by the coupling reaction between Fe(II) and Cu(II) resulting in a depression of $\gamma(\text{HO}_2)$. At a $[\text{TMI}]_{\text{aerosol}}$ of $1 \times 10^{-3}$ M sections 3.2 and 3.3 showed that a decrease in predicted $H_{\text{eff}}$ was not necessary to achieve agreement with measured and calculated $\gamma(\text{HO}_2)$ as the reaction occurs within the interfacial layer of the aerosol or very close to it, which seems to be unaffected by an increase of the salting out effects in the bulk of the aerosol that decreases HO$_2$ solubility.
Figure 3.21: Comparison between measured $\gamma$(HO$_2$) onto Cu(II) and Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols (red circles = [TMI]$_{atomiser}$ 1 and calculated $\gamma$(HO$_2$) based on the sum of the parameterisations of $\gamma$(HO$_2$) for (NH$_4$)$_2$SO$_4$ aerosols doped with either Cu(II) or Fe(II) individually at different Cu(II):Fe(II) mole fractions and a RH of 43%.

Figure 3.22 shows the consistent values of $H_{eff}$ to achieve agreement with measured $\gamma$(HO$_2$) onto (NH$_4$)$_2$SO$_4$ aerosols doped with Fe(II) and Cu(II) at different mole fractions at a RH of 43% and the sum of parameterisations of $\gamma$(HO$_2$) determined in section 3.2 and 3.3. It shows a consistent trend for both datasets. As the mole fraction of [Cu(II)]$_{aerosol}$ increases in the aerosol the required consistent value of $H_{eff}$ for agreement decreases up until a minima is reached around a mole fraction of 0.55, above which the required value of $H_{eff}$ increases. This could suggest that the observed dependence of $\gamma$(HO$_2$) with mole fraction of [Cu(II)]$_{aerosol}$ and [Fe(II)]$_{aerosol}$ was likely due to the effects of the TMI to $H_{eff}$. Another hypothesis that could explain the observed dependence of $\gamma$(HO$_2$) with mole fraction of [Cu(II)]$_{aerosol}$ and [Fe(II)]$_{aerosol}$ is the location of TMI within the aerosols. As the mole fraction of [Cu(II)]$_{aerosol}$ increases in the aerosol from 0 to around 0.1 all Cu(II) added resides in or around the interfacial layer, much like halide ions, resulting in a large increase of $\gamma$(HO$_2$). Like halide ions, the larger the ion the higher the affinity to reside in the interfacial layer. Between the mole fractions of [Cu(II)]$_{aerosol}$ of 0.1 – 0.6 additional Cu(II) will reside in the bulk and most accommodated HO$_2$ will react with existing Cu(II) in or around the interfacial layer or at a much slower rate with Fe(II) in the bulk resulting on observable increase of $\gamma$(HO$_2$). At mole fractions of [Cu(II)]$_{aerosol}$ > 0.6 more Cu(II) will reside in the bulk and the probability of any accommodated HO$_2$ that manages to diffuse into the bulk of the aerosol will react with Cu(II) increases resulting in a gradual observed increase of $\gamma$(HO$_2$). Both hypotheses suggest that the Mao hypothesis for this system is unlikely.
Chapter 3 – HO₂ Uptake on Aerosols relevant to the Troposphere

3.5.2 Measurements of γ(HO₂) onto irradiated deliquesced mixed Cu and Fe-doped inorganic aerosols

The effect of irradiating deliquesced mixed Cu and Fe-doped (NH₄)₂SO₄ aerosols to γ(HO₂) was investigated. Experiments were conducted as described in sections 2.4 and 3.2.3. Figures 3.23 and 3.24 show plots of $k'$ for the heterogeneous reaction between irradiated and non-irradiated deliquesced (NH₄)₂SO₄ aerosols doped with Cu(II) and Fe(II) (Figure 3.23 [TMI]atomiser = 1 × 10⁻³ M and Cu:Fe mole ratio = 1:9, Figure 3.24 [TMI]atomiser = 1 × 10⁻⁴ M and Cu:Fe mole ratio = 1:1) and HO₂ at different $S_a$. Figures 3.23 and 3.24 show that upon irradiation of such aerosols γ(HO₂) increases. The increase in γ(HO₂) was dependent on the molar ratio, with a 1:1 molar ratio resulting in a larger increase. This finding was contrary to the findings in section 3.2.3, which showed that γ(HO₂) decreases upon irradiation of Cu-doped (NH₄)₂SO₄ aerosols. It could be that the increase in γ(HO₂) upon irradiation of mixed Cu and Fe-doped (NH₄)₂SO₄ aerosols could be a consequence of a photochemical reaction mechanism (R3.17 – R.3.23) similar to that proposed by Mao ⁶² i.e. conversion of HO₂ to H₂O. As discussed in section 3.2.3, the presence of Cu(II) in solution has been shown to increase the quantum yield of H₂O₂ photolysis. H₂O₂ is formed as a result of the reaction between Cu(I) or Fe(II) and accommodated HO₂. The resulting OH produced by H₂O₂ photolysis, rather than possibly causing Cu ions to precipitate out of the aqueous phase, will react with

![Figure 3.22: Consistent values of $H_{eff}$ required to achieve agreement with measured γ(HO₂) onto (NH₄)₂SO₄ aerosols doped with Fe(II) and Cu(II) at different mole fractions at a RH of 43%.](image-url)
Fe(II) and H⁺ producing H₂O. Fe(OH)²⁺ can also photolyse producing further OH. The observed increase of γ(HO₂) upon irradiation can explained by the destruction of H₂O₂ within the aerosol, which has the potential to reform HO₂ which can then desorb out of the aerosol back into the gas-phase ⁷⁸. The effect to γ(HO₂) is greater onto aerosols with a higher content of Cu ions as H₂O₂ will be produced at a faster rate. This hypothesis suggests that rather than a coupling reaction between the two TMIs that may be limited somewhat by diffusion is responsible for the recycling of Fe(II) which can then undergo catalysis of HO₂ conversion to H₂O, that the presence of Cu(II) aids the photolysis of H₂O₂ resulting in the production of OH which can be converted to H₂O by Fe(II), which is recycled by Fe(III) photolysis or reaction with HO₂.

\[
\text{Cu(II)/Fe(III)}(\text{aq}) + \text{HO}_2(\text{aq}) \rightarrow \text{Cu(I)/Fe(II)}(\text{aq}) + \text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) \quad \text{(R3.17)}
\]

\[
\text{Cu(I)/Fe(II)}(\text{aq}) + \text{HO}_2(\text{aq}) \rightarrow \text{Cu(II)/Fe(III)}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{(R3.18)}
\]

\[
\text{H}_2\text{O}_2(\text{aq}) + \text{hv} \rightarrow 2\text{OH}(\text{aq}) \quad \text{(R3.19)}
\]

\[
\text{Fe(III)}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}^{2+}(\text{aq}) \quad \text{(R3.20)}
\]

\[
\text{Fe(OH)}^{2+}(\text{aq}) + \text{hv} \rightarrow \text{Fe(II)}(\text{aq}) + \text{OH}(\text{aq}) \quad \text{(R3.21)}
\]

\[
2\text{Fe(II)}(\text{aq}) + 2\text{OH}(\text{aq}) + (2\text{H}^+(\text{aq})) \rightarrow 2\text{Fe(III)}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \quad \text{(R3.22)}
\]

Net: \[
2\text{HO}_2(\text{aq}) + 2\text{hv} + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{aq}) \quad \text{(R3.23)}
\]

**Figure 3.23:** First order rate coefficient for loss of HO₂ due to heterogeneous reaction with irradiated (purple circles, γ(HO₂) = 0.149 ± 0.007) and non-irradiated (black squares, γ(HO₂) = 0.117 ± 0.004) Cu and Fe-doped (NH₄)₂SO₄ aerosols ([Fe(II)]ₐerosol = 0.333 M and [Cu(II)]ₐerosol = 0.037 M, Fe(II) mole fraction = 0.9 and Cu(II) mole fraction = 0.1) at different total surface areas and at a RH of 43%.
Figure 3.24: First order rate coefficient for loss of HO$_2$ due to heterogeneous reaction with irradiated (purple circles, $\gamma$(HO$_2$) = 0.230 ± 0.007) and non-irradiated (black squares, $\gamma$(HO$_2$) = 0.144 ± 0.004) Cu and Fe-doped (NH$_4$)$_2$SO$_4$ aerosols ([Fe(II)]$_{\text{aerosol}}$ = 0.019 M and [Cu(II)]$_{\text{aerosol}}$ = 0.019 M, Fe(II) mole fraction = 0.5 and Cu(II) mole fraction = 0.5) at different total surface areas and at a RH of 43%.

3.6 Measurements of the Reactive HO$_2$ Uptake Coefficient onto Deliquesced Inorganic Salt Aerosols Doped with KI and Cu(II) or Fe(II) or Fe(III) ions

Initially, to determine whether the heterogeneous reaction between HO$_2$ and aerosols containing I$^-$ could be significant, measurements of $\gamma$(HO$_2$) onto KI aerosols at a RH of 65% were conducted a number of times. Values of $\gamma$(HO$_2$) measured ranged from 0.195 ± 0.022 to 0.382 ± 0.013 suggesting that reactive uptake of HO$_2$ onto deliquesced aerosols containing I$^-$ could be significant. However, an increase of measured $\gamma$(HO$_2$) onto NaCl aerosols doped with KI was not observed above that measured onto pure NaCl aerosols (see Figure 3.25, Experiments 1 – 2). The reaction between HO$_2$ and I$^-$ in the aqueous phase is particularly slow ($k < 1 \times 10^3$ M$^{-1}$ s$^{-1}$) [132], however the reaction between O$_2^-$ and I$_2$ is rapid ($k = 5.5 \times 10^9$ M$^{-1}$ s$^{-1}$) [117], around five times greater than the reaction between O$_2^-$ and Cu(II). As NaCl aerosols are likely to have a pH of around 7 most HO$_2$ within the aqueous phase will dissociate to O$_2^-$. Large values of $\gamma$(HO$_2$) onto pure KI aerosols could be caused by a combination of heterogeneous reactions of enhanced interfacial I$^-$ with trace amounts of O$_3$ produced by O$_2$ photolysis during production of HO$_2$ within the injector and possible contamination with TMI due to artefacts within the apparatus. In order to investigate how TMI contamination could affect measurements of $\gamma$(HO$_2$), shown in Figure 3.25, onto NaCl aerosols doped with KI and Cu(II) or Fe(II) or Fe(III) were conducted at a RH of 65%. 

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Figure 3.25 shows that $\gamma$($\text{HO}_2$) onto NaCl aerosols doped with Fe(II) or Fe(III) does not increase upon the addition of KI (Experiments 3 – 5), however upon addition of KI to NaCl aerosols doped with Cu(II) a significant increase of $\gamma$($\text{HO}_2$) was observed (Experiments 6 – 10). Experiments 7 and 8 show that doubling the concentration of KI from $5 \times 10^{-4}$ M to $1 \times 10^{-3}$ M in the atomiser solution of NaCl (0.02 M) and Cu(II) ($1 \times 10^{-4}$ M) does not result in an increase of $\gamma$($\text{HO}_2$) onto the resulting aerosols suggesting that I$^-$ was in excess above a stoichiometric Cu(II):I$^-$ ratio of 1:5. An increase of $\gamma$($\text{HO}_2$) was observed when the concentration of Cu(II) was increased from $1 \times 10^{-4}$ M to $5 \times 10^{-4}$ M in an atomiser solution of NaCl (0.02 M) and KI ($5 \times 10^{-4}$ M) suggesting more reactive products in the aerosol were present. Figure 3.26 shows upon addition of KI to a solution containing aerosol equivalent concentrations of NaCl and CuSO$_4$ a black precipitate formed and the solution turned an orange colour suggesting iodine was formed, which is consistent with the reduction of Cu(II) by I$^-$ forming a CuI precipitate and I$_2$ (R3.24). It is likely that I$_2$ rather than I$^-$, produced from reaction with O$_3$ or contamination of aerosols with Cu(II), resulted in the high values of $\gamma$($\text{HO}_2$) onto pure KI aerosols and that I$_2$ is more reactive with HO$_2$ than Cu(II) as suggested by kinetic studies in bulk solution (R3.24). Figure 3.27 compares normalised average aerosol size distributions of NaCl aerosols doped with KI (Experiment 2) and NaCl aerosols doped with KI and CuSO$_4$ (Experiment 9). It shows that the geometric mean midpoint aerosol diameter measured during Experiment 9 was larger (49 nm) than measured during Experiment 2 (44
nm) which could indicate that any CuI precipitate formed stayed accommodated within the NaCl aerosols. It is not clear whether CuI accounts for any of the aerosols reactivity towards HO$_2$. These experiments show that aerosols containing I$_2$ within the marine boundary layer could be a significant sink of HO$_2$ in these environments.

$$2\text{Cu(II)}_{(aq)} + 4\text{I}^-_{(aq)} \rightarrow 2\text{CuI(s)} + \text{I}_2(aq)$$  \hspace{1cm} (R3.24)

**Figure 3.26:** Photographs of solutions of CuSO$_4$ (0.363 M) and NaCl (7.27 M, left) and CuSO$_4$ (0.363 M), NaCl (7.27 M) and KI (0.363 M, right).

**Figure 3.27:** Normalised average size distributions of NaCl aerosols doped with KI (Experiment 2, black line) and NaCl aerosols doped with KI and CuSO$_4$ (Experiment 9, red line) at a RH of 65%.
3.7 Summary

This chapter has presented measurements of $\gamma$(HO$_2$) onto deliquesced inorganic aerosols doped with TMI and I, which are commonly found in the troposphere. Deliquesced inorganic aerosols containing TMI are likely to be not as reactive with HO$_2$ as originally thought in most cases. When such aerosols are within proximity to their efflorescence point, the Thornton expression, used in global modelling studies, over predicts values of $\gamma$(HO$_2$) at [TMI]$_{aerosol}$ < 0.1 M as it is likely that HO$_2$ solubility decreases as HO$_2$ diffuses into the bulk of the aerosol due to a salting out effect. Cu-doped NaCl aerosols showed much less reactivity with HO$_2$ than predicted by the Thornton expression, possibly due to enhanced concentrations of Cl$^-$ ions within the interfacial layer repelling [Cu(Cl)$_4$]$^{2-}$ ions into the bulk making diffusion of HO$_2$ to Cu ions a limiting factor. Also, upon irradiation Cu-doped (NH$_4$)$_2$SO$_4$ aerosols showed a lowering of reactivity with HO$_2$ possibly due to H$_2$O$_2$ photolysis causing Cu to precipitate out of the aerosol. However, $\gamma$(HO$_2$) onto Fe-doped NaCl aerosols show good agreement with the Thornton expression and relatively high reactivity with HO$_2$ due to enhanced HO$_2$ solubility caused by near total HO$_2$ dissociation at a pH likely associated with NaCl aerosols and the high reactivity of O$_2$ with TMI. Upon irradiation, Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols have shown to possibly produce OH radicals in gas-phase and further studies in the future should be conducted to investigate this possible phenomena further. The presence of Mn ions within deliquesced inorganic aerosols have also shown they too can catalyse the conversion the destruction of accommodated HO$_2$. Measurements of $\gamma$(HO$_2$) onto mixed Cu(II) and Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% could not determine whether the Mao hypothesis that an electron transfer reaction between Cu(I) and Fe(III) results in the conversion of HO$_2$ to H$_2$O, rather than H$_2$O$_2$. However, values of $\gamma$(HO$_2$) did not simply equal the sum of $\gamma$(HO$_2$) onto Cu or Fe-doped aerosols individually, indicating that the presence of both TMI in the aerosol does alter the chemistry of the aerosol in some way. Irradiation of Cu(II) and Fe(II)-doped aerosols resulted in an enhancement of $\gamma$(HO$_2$) possibly indicating an alternative mechanism than that proposed by Mao where HO$_2$ is converted to H$_2$O due to photochemical reactions within deliquesced aerosols. The presence of I within NaCl aerosols does not result in any change of $\gamma$(HO$_2$), however the when converted to I$_2$ by reaction with Cu(II) an enhancement of $\gamma$(HO$_2$) was observed. The measurements of $\gamma$(HO$_2$) onto deliquesced aerosols presented in this chapter suggest that heterogeneous reactions cannot fully account for discrepancies between measured and modelled tropospheric HO$_2$ concentration within the marine boundary. It is only until values of $\gamma$(HO$_2$) were equal to the theoretical maximum value of 1 within atmospheric models when agreement between modelled and measured concentration of HO$_2$ was observed \textsuperscript{13}, which is much higher than values of $\gamma$(HO$_2$) measured in this work.
Chapter 4 – HO$_2$ Uptake and Production on Aerosols relevant to the Stratosphere

This chapter presents the results and interpretation of experiments conducted on airborne TiO$_2$ nanoparticles.
4.1 Introduction

Injection of TiO$_2$ particles into the dynamically stable stratosphere is considered a means to mitigate global warming as they will back-scatter some incoming solar light back into space (see section 1.10). However, before this kind of geoengineering solution can be considered, the impacts of the presence of TiO$_2$ particles on stratospheric chemistry should be determined. Removal and production of trace gases into the stratosphere may significantly perturb concentrations of O$_3$. HO$_2$ is one such trace species that is involved in controlling stratospheric ozone levels (see section 1.8). It is important when assessing the potential impact of such a mitigation scheme to evaluate the kinetics of likely heterogeneous chemistry. The kinetics of the heterogeneous reaction of HO$_2$ onto Arizona Test Dust (ATD), a proxy of mineral dust, has been previously investigated $^{66,134}$, however uptake of HO$_2$ with TiO$_2$ particles has not. The reactive uptake coefficient, $\gamma$, was measured to be more than an order of magnitude larger for HO$_2$ onto ATD than for N$_2$O$_5$ and ClONO$_2$ onto TiO$_2$ sub-micron particles with contrasting dependences of $\gamma$ with relative humidities (RH) were observed $^{49,135}$. Therefore, it is expected that HO$_2$ uptake onto TiO$_2$ may be faster than N$_2$O$_5$ uptake. Uptake of ClONO$_2$ by TiO$_2$ particles resulted in similar values of $\gamma$, however, no dependency of $\gamma$ with RH between 7 – 33% was observed $^{49}$. Another possible way the presence of TiO$_2$ particles in the stratosphere could perturb stratospheric chemistry is through production of HO$_x$ radicals. TiO$_2$ is a well-known photocatalyst and studies have shown possible production of OH formed via the oxidation of water and HO$_2$ via the decomposition of H$_2$O$_2$ which can desorb into the gas-phase from its surface (see section 1.15).

The kinetics of the heterogeneous reaction of HO$_2$ with airborne TiO$_2$ nanoparticles at different RH was investigated using the moving injector methodology (see section 2.4.3). While it has been possible here to study such kinetics over a range of RH representative to those typically found in the lower stratosphere ($< 40\%$) $^{136}$, due to experimental limitations experiments were only conducted at room temperature ($\sim 293 \pm 3$ K). The TOMCAT off-line three-dimensional (3D) chemical transport model $^{137}$ has also been used to predict the likely impact of HO$_2$ uptake by TiO$_2$ particles on the stratospheric concentrations of HO$_2$ and O$_3$.

In addition to this, a UVA lamp was placed above the aerosol flow tube in order to irradiate TiO$_2$ aerosols and activate their photocatalytic properties. Production of gas-phase HO$_2$ and OH from irradiated TiO$_2$ aerosol surfaces was investigated. The study examines the dependency of HO$_2$ production on parameters such as [O$_2$], time, photon flux and RH. Comparisons with previous studies $^{83,84}$ of gas-phase HO$_2$ production from irradiated TiO$_2$ surfaces (see section 1.15) using a Knudsen cell style experimental setup are discussed. These studies showed gas-phase HO$_2$ production only when H$_2$O$_2$ was present and a dependence with [O$_2$] was not observed.
4.2 Measurements of the Reactive HO₂ Uptake Coefficient onto Airborne Particles of TiO₂

4.2.1 Results & Discussion

Measurements of the reactive HO₂ uptake coefficient, \( \gamma(\text{HO}_2) \), were made on airborne Degussa TiO₂ nanoparticles (Aldrich Chemistry 718467, 99.5% Degussa). These nanoparticles are composed of a blend of 80% anatase and 20% rutile; both polymorphs of TiO₂. Similar formulations of TiO₂, such as Degussa P25 (75% anatase and 25% rutile), are widely used in laboratory studies\(^{138} \). The TiO₂ nanoparticles were entrained into a flow of N₂ using a commercial atomiser as it was judged that suspending these particles within a solution of milli-Q water would not alter the chemical characteristics of the particles. This meant that a constant and stable output of aerosols could be generated allowing determination of \( \gamma(\text{HO}_2) \) via the sliding injector experimental methodology. Examples of typical number and surface area weighted size distributions measured during an experiment are presented in Figure 4.1. The average radius of the particles for this distribution is 68 nm.

![Figure 4.1](image)

**Figure 4.1:** Typical surface area (left y axis, black filled squares) and particle number (right y axis, blue open squares) size distributions measured by the SMPS of TiO₂ aerosols at 11% RH, \( T = 296 \text{ K} \)

Figure 4.1 shows that it is possible that particles beyond the detection range (> 750 nm) of the SMPS may have been present within aerosol flow tube, however, the aerosol flow was passed through an impactor (\( D_{50} = 685 \text{ nm} \)) before entering the aerosol flow tube to remove the majority of these particles. The average radius varied for each experiment, for example the average diameter of the TiO₂ particles was measured to vary from 136 nm at RH = 11% to 173 nm and RH = 37%. An increase of this magnitude in RH has been measured\(^{139} \) to result in an
additional 0.5 monolayers of water adsorbed onto the TiO$_2$ particle surface which would not cause the observed increase in particle size. The dependency of the size distribution of airborne TiO$_2$ nanoparticles with RH was investigated and shown in Figure 4.2. It shows that there was no observable change in the size distributions as RH was increased in the aerosol flow tube from 10% to 52% RH, however the particles did grow when the RH was increased to 76% RH. At 76% RH the coverage of water around the particle is 3.1 monolayers, enough so that the influence of the TiO$_2$ surface to additional water adsorption is no longer apparent and water adsorption at this RH could be characterised by bulk water condensation. This evidence shows that observed variations in average aerosol diameter was mostly likely associated with differences during aerosol generation such as slight blockages in the atomiser, variation in cylinder backing pressure or differences in mixing of the atomiser solution during the experiments.

![Figure 4.2: Size distributions of airborne TiO$_2$ nanoparticles used within this study at different RH (black = 10%, red = 25%, blue 37%, purple = 52% and green = 76%).](image)

Initial HO$_2$ concentrations used within these experiment (defined as [HO$_2$]$_0$) were $\sim 1.6 \times 10^9$ molecule cm$^{-3}$, which are approximately 38 times higher than stratospherically relevant concentrations ($\sim 4.3 \times 10^7$ molecule cm$^{-3}$) $^{31}$. Figure 4.3 shows plots of the natural log of HO$_2$ measurements at different injector positions, which corresponds to different aerosol/analyte interaction times, with and without aerosols present used to calculate $k_{ab}$ (see section 2.4.3). From inspection, it is clear that as aerosols are introduced into the aerosol flow tube lower concentrations of HO$_2$ are measured and the slope of the line increases indicating reactive uptake of HO$_2$ on the aerosols surfaces.
Figure 4.3: Measured HO\textsubscript{2} signal at different interaction times, in the presence of TiO\textsubscript{2} particles (surface area density 1.21 × 10\textsuperscript{-4} cm\textsuperscript{2} cm\textsuperscript{-3} and 2.57 × 10\textsuperscript{-4} cm\textsuperscript{2} cm\textsuperscript{-3}, green circles and red triangles respectively) and in their absence (blue squares). The RH in the aerosol flow tube was 11%, the lowest used in this study. The lines represent linear-least squares fits to the data yielding \( k_{\text{obs}} = 0.079 \pm 0.005 \text{ s}^{-1} \) and \( k_{\text{obs}} = 0.093 \pm 0.003 \text{ s}^{-1} \) (aerosols present, green circles and red triangles respectively) and 0.049 ± 0.003 s\textsuperscript{-1} (no aerosols, \( k_{\text{wall}} \)).

Values of \( k_{\text{obs}} \) were determined for a number of runs at different aerosol concentrations and then corrected, as described in section 2.4, and plotted against surface area concentration of TiO\textsubscript{2} aerosols (see Figure 4.4) in order to calculate the reactive uptake coefficient, \( \gamma(\text{HO}_2) \).

Figure 4.4: First order rate coefficient for loss of HO\textsubscript{2} due to heterogeneous reaction with TiO\textsubscript{2} particles at different total surface areas for \( T = 296 \text{ K} \) and \( RH = 37\% \). The gradient yielded a value of \( \gamma(\text{HO}_2) = (2.68 \pm 0.01) \times 10^{-2} \), with the uncertainty representing 2\( \sigma \) random errors from the fit (95% confidence limits).
Table 4.1 and Figure 4.5 presents the measurements of $\gamma$(HO$_2$) across a range of RH. This was done in order to shed possible light on the reaction mechanism. Measurement of $\gamma$(HO$_2$) at the lowest RH possible within the experimental setup (~ 10%) is the most representative achievable RH for the lower stratosphere. The number of monolayers of water adsorbed onto the surface of TiO$_2$ particles has been previously determined experimentally by transmission FTIR spectroscopy $^{139}$, and is also shown as a function of RH in Figure 4.5.

Table 4.1: Reactive HO$_2$ uptake coefficients, $\gamma$(HO$_2$), for TiO$_2$ particles at different RH.

<table>
<thead>
<tr>
<th>RH (%) ± 1.0</th>
<th>$\gamma$(HO$_2$) / 10$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>2.08 ± 0.11</td>
</tr>
<tr>
<td>11.8</td>
<td>2.11 ± 0.13</td>
</tr>
<tr>
<td>24.9</td>
<td>2.48 ± 0.33</td>
</tr>
<tr>
<td>29.1</td>
<td>2.54 ± 0.18</td>
</tr>
<tr>
<td>37.5</td>
<td>2.68 ± 0.09</td>
</tr>
<tr>
<td>45.1</td>
<td>2.90 ± 0.53</td>
</tr>
<tr>
<td>45.3</td>
<td>2.92 ± 0.37</td>
</tr>
<tr>
<td>63.1</td>
<td>3.43 ± 0.27</td>
</tr>
<tr>
<td>66.4</td>
<td>3.65 ± 0.70</td>
</tr>
</tbody>
</table>

Figure 4.5: Reactive uptake coefficients of HO$_2$, $\gamma$(HO$_2$), onto airborne TiO$_2$ particles (black squares, left y axis) at different RH for $T = 295 \pm 2$ K. The number of monolayers of the adsorbed water on TiO$_2$ particles (red curve, right y axis) at 296 K is also plotted as a function of RH, determined using FTIR spectroscopy $^{139}$. 

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The results show a clear positive dependence of $\gamma$(HO$_2$) across the range of RH investigated, and as shown in Figure 4.6, $\gamma$(HO$_2$) correlates well with the number of monolayers of water adsorbed onto the TiO$_2$ aerosols, $V$, which was parameterised by Eqn. 4.1:

$$V = \left[ V_m \left( \frac{P}{P_0} \right)^n \right] \left[ \frac{1-(n+1)\left( \frac{P}{P_0} \right)^n + n\left( \frac{P}{P_0} \right)^{n+1}}{1+(c-1)\left( \frac{P}{P_0} \right)^{n-1} - c\left( \frac{P}{P_0} \right)^n} \right]$$

(E4.1)

where $V$ is the volume of gas (water vapour) in the units of monolayers of coverage adsorbed at equilibrium pressure $P$, $V_m$ is volume of gas necessary to cover the surface of the adsorbent TiO$_2$ particles with a complete monolayer, $P$ is the equilibrium pressure of the adsorbing gas, $P_0$ is the saturation vapour pressure of the adsorbing gas at that temperature, $c$ is a temperature-dependent constant related to the enthalpies of adsorption of the first and higher layers (78.4) and $n$ is the asymptotic limit of monolayers (8) at large values of $P/P_0$.

![Figure 4.6: Variation of the reactive uptake coefficient, $\gamma$(HO$_2$), with the number of monolayers of water surrounding TiO$_2$ particles (as determined by Goodman et al., 2001) for $T = 295 \pm 2$ K. The red line represents a linear least-squares fit to the data ($r^2 = 0.987$).](image)

As discussed in section 1.13.2, $\gamma$(HO$_2$) shows a negative dependence on [HO$_2$] within the experimental set-up. Previous work on this apparatus has shown that $\gamma$(HO$_2$) for uptake on Arizona Test Dust (ATD) aerosols increases as the [HO$_2$]$_0$ was lowered 66, possibly due to surface saturation. The conclusions of that study were that the observed positive dependence of $\gamma$(HO$_2$) with RH could be associated with the [HO$_2$] impinging on the aerosol for a given injector position decreasing with RH as wall losses of HO$_2$ also increase as RH is increased.
within the aerosol flow tube. To investigate the dependence of $\gamma$(HO$_2$) for uptake on to TiO$_2$ aerosols with [HO$_2$], uptake onto TiO$_2$ aerosols at a RH of 11% was measured at two different [HO$_2$]$_0$ exiting the injector, and $\gamma$(HO$_2$) increased from $2.08 \times 10^{-2}$ to $2.72 \times 10^{-2}$ as [HO$_2$]$_0$ was decreased from $1.6 \times 10^9$ molecule cm$^{-3}$ to $8.9 \times 10^8$ molecule cm$^{-3}$. The wall loss rate for HO$_2$ increased from 0.049 to 0.079 s$^{-1}$ across the entire range of RH (11% to 66%) resulting in only a small decrease in [HO$_2$] of $\sim 2.6 \times 10^8$ molecule cm$^{-3}$ and $2.7 \times 10^8$ molecule cm$^{-3}$ at the first and last injector position, respectively. The study of HO$_2$ uptake onto ATD$^{66}$ showed that within this range of [HO$_2$] the dependence of $\gamma$(HO$_2$) upon [HO$_2$] is linear. Assuming the same behaviour for uptake onto TiO$_2$ particles, the change in $\gamma$(HO$_2$) from RH across the range 11 - 66% due to the change in initial HO$_2$ concentration alone is only 0.0023 (or $\sim$ 6% of the averaged measured $\gamma$(HO$_2$) across this range), which does not explain the 75 % increase in $\gamma$(HO$_2$) observed in Figure 4.5 across this range of RH.

For the range of RH studied, Figure 4.6 shows that $\gamma$(HO$_2$) is a linear function of the number of monolayers of water surrounding a TiO$_2$ particle. Uptake of water must therefore play an important role in the reactive HO$_2$ uptake process on TiO$_2$ particles. Figure 4.7 presents a molecular diagram showing how water interacts and adsorbs onto the surface of TiO$_2$ and then how HO$_2$ can interact with that adsorbed water and react on the TiO$_2$ surface.

**Figure 4.7:** Simplified diagram of the important steps of HO$_2$ reactive uptake onto the surface of TiO$_2$. Grey circles = Ti, blue circles = O, orange circles = H, green circles = oxygen vacancy (V$_{bridge}$), solid black lines = chemical bond and dashed lines = hydrogen bond. Panel 1 shows the diffusion of water molecule towards a bridging O vacancy. Panel 2 shows the resultant formation of two neighbouring bridging OH groups at the original site of the O vacancy. Panel 3 shows the bridging OH groups acting as anchoring sites for water and HO$_2$ adsorption via hydrogen bonding leading to multilayer water adsorption and HO$_2$ self-reaction via an Eley-Rideal type mechanism. Panel 4 shows the build-up of a more extensive hydrogen bonded network as more water molecules adsorb onto the particle, which stabilises HO$_2$ increasing its desorption lifetime and hence probability that it will react.
Studies using ambient pressure photoelectron spectroscopy (APPES) have shown that water adsorption on rutile, a polymorph of TiO$_2$ (110), occurs in a number of distinct steps. Firstly, water molecules dissociate at O-vacancies ($V_{\text{bridge}}$) in bridge sites which produces a stoichiometric amount of bridging OH groups (OH$_{\text{bridge}}$) equal to twice the initial vacancy concentration upon initial exposure of rutile:

$$\text{H}_2\text{O} + V_{\text{bridge}} + O_{\text{bridge}} = 2\text{OH}_{\text{bridge}} \quad (R4.1)$$

Reaction 4.1 takes place even at very low concentrations of water vapour, with these bridging OH groups acting as nucleation sites that anchor water molecules to form strongly bound OH.H$_2$O complexes. The OH.H$_2$O complexes remain to act as nucleation centres for further water adsorption. TiO$_2$(110) wetting properties are thus driven by modest amounts of strongly attractive OH sites that nucleate water molecules. These OH.H$_2$O complexes have a relatively high enthalpy of adsorption for water of -72 kJ mol$^{-1}$, whereas additional adsorption of water beyond a monolayer of water coverage enthalpies tend to that associated with the bulk enthalpy of water condensation (-45 kJ mol$^{-1}$), and explains the distribution of the number of monolayers of water on the TiO$_2$ particle with RH as shown in Figure 4.5. Computational studies have shown that HO$_2$ can also readily form complexes with water through hydrogen bonding with a binding energy of 28.9 kJ mol$^{-1}$ (6.9 kcal mol$^{-1}$). It is likely that the observed correlation of $\gamma$(HO$_2$) with the number of monolayers of water surrounding TiO$_2$ particles is related with either an increase in the network of hydrogen bonding with each hydrogen bond increasing the stability of a molecular system by $\sim$ 20.9 kJ mol$^{-1}$ or merely that the number of available sites to hydrogen bond to increases meaning more HO$_2$ can adsorb on to the surface of the particle which in turn will increase the rate of reaction. An increase in the hydrogen bond network around the particle leads to a longer adsorption lifetime of HO$_2$ leading to an increase of the probability of HO$_2$ reacting on the surface of the particle.

Following the adsorption of HO$_2$ onto the TiO$_2$ surface, HO$_2$ self-reaction (R8-R9) plays a key role in the removal of HO$_2$ which is represented by the value of $\gamma$(HO$_2$):

$$\text{HO}_2(g) \rightleftharpoons \text{HO}_2(ad) \quad (R4.2)$$

$$\text{HO}_2(ad) + \text{HO}_2(g) \rightarrow \text{H}_2\text{O}_2(ad) + \text{O}_2(ad) \quad (R4.3)$$

It is likely that the mechanism of the reaction will, up to 2 monolayers, mostly follow the Eley-Rideal mechanism rather than the Langmuir-Hinshelwood mechanism. The coverage of $V_{\text{bridge}}$ across the surface of TiO$_2$ (110) has been determined to be 0.125 monolayers (i.e. one vacancy for every eight unit cells) meaning water will adsorb onto the surface of the particle in clusters. In order for HO$_2$ to react another molecule of HO$_2$ they must either adsorb on the same water cluster and diffuse across it or desorb and diffuse to a neighbouring cluster. As the
binding energy of HO₂ and water complexes is relatively strong one would imagine this process to be slow. The Eley-Rideal mechanism overcomes the problem of surface diffusion allowing for HO₂ in the gas phase to readily diffuse around the surface until reaction with an adsorbed molecule of HO₂. It is only until 2 monolayers of water are adsorbed onto the surface of the particle that the water clusters are big enough to interact with each other. The water binding structure is then more characteristic of bulk liquid allowing HO₂ to diffuse around the thin surface film of water with thermodynamic properties similar to liquid water¹⁴³.

To determine with some certainty whether indeed the Eley-Rideal mechanism is at play within this system is beyond the capability of the measurement and further experiments would be required.

The superoxide ion, O₂⁻, which is the conjugate base of HO₂, reacts with HO₂ over a hundred times quicker than with HO₂¹¹⁷ via (also see section 1.11.2):

\[ \text{HO}_2 + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- \]  \hspace{1cm} (R4.4)

It is unlikely that O₂⁻ will form readily on the surface of the particle at low coverages of water. O₂⁻ can form on surfaces via direct surface–oxygen electron transfer, photo-induced electron transfer, surface intermolecular electron transfer or decomposition of hydrogen peroxide (H₂O₂)¹⁴⁴. The dissociation of HO₂ to O₂⁻ occurs in bulk liquid (pKₐ = 4.7),⁵¹ however water surrounding the particles only begins to acquire liquid like properties once the coverage of water is greater than ~2 monolayers. If significant formation of O₂⁻ does occur above ~2 monolayers of H₂O, then owing to its much higher reactivity, some deviation from linearity of \( \gamma(\text{HO}_2) \) versus monolayers of water (Figure 4.6) might be expected. However, this was not observed, although the number of data points is very limited.

### 4.2.2 Comparison of \( \gamma(\text{HO}_2) \) with literature values

There are previous studies of HO₂ uptake onto ATD⁶⁶, a proxy for mineral dust, and both N₂O₅⁴⁸ and ClONO₂⁴⁹ uptake onto TiO₂ particles. Values of \( \gamma(\text{HO}_2) \) measured for ATD are comparable to those measured onto TiO₂ particles at similar concentrations of HO₂ in the aerosol flow tube (\( \gamma(\text{HO}_2)_{\text{ATD}} \sim 0.008 – 0.030 \)). For ATD, \( \gamma(\text{HO}_2) \) was only determined at 4 values of RH, but a general increase with RH was observed (although there was a dip around a RH of 50% before a further increase), consistent with HO₂ uptake being driven by the number of defects in the crystal lattice of mineral dust surfaces which provides bridging OH groups upon exposure to water and subsequently by the number of monolayers of water adsorbed onto the surface of such aerosols. The number of monolayers of water on the ATD surface at different RH has been determined¹⁴⁵, and also showed a general increase with RH but with a shoulder around a RH of 50% where the observed \( \gamma(\text{HO}_2) \) also contained a small dip (Figure 4.8).
Chapter 4 – HO₂ Uptake and Production on Aerosols relevant to the Stratosphere

Figure 4.8: \( \gamma(\text{HO}_2) \) onto airborne ATD particles (black squares, right y axis) at different RH taken from reference 66. The number of monolayers of the adsorbed water on ATD particles (white circles black curve, left y axis) also plotted as a function of RH, as previously determined using thermogravimetric analysis 145.

Values of \( \gamma(\text{N}_2\text{O}_5) \) and \( \gamma(\text{ClONO}_2) \) onto TiO₂ particles were an order of magnitude lower than \( \gamma(\text{HO}_2) \) and may be associated with the lower polarity of these molecules compared to HO₂. It is likely that, as with uptake of HO₂, both N₂O₅ and ClONO₂ react with TiO₂ via complexing with bridging OH groups and adsorbed H₂O, therefore, and less polar molecules will be less bound to the surface and more likely to desorb back into the gas phase, leading to a smaller \( \gamma \). The dependence of \( \gamma(\text{N}_2\text{O}_5) \) for TiO₂ with RH is also different to that for HO₂ observed here, with a small decrease of \( \gamma(\text{N}_2\text{O}_5) \) observed as the RH is increased from \( \sim 5 – 23\% \) where a minimum is reached, beyond 23\% \( \gamma(\text{N}_2\text{O}_5) \) increases as RH is increased. Competition between water and N₂O₅ for surface active OH groups was suggested for the initial observed decrease in \( \gamma(\text{N}_2\text{O}_5) \) with RH, whereas for RH > \( \sim 23\% \) heterogeneous hydrolysis of N₂O₅ to form HNO₃ starts to drive reactive uptake resulting in an increase of \( \gamma(\text{N}_2\text{O}_5) \) 135. Measurements of \( \gamma(\text{ClONO}_2) \) onto TiO₂ particles were only made at two values of RH, insufficient to determine any systematic dependence, it is expected that \( \gamma(\text{ClONO}_2) \) increases as more water adsorbs onto the surface of TiO₂ particles.

George et al. 9 previously measured \( \gamma(\text{HO}_2) \) onto dry salt aerosols. Values of \( \gamma(\text{HO}_2) \) for NaCl and (NH₄)₂SO₄ at RH values (33 – 54\%) below their deliquescence point were below the limit of detection (<0.004). Measured values of \( \gamma(\text{HO}_2) \) for TiO₂ (Figure 4.5 and Table 4.1) are more than an order of magnitude greater than that of solid salts, even for the dry conditions (RH = 11\%). A possible explanation for the difference in \( \gamma(\text{HO}_2) \) values could be that even though the size of the aerosol determined by the SMPS is similar, dry salt aerosols are more spherical in shape than TiO₂ particles which may be more fractal in nature. As the SMPS
indirectly measures the surface area of aerosols by measuring their mobility through an electric field, an assumption that the aerosol is spherical has to be made. Hence this may lead to a significant under-prediction of the surface area of non-spherical aerosols and therefore an over-prediction of $\gamma$(HO$_2$). In order to measure the geometry of the TiO$_2$ particles, a scanning electron microscope (SEM, FEI Nova NanoSEM 450) operating at 3 kV was used to image the TiO$_2$ nanoparticles used within these experiments. Samples for the SEM were prepared by dispersing the nanoparticles in ethanol and allowing a drop of this solution to dry on a silicon wafer. The wafer with nanoparticles was then mounted on SEM stubs using conductive carbon tapes and coated with 2 nm of Ir, using a Cressington 208HR high resolution sputter coater. Figure 4.9 shows an example of an SEM image providing evidence that the TiO$_2$ particles are spherical and therefore any error associated with SMPS measurements of surface area is minimal. A more likely explanation for the higher $\gamma$(HO$_2$) for TiO$_2$ particles is that dry salt aerosols do not adsorb a significant amount of water onto their surface, until the deliquescence point reached, whereas at a RH of 11% the TiO$_2$ particles already have a monolayer coverage which can form relatively strongly bound complexes with HO$_2$. Measurements of $\gamma$(HO$_2$) onto aqueous salt aerosols show that $\gamma$(HO$_2$) significantly increases above the deliquescence point and is comparable to $\gamma$(HO$_2$) measured for TiO$_2$ ($\gamma$(HO$_2$) $\sim$ 0.01).

![SEM image of a single TiO$_2$ particle magnified 80,000× used within this study.](image)

**Figure 4.9:** SEM image of a single TiO$_2$ particle magnified 80,000× used within this study.

### 4.2.3 Implications of HO$_2$ uptake by TiO$_2$ for stratospheric chemistry

The TOMCAT off-line three-dimensional (3D) chemical transport model (CTM) was used by Professor Chipperfield to predict the impact of the heterogeneous reaction of TiO$_2$ with HO$_2$ to stratospheric concentrations of O$_3$ and HO$_2$. At RH relevant to the lower stratosphere (< 40%), this study showed that $\gamma$(HO$_2$) is in the range 0.020 - 0.028 at 295 K. Although there have been no systematic experimental studies of the temperature dependence of $\gamma$(HO$_2$) an inverse temperature dependence of $\gamma$(HO$_2$) onto dry sea-salt aerosols has
previously been observed and parameterisations have developed (see section 1.13.2). It is likely that \( \gamma(\text{HO}_2) \) will be considerably larger at stratospherically relevant temperatures (200 - 220 K) than observed at 295 K. In light of this, \( \gamma(\text{HO}_2) = 1 \) was used in the model simulations which represents an upper limit value. Three TOMCAT simulations were run as shown below. Where TiO\(_2\) aerosols were included within TOMCAT simulations, a specified latitude-height distribution of the aerosol was applied with an effective aerosol surface area density equal to that of sulphate aerosols in 1992, the year after the eruption of Mt. Pinatubo. This assumption allows for the fact that less TiO\(_2\) mass is required to produce the same radiative impact as sulphate aerosols from Mt. Pinatubo but the TiO\(_2\) particle size is smaller, hence these effects largely cancel.

1. A control simulation which did not include TiO\(_2\) aerosols;
2. A simulation which included only the loss of N\(_2\)O\(_5\) on TiO\(_2\) particles with \( \gamma(\text{N}_2\text{O}_5) = 0.005 \), which allows comparison with previous studies; and
3. A simulation which also included the loss of HO\(_2\) on TiO\(_2\) particles with a \( \gamma = 1 \).

Figure 4.10 shows results from the simulation which also included the loss of HO\(_2\) on stratospheric TiO\(_2\) particles using \( \gamma(\text{HO}_2) = 1 \). It is apparent that HO\(_2\) loss due to heterogeneous reaction between HO\(_2\) and TiO\(_2\) particles in 2008 is < 1% and is restricted to the lower stratosphere where it is assumed TiO\(_2\) particles would be located. Figure 4.10 also shows that the predicted subsequent effect of the TiO\(_2\) particles on the O\(_3\) concentrations through the effects of HO\(_2\) uptake is also small (< 0.1%), with a small decrease in the tropical upper troposphere/lower stratosphere and a small increase at all latitudes in the lower stratosphere. The small predicted effect of TiO\(_2\) particles on stratospheric HO\(_2\) and O\(_3\) concentrations is due to the high reactivity and short lifetime of HO\(_2\). HO\(_2\) will readily react with other gas phase species (e.g. O\(_3\)) and so loss on TiO\(_2\) surfaces is unlikely to compete significantly.

![Figure 4.10: Annual mean change (%) in atmospheric O\(_3\) (a) and HO\(_2\) (b) calculated using the TOMCAT 3-D model from inclusion of heterogeneous loss of HO\(_2\) on TiO\(_2\) particles for 2008, and using \( \gamma(\text{HO}_2) = 1 \).](image-url)
4.3 \textbf{HO}_2 \textbf{Production from Irradiated Airborne TiO}_2 \textbf{particles}

4.3.1 \textit{Results}

Initial experiments (see section 2.4.6 for experimental methodology) were performed using a carrier gas consisting of firstly nitrogen and secondly a mixture of air and nitrogen (28\% air and 72\% N\textsubscript{2}, resulting in [O\textsubscript{2}] in aerosol flow tube of 5.9\%) at the driest conditions possible within the experimental setup (RH = 7.8\%) in order to reduce potential wall losses. The Limit of Detection (LOD) of the FAGE instrument for detection of \textit{HO}_2 was calculated to be 9.18 × 10\textsuperscript{5} molecule cm\textsuperscript{-3}. Figure 4.11 displays the concentration of \textit{HO}_2 measured at the end of the aerosol flow tube as a function of the surface area density of airborne TiO\textsubscript{2} nanoparticles, \textit{S}_a. The results showed significant production of gas-phase \textit{HO}_2 within the aerosol flow tube as a function of the TiO\textsubscript{2} aerosols \textit{S}_a in the presence of O\textsubscript{2}, confirming the source of \textit{HO}_2 was from aerosol surfaces. \textit{HO}_2 production was small when the carrier gas was composed of solely compressed nitrogen at similar RH. The small amount of \textit{HO}_2 produced was likely associated with impurities of oxygen in the compressed nitrogen. Therefore, the presence of gas phase molecular oxygen was necessary for \textit{HO}_2 production to occur. There is a large gap of measurements between a range of \textit{S}_a as the valves within the by-pass loop of HEPA filters, used to control the number of airborne particles entering the aerosol flow tube, beyond a \textit{S}_a of around 2.5 × 10\textsuperscript{-5} cm\textsuperscript{2} cm\textsuperscript{-3} could not be controlled with the same sensitivity.

![Graph](image-url)

\textit{Figure 4.11}: Gas phase HO\textsubscript{2} produced by airborne irradiated TiO\textsubscript{2} nanoparticles as a function of surface area density, \textit{S}_a, with a carrier gas composed of compressed nitrogen (solid black squares) at RH = 24.0\% and a mixture of compressed nitrogen and air (unfilled red squares) at RH = 16.4\%. Illumination time was 14 s.
A small HO$_2$ signal was detected when TiO$_2$ nanoparticles were not present in the aerosol flow tube from the deposition of TiO$_2$ nanoparticles on the walls of the aerosol flow tube. No such HO$_2$ signal was observed after the aerosol flow tube had been cleaned. This small signal was included within the model as $k_{\text{prod\;wall}}$.

The dependence of the HO$_2$ produced to $S_a$ shows that HO$_2$ rises as more airborne nanoparticles enter the system until a maximum was reached (see Figure 4.11). Adding more particles beyond this results in a decrease of HO$_2$ concentration. There are two possible reasons for such observation. On one hand, as TiO$_2$ aerosols have a large refractive index (2.5 at 500 nm) it is expected that this system would be affected by Mie scattering. As aerosol loading is increased within the aerosol flow tube more light will be Mie scattered back out of the flow tube shading particles below, therefore reducing the number of photons within the aerosol flow tube and the photocatalytic activity of TiO$_2$ aerosols, hence a drop in the total rate of production of HO$_2$. On the other hand, as aerosol loading of the flow tube increases HO$_2$ heterogeneous uptake by TiO$_2$ aerosols will become more significant.

Figure 4.12 shows the difference in HO$_2$ produced as a function of $S_a$ when the 8 W and 15 W UVA lamp was used to illuminate the aerosol flow tube. As expected, the higher-powered lamp results in more gas-phase HO$_2$ being produced. A maximum of HO$_2$ formation using the 8 W UVA lamp occurred at a slightly higher aerosol loading within the aerosol flow tube suggesting that experiments using the higher-powered lamp (15 W) was more affected by Mie scattering.

**Figure 4.12:** Gas phase HO$_2$ produced from airborne irradiated TiO$_2$ nanoparticles as function of total surface area density ($S_a$) at RH = 8.0% and [O$_2$] = 5.9% using an 8 W UVA lamp (red crosses) and a 15 W UVA lamp (black squares) to illuminate the aerosol flow tube.
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Using the model described in section 2.4.6, it was possible to calculate the rate of production of HO₂ by TiO₂ aerosols, \( k_{\text{prod}} \), as a function of \( S_a \) for these experiments (see Figure 4.13). This shows that \( k_{\text{prod}} \) decreases exponentially (exponential decay fit to data presented in Figure 4.13) with both lamps as a function of \( S_a \). The rate at which \( k_{\text{prod}} \) decreases with \( S_a \) was much greater (~ 3 ×) with the 15 W lamp, suggesting that Mie scattering effects are greater using this lamp than the 8 W lamp as discussed before, since the 15 W lamp emits a higher flux of the photons (see Figure 4.13).

\[ k_{\text{prod}} \text{ / molecule cm}^{-2} \text{s}^{-1} \]

\[ S_a / \text{cm}^2 \text{cm}^{-3} \]

**Figure 4.13:** The rate coefficient describing production of HO₂ (\( k_{\text{prod}} \)) from airborne irradiated TiO₂ nanoparticles as function of total surface area density (\( S_a \)) at RH = 8.0% and \([O_2] = 5.9\%\) using an 8 W UVA lamp (black squares) and a 15 W UVA lamp (red circles) to illuminate the aerosol flow tube. Solid lines represent exponential decays (i.e., \( y = y_0 + Ae^{-x/t} \)) fitted to experimental data.

Due to these findings, further experiments were conducted at a small and constant aerosol surface area density (~ 1 - 2 × 10⁵ cm² cm⁻³) to try to ensure photon scattering effects and aerosol uptake of HO₂ were negligible (< 1%), meaning any changes in \( k_{\text{prod}} \) was predominantly due to changes in the conditions to be investigated.

By shading different proportions of the lamp, the length of time that aerosols are exposed to UV light flux could be controlled. Figure 4.14 shows that the rate of HO₂ production changes the longer aerosols were irradiated. HO₂ was produced at a fast and broadly constant rate within the first few seconds upon irradiation of the aerosols, beyond three seconds the net rate of HO₂ production begins to slow down. Projection of the production rate trends shows that at both initial \( O_2 \) concentrations the rate of HO₂ production reaches zero at around a residence
time of \( \sim 30 \text{ s} \). This points to two processes operating here; a \( \text{HO}_2 \) production process which shows a strong dependence to \( \text{O}_2 \) concentrations and is also dependent on the rate of a second aging process that is dependent on the residence time spent within the illuminated region of the flow tube. It is unlikely that the observed decrease of \( k_{\text{prod}} \) with time is associated with a reduction of available \( \text{O}_2 \) for reaction as the reaction proceeds. Concentrations of \( \text{O}_2 \) far exceed the concentrations of \( \text{HO}_2 \) produced and the rate of aging seems to be independent of \([\text{O}_2]\), however without measurement of \( \text{O}_2 \) at the end of the flow tube it cannot be entirely ruled out. It should be noted that these findings show that the calculation of \( k_{\text{prod}} \) using the model is somewhat limited as it is characterised as a first-order reaction which does not capture this behaviour, therefore, \( k_{\text{prod}} \) calculated by the model is an average over the residence time of aerosols within the illuminated region of the flow tube.

![Graph](image)

**Figure 4.14:** Gas-phase \( \text{HO}_2 \) produced from airborne irradiated TiO\(_2\) nanoparticles as a function of time. Black squares and red circles represent \([\text{O}_2]\)\(_{t=0} = 7.3\%\) and 4.4\% respectively, RH = 11.0\%. Solid lines represent box-lucus best-fits to experimental data.
The dependence of $k_{prod}$ with O$_2$ concentration (expressed as the partial pressure, $p_{O_2}$) was investigated at two different RH and for a reaction time of 14 s and is presented in Figure 4.15. The relationship between $k_{prod}$ and $p_{O_2}$ shows a typical Langmuir adsorption saturation curve.

Comparison of the dependence of $k_{prod}$ with $p_{O_2}$ at a RH of 8.7% and 22.1% shows that the rate of change of $k_{prod}$ at low $p_{O_2}$ (< 4000 Pa) was more than three times greater at a RH of 8.7% than a RH of 22.1%. The maximum value of $k_{prod}$ at high $p_{O_2}$ was around twice as great at a RH of 8.7% than at a RH of 22.1%. The presence of water inhibits $k_{prod}$ showing that water and oxygen are either competing for the same adsorption sites on the TiO$_2$ aerosol surface or that the adsorption of water affects the number of adsorption sites of O$_2$. The reaction of O$_2$ with the surface of a TiO$_2$ particle can be described by R4.5. The adsorption of water inhibits $k_{prod}$ by reducing the number of available sites on the TiO$_2$ particle surface that O$_2$ can adsorb and react on. With this in mind, the total number of active sites is therefore equal to the number of available active sites plus the number of active sites occupied by water and O$_2$ (E4.6). The equilibrium constant for adsorption, $K$, of O$_2$ or water vapour is defined in E4.3. By combining E4.2 with E4.3, the fractional coverage of O$_2$, $\theta_{O_2}$ defined as the fraction of active sites on the TiO$_2$ nanoparticle surface occupied by O$_2$, can be expressed as in E4.4.
\[ \text{O}_2 + \text{H}^* + e^- \rightarrow \text{HO}_2 \]  \hspace{1cm} (R4.5)

\[ [\text{O}_2(g)] \leftrightarrow [\text{O}_2(\text{ad})] \rightarrow [\text{HO}_2] \]  \hspace{1cm} (R4.6)

\[ [S_0] = [S] + [\text{H}_2\text{O}(\text{ad})] + [\text{O}_2(\text{ad})] \]  \hspace{1cm} (E4.2)

\[ K = \frac{k_1}{k_{-1}} = \frac{[A(\text{ad})]}{p[A][S]} \text{ where } A = \text{O}_2 \text{ or H}_2\text{O} \]  \hspace{1cm} (E4.3)

\[ \theta_{\text{O}_2} = \frac{[S_0] - [O_2(\text{ads})]}{[S_0]} = \frac{K_{\text{O}_2}p_{\text{O}_2}}{1 + K_{\text{O}_2}p_{\text{O}_2} + K_{\text{H}_2\text{O}}p_{\text{H}_2\text{O}}} \]  \hspace{1cm} (E4.4)

where \( K_{\text{O}_2} \) is the adsorption equilibrium constant of oxygen, \( p_{\text{O}_2} \) is the pressure of oxygen, \( K_{\text{H}_2\text{O}} \) is the adsorption equilibrium of water and \( p_{\text{H}_2\text{O}} \) is the partial pressure of water.

The rate of the production of HO\(_2\) (\( k_{\text{prod}} \)) is equal to \( k_2 \) multiplied by \( \theta_{\text{O}_2} \) (E4.5). At high partial pressures of \( \text{O}_2 \), \( k_{\text{prod}} \) is effectively equal to \( k_2 \) and is referred to as the maximum rate of production of HO\(_2\), \( k_{\text{prod, max}} \). Taking this into account then \( k_{\text{prod}} \) can be expressed as follows:

\[ k_{\text{prod}} = k_2\theta_{\text{O}_2} = \frac{k_{\text{prod, max}}K_{\text{O}_2}p_{\text{O}_2}}{1 + K_{\text{O}_2}p_{\text{O}_2} + K_{\text{H}_2\text{O}}p_{\text{H}_2\text{O}}} \]  \hspace{1cm} (E4.5)

Figure 4.15 shows a fit of the experimental data to E4.5 which yielded values for \( k_{\text{prod, max}}, K_{\text{O}_2} \) and \( K_{\text{H}_2\text{O}} \) presented in Table 1.

**Table 4.2:** Parameters yielded from fitting experimental data in Figure 4.15 to E4.5 (error = 2\( \sigma \)). Illumination time was 14 s.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment at RH = 8.7%</th>
<th>Experiment at RH = 22.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{prod, max}} )/ molecule cm(^{-2}) s(^{-1})</td>
<td>(5.93 ± 0.07) \times 10^{12}</td>
<td>(3.21 ± 0.02) \times 10^{12}</td>
</tr>
<tr>
<td>( K_{\text{O}_2} )/ Pa(^{-1})</td>
<td>0.269 ± 0.016</td>
<td>0.184 ± 0.004</td>
</tr>
<tr>
<td>( K_{\text{H}_2\text{O}} )/ Pa(^{-1})</td>
<td>2.16 ± 0.12</td>
<td>1.33 ± 0.04</td>
</tr>
</tbody>
</table>

The relationship between the rate of HO\(_2\) formation and the amount of water vapour within the aerosol flow tube was investigated. Figure 4.16 shows that the concentration of HO\(_2\) produced per unit of \( S_a \) and \( k_{\text{prod}} \) from the model decreases exponentially as the relative humidity was increased within the aerosol flow tube. Increasing the concentration of \( \text{O}_2 \) in the aerosol flow tube increased HO\(_2\) produced proportionally.
The OH production from irradiated TiO$_2$ aerosols was also investigated. The LOD of the FAGE instrument for detection of OH was calculated to be $2.24 \times 10^6$ molecule cm$^{-3}$. Direct detection of OH using the FAGE instrument showed no OH was produced by TiO$_2$ aerosols within the aerosol flow tube, possibly due to high losses to the aerosol flow tube walls. Therefore, CO (0.5 L min$^{-1}$, 5% in air) was added to the carrier gas prior to the conditioning tube in order to act as a OH scavenger rapidly ($\tau$(OH) = $5.5 \times 10^{-5}$ s) converting OH to HO$_2$ (R4.7).
CO + OH (+ O\(_2\)) \rightarrow CO\(_2\) + HO\(_2\) \hspace{1cm} (R4.7 \ k = 1.53 \times 10^{-13} \ \text{molecule}^{-1} \ \text{cm}^3 \ \text{s}^{-1})

Figure 4.17 shows that at \(S_a\) lower than \(2 \times 10^{-4} \ \text{cm}^2 \ \text{cm}^{-3}\) there was no difference between HO\(_2\) produced with and without CO present, however when \(S_a\) was greater than \(2 \times 10^{-4} \ \text{cm}^2 \ \text{cm}^{-3}\) a noticeable difference (~ \(8 \times 10^8 \ \text{molecule} \ \text{cm}^{-3}\)) was observed. It could be that the amount of gas-phase OH produced is relatively small and large concentrations of TiO\(_2\) aerosols are necessary to generate an observable amount. A more likely explanation is OH was produced by the photocatalytic decomposition of H\(_2\)O\(_2\) (R11) formed by HO\(_2\) uptake, which is more prevalent at high [HO\(_2\)] and \(S_a\). The mechanism of H\(_2\)O\(_2\) decomposition producing OH seen in this study is likely to be that observed by Yi \textit{et al.} \(^{84}\) (R11). Whilst this study is contrary to the findings of Murikami \textit{et al.} \(^{82}\) who directly observed gas-phase production of OH from irradiated TiO\(_2\) surfaces, other studies \(^{148}\) have shown OH formed by water oxidation on anatase is likely to remain adsorbed on the surface rather than desorbing into the gas-phase and on rutile peroxy intermediates are formed rather than OH.

![Figure 4.17](image)

**Figure 4.17**: Gas-phase HO\(_2\) produced by irradiated airborne TiO\(_2\) nanoparticles at different \(S_a\) at [O\(_2\)] = 5.9\% without (black squares) and with (red circles) CO present within the flow tube. Illumination time was 14 s.

### 4.3.2 Discussion

From our knowledge, this study provides the first direct observations of significant quantities of gas-phase HO\(_2\) radicals formed on aerosol surfaces and the first time such observations have been made from TiO\(_2\) in the presence of light and O\(_2\) and without the initial presence of H\(_2\)O\(_2\).
Previous studies by Yi et al. did not observe the same phenomena as the presence of added H$_2$O$_2$ was necessary for HO$_2$ emission. Some possible reasons for the non-observation of HO$_2$ emission in the absence of H$_2$O$_2$ could be as follows:

- Studies involving aerosols often show different findings to studies with films as they are not diffusion limited due to the high surface area to volume ratio of aerosol experiments. Nanoparticles provide a significantly larger surface area density for adsorption and interaction of reactants than TiO$_2$ films. To overcome diffusion limitations surface or thin film experiments are often performed under low pressure, however this will not favour adsorption of species with a high vapour pressure, such as water;
- The HO$_2$ limit of detection (LOD) of Yi et al.’s cw-CRDS set-up was $3.3 \times 10^9$ molecule cm$^{-3}$ vs. our LOD of $9.18 \times 10^5$ molecule cm$^{-3}$. This LOD is above many of the measurements of concentrations of HO$_2$ produced by TiO$_2$ nanoparticles in this study; and
- Surface or thin film experiments often take a number of minutes so surface saturation and product accumulation may occur on the surface of the sample and could change its chemical characteristics.

Figure 4.15 and 4.16 shows that water acts as an inhibitor to the production of HO$_2$ as water competes with O$_2$ for adsorption onto active sites or water adsorption reduces the number of O$_2$ adsorption sites. The value of $K_{H2O}$, obtained from Figure 4.15, shows that $K_{H2O}$ was greater than $K_{O2}$ suggesting H$_2$O adsorption is more favoured than O$_2$ adsorption, probably due to water having a great enthalpy of adsorption than oxygen with TiO$_2$ surfaces and hence a longer adsorption lifetime. As $K_{O2} < 1$ the rate constant of desorption of oxygen ($k_{-1}$) must be greater than the rate constant of adsorption ($k_1$), whereas when $K_{H2O} > 1$ the rate of adsorption is greater than the rate of desorption. Both $K_{O2}$ and $K_{H2O}$ decrease as RH was increased within the system suggesting that the enthalpy of adsorption of both species will be RH dependent. It is known that bridging hydroxyl groups (OH$_{br}$) provide an anchoring point for water molecules to adsorb onto TiO$_2$ surfaces forming OH$_{br}$-H$_2$O complexes which are acidic in character (i.e. OH$_{br}$ groups act as H-donors). The enthalpy of water adsorption on these sites is ~ 70 kJ mol$^{-1}$. As RH is increased within the system more H$_2$O attaches to OH$_{br}$-H$_2$O complexes and the acidic nature of the complexes decreases, resulting in the water binding structure tending to be more characteristic of bulk water. This results in a lowering of the H$_2$O adsorption enthalpy which is observed in this work. Density functional theory (DFT) calculations have shown that O$_2$ adsorption onto TiO$_2$ (110, i.e. the rutile polymorph of TiO$_2$) surfaces is also entirely dependent on the presence of OH$_{br}$ groups. These calculations show that the most stable configuration for adsorption is over two fivefold coordinated Ti sites (Ti$_{5c}$) adjacent to a
OH\textsubscript{br} group and has an adsorption enthalpy of 0.8 eV (~77 kJ mol\textsuperscript{-1}), however many other configurations have an adsorption enthalpy only 0.2 eV less (~58 kJ mol\textsuperscript{-1}), e.g. adsorption is over one Ti\textsubscript{5c} site adjacent to a OH\textsubscript{br} group. They also show that the adsorption enthalpy is dependent on the coverage of OH\textsubscript{br}, with higher levels of OH\textsubscript{br} resulting in a higher enthalpy of adsorption and hence a higher adsorption lifetime, although the distance between adsorbed O\textsubscript{2} and OH\textsubscript{br} does not significantly affect the adsorption enthalpy meaning OH\textsubscript{br} possess a long-range effect on O\textsubscript{2} adsorption. It is suggested that these effects are caused by OH\textsubscript{br} groups donating electrons to TiO\textsubscript{2} which delocalise amongst Ti\textsubscript{5c} atoms. Upon O\textsubscript{2} adsorption, there is a charge transfer from the Ti\textsubscript{5c} atoms to O\textsubscript{2}, the magnitude of which determines the enthalpy of adsorption. The same mechanism was true for calculations of O\textsubscript{2} adsorption onto TiO\textsubscript{2}(101, anatase)\textsuperscript{150}. The decrease of K\textsubscript{O2} with RH and the inhibiting effects of H\textsubscript{2}O adsorption to the rate of HO\textsubscript{2} production observed in this work are likely associated with the formation of OH\textsubscript{br}-H\textsubscript{2}O complexes which inhibits the ability of OH\textsubscript{br} groups to donate electron density to Ti\textsubscript{5c} atoms thereby reducing the adsorption enthalpy of O\textsubscript{2} and adsorption of H\textsubscript{2}O on this site, blocking favourable O\textsubscript{2} absorptions sites near OH\textsubscript{br}.

The likely mechanism for the production of HO\textsubscript{2} upon TiO\textsubscript{2} in the presence of O\textsubscript{2} is initiated by the production of photogenerated electrons in the conduction band (e\textsuperscript{-CB}) and holes within the valence band (h\textsuperscript{+VB}) by irradiated TiO\textsubscript{2}(R4.8), which can either recombine or reside in a trapped state or within the respective band. In photocatalysis, O\textsubscript{2} is an effective electron scavenger forming either O\textsubscript{2}\textsuperscript{-} or O\textsubscript{2}\textsuperscript{2-}. A study of this process on TiO\textsubscript{2}(101) surfaces\textsuperscript{151} showed that photogenerated e\textsuperscript{-} can exist on paramagnetic Ti\textsuperscript{3+} sites or delocalise within the conduction band. At room temperature, most photogenerated e\textsuperscript{-} remains stable within the conduction band rather than in trapped Ti\textsuperscript{3+} states, however at cooler temperatures e\textsuperscript{-} can reside in these traps which could lead to a higher rate of O\textsubscript{2}\textsuperscript{-} formation. That study observed the production of long-lived O\textsubscript{2}\textsuperscript{-}, which was judged to be very efficient as all photoexcited e\textsuperscript{-} were transferred to adsorbed O\textsubscript{2}. It is likely that the mechanism for HO\textsubscript{2} production would therefore have to involve the reduction of adsorbed O\textsubscript{2} with e\textsubscript{-CB} forming adsorbed O\textsubscript{2}\textsuperscript{-} (R4.12). O\textsubscript{2}\textsuperscript{-} can then go on to react with a proton (R4.13) formed by the oxidation of adsorbed water via its reaction with a photogenerated h\textsuperscript{+} (R4.10) located at bridging oxygen sites (O\textsubscript{bc}) for TiO\textsubscript{2} (110) and OH\textsubscript{br} groups for TiO\textsubscript{2} (101)\textsuperscript{152, 153} to form adsorbed HO\textsubscript{2}. This mechanism highlights the contradictory role that water plays in the photocatalytic activity of TiO\textsubscript{2}, on the one-hand producing active species on the surface of photocatalytically active TiO\textsubscript{2} available for reaction and on the other hand reducing effective adsorption of gas-phase species. It is also possible that the desorption of HO\textsubscript{2} (R4.14) could be aided by light (i.e. photodesorption) as photogenerated e\textsuperscript{-} populates Ti sites, hence why HO\textsubscript{2} is desorbed back into the gas-phase rather than remain adsorbed on the TiO\textsubscript{2} surface as given below:
Chapter 4 – HO\textsubscript{2} Uptake and Production on Aerosols relevant to the Stratosphere

\[ \text{TiO}_2 + h\nu (\lambda < 388 \text{ nm}) \rightarrow \text{TiO}_2 + h^*_{\text{VB}} + e^-_{\text{CB}} \] \hspace{1cm} (R4.8)

\[ \text{OH}_{\text{br}} + \text{H}_2\text{O}(g) \rightleftharpoons \text{OH}_{\text{br}}\text{OH}_2(\text{ad}) \] \hspace{1cm} (R4.9)

\[ \text{OH}_{\text{br}}^- \text{OH}_2(\text{ad}) + h^* \rightarrow \text{OH}(\text{ad}) + \text{H}^+_{\text{ad}} + \text{OH}_{\text{br}} \] \hspace{1cm} (R4.10)

\[ \text{Ti} + \text{O}_2(g) \rightleftharpoons \text{Ti-O}_2(\text{ad}) \] \hspace{1cm} (R4.11)

\[ \text{Ti-O}_2(\text{ad}) + e^-_{\text{CB}} \rightarrow \text{Ti-O}_2(\text{ad}) \] \hspace{1cm} (R4.12)

\[ \text{Ti-O}_2(\text{ad}) + \text{H}^+_{\text{ad}} \rightarrow \text{Ti-O}_2\text{H}(\text{ad}) \] \hspace{1cm} (R4.13)

\[ \text{Ti-O}_2\text{H}(\text{ad}) \rightleftharpoons \text{Ti} + \text{HO}_2(g) \] \hspace{1cm} (R4.14)

This study has also shown that \( k_{\text{prod}} \) reduces the longer TiO\textsubscript{2} particles spend irradiated, with no further HO\textsubscript{2} being produced beyond \(~30\) s, eluding to an aging process dependent on UV irradiation. It is likely that the destruction of OH\textsubscript{br} groups was the cause for the slowing down of \( k_{\text{prod}} \) as they are required for both adsorption of O\textsubscript{2} and H\textsubscript{2}O and provide a site for hole trapping required for H\textsubscript{2}O oxidation\(^{153}\). It has been shown that isolated OH\textsubscript{br} groups or OH\textsubscript{br} pairs, formed by water dissociation at oxygen vacancy sites (O\textsubscript{vac}) (R4.15), can react with gas-phase O\textsubscript{2} to form adsorbed HO\textsubscript{2} (R4.16 – R4.17)\(^{154,156}\). It could be that the aging process observed in this work was a result of the formation of O\textsubscript{2}‘, a more reactive species of O\textsubscript{2}, close to an OH\textsubscript{br} group extracting the proton from it and converting it to O\textsubscript{br}, causing in a reduction of \( k_{\text{prod}} \).

\[ \text{H}_2\text{O} + \text{O}_{\text{vac}} + \text{O}_{\text{br}} \rightarrow 2\text{OH}_{\text{br}} \] \hspace{1cm} (R4.15)

\[ \text{OH}_{\text{br}} + \text{O}_2(g) \rightarrow \text{O}_{\text{br}} + \text{HO}_2(\text{ad}) \] \hspace{1cm} (R4.16)

\[ 2\text{OH}_{\text{br}} + \text{O}_2(g) \rightarrow \text{OH}_{\text{br}} + \text{O}_{\text{br}} + \text{HO}_2(\text{ad}) \] \hspace{1cm} (R4.17)

Both this (R4.14 – R4.16) and the previous mechanism (R4.7 – R4.13) produce HO\textsubscript{2} and are probably occurring concertedely. If this was the only mechanism at play then it could be expected the rate of HO\textsubscript{2} production would reduce rapidly upon irradiation and the quantities of HO\textsubscript{2} produced would be independent of the concentration of O\textsubscript{2} in the gas-phase, both are not the case. However, this mechanism does suggest that in the absence of a mechanism for OH\textsubscript{br} regeneration production of HO\textsubscript{2} is not continuous and consequently it would mean that radical production would get reduced with aging.

4.3.3 Atmospheric Implications

Whilst this study has shown that irradiation of airborne TiO\textsubscript{2} nanoparticles in the presence of O\textsubscript{2} does result in the production of gas-phase HO\textsubscript{2}, which has the potential perturb stratospheric chemistry, it also shows that this process is likely not to be continuous as
photochemical aging slows the rate of the HO$_2$ production until it reaches zero when all OH$_{br}$ groups have been converted to O$_{br}$. The aging of particles will have an additional beneficial effect, with regards to SRM application, as OH$_{br}$ groups are likely nucleation sites for uptake of trace gases. Other studies$^49$ and this work have shown that uptake of trace gas species does correlate with the number of monolayers of water surrounding the TiO$_2$ aerosol. Removal of OH$_{br}$ from the surface of TiO$_2$ particles, creating an almost perfect TiO$_2$ surface (i.e. without O defects), is likely to result in the lowering of its reactivity to trace gases, therefore reducing the potential for reactions that could perturb stratospheric chemistry to occur upon its surface. However, this result could have particular repercussions for its use as an environmental catalyst within the troposphere. NO, an important air pollutant within the urban environment, adsorbed onto illuminated TiO$_2$ surfaces is predominantly converted to nitrates in the presence of O$_2$$^{157}$ demonstrating the use of TiO$_2$ as a possible environmental catalyst. Like O$_2$, adsorption of NO is only possible in the proximity of surface hydroxyl groups, such as OH$_{br}$$^{158}$. If O$_2$ does efficiently extract protons from hydroxyl groups then the effectiveness of TiO$_2$ as an environmental catalyst is reduced as NO will not be able to adsorb onto the surface of TiO$_2$. Indeed, a number of field studies have shown little or no reduction in ambient levels of NO or NO$_2$ in areas where TiO$_2$ coatings have been applied$^{159-161}$ and that such coatings were not durable and require frequent re-application in order to retain their effectiveness$^{159}$.

4.4 Summary

HO$_2$ uptake coefficients on TiO$_2$ nanoparticles were measured to be from $\gamma$(HO$_2$) = 0.021 ± 0.001 to 0.036 ± 0.007 over a range of RH from 11% to 66% respectively. Measured HO$_2$ uptake coefficients showed a positive dependence on RH which correlated with the number of monolayers of water adsorbed onto the TiO$_2$ nanoparticle suggesting a mechanism by which HO$_2$ adsorbs to the surface of the TiO$_2$ particle by forming complexes with water molecules bound to bridging OH groups. As RH increases so does the number of water molecules adsorbed to the surface of the TiO$_2$ nanoparticle. This increases the network of hydrogen bonds that stabilises HO$_2$ leading to a longer adsorption lifetime and increased $\gamma$(HO$_2$). The TOMCAT chemical transport model was used by Professor Chipperfield to predict the possible effects of HO$_2$ uptake (using an upper limit of $\gamma$(HO$_2$) = 1) onto the surface of TiO$_2$ nanoparticles on the stratospheric concentrations of HO$_2$ and O$_3$. The amount of TiO$_2$ used was chosen to achieve a similar cooling to that following the Mt. Pinatubo eruption, but the model predicted a very small loss of both stratospheric HO$_2$ and O$_3$.

As TiO$_2$ possesses photocatalytic properties, water adsorbed onto its surface may dissociate under stratospheric illumination providing a source of HO$_3$$^{138,162}$. Production of HO$_3$ radicals by irradiated airborne TiO$_2$ was therefore investigated. This work presents the first direct observations of radicals emitted from the surface of airborne particles and provides an insight
into the photocatalytic reactions occurring on the surfaces of TiO$_2$. Upon illumination of airborne TiO$_2$ nanoparticles with UV light, significant quantities of HO$_2$ was formed within the gas-phase. The reaction is dependent on the presence of gas-phase O$_2$ within the system. The production of HO$_2$ has shown to slow down as a function of irradiation pointing towards a photochemical aging process occurring. The dependence of HO$_2$ production on O$_2$ and H$_2$O concentrations has been determined which shows a typical Langmuir adsorption saturation curve for O$_2$ suggesting it is the gas-phase reactant in this process. The addition of H$_2$O into the system inhibits the reaction and reduces the adsorption equilibrium coefficient for both species. Reduction of O$_2$ by photogenerated electrons is likely to be the initial step in this process followed by reaction with a proton. Hydrogen extraction from OH$_{br}$ groups by O$_2^-$ could explain the slow down observed in the rate of HO$_2$ production. Production of gas-phase OH radicals were investigated and showed OH was produced only when large concentrations of TiO$_2$ aerosols entered the aerosol flow tube, probably associated with the decomposition of H$_2$O$_2$ formed from reactive uptake. Although the production of HO$_2$ by TiO$_2$ aerosols initially would not be advantageous for its use within SRM schemes, the reaction ceases upon prolonged photocatalytic aging of the aerosol surface.
Chapter 5 – HO₂ Uptake on Aerosols relevant to the Mesosphere

This chapter presents the results and interpretation of experiments conducted on airborne analogues of mesospheric smoke particles.
5.1 Introduction
Discrepancies between observations and photochemical model predictions of mesospheric HO₂, known as the “HOₓ Dilemma” 32, have highlighted limitations in our understanding of the chemistry occurring within the middle atmosphere. Observed vertical profiles of OH have brought into question the current understanding of the key reactions that dominate OH/HO₂ partitioning within the mesosphere and stratosphere 34 and widely used models, such as Whole Atmosphere Community Climate Model (WACCM), systematically under predicts mesospheric HO₂ concentrations 32. However, these modelling studies only consider gas-phase chemistry and so heterogeneous chemistry between HO₂ and meteoric smoke particles (MSP), the only known source of potentially reactive surfaces in the mesosphere below 80 km 163, could be a key reaction within the mechanism that partitions HOₓ within this region of the atmosphere. Previous studies have shown that reactive uptake on MSP may considerably affect stratospheric and mesospheric concentrations of HNO₃ and H₂SO₄ 52, 164 and that heterogeneous recombination of O and H₂ on the surface of MSP could be a missing source of H₂O in the lower mesosphere 165. Therefore, a study on the kinetics of heterogeneous HO₂ uptake on analogues of MSP (known as olivines, Mg₂Fe₂-xSiO₄) was conducted in this work. Uptake of acetylene (C₂H₂) 166, H₂O, NO, NO₂ and HNO₃ 164 onto olivine surfaces have previously been conducted, however as such experiments were performed on surfaces rather than airborne particles gas-phase diffusion limitations would likely offer a lower estimate of the reactive uptake coefficient (γ). The uptake coefficient of C₂H₂ onto olivine surfaces was measured to be on average (1.6 ± 0.4) × 10⁻⁴ and shown to be independent of the number of Mg or Fe active sites. Measurements of the uptake coefficient of HNO₃, H₂O, NO₂ and NO onto a surface of MgFeSiO₄ were (1.8 ± 0.3) × 10⁻³, (4.0 ± 1.3) × 10⁻³, (5.7 ± 0.2) × 10⁻⁴ and < 3 × 10⁻⁴ respectively.

5.2 Measurements of the Reactive HO₂ Uptake Coefficient onto analogues of MSP
Measurements of the reactive HO₂ uptake coefficient, γ(HO₂), were made on three analogues of MSP; a synthetic amorphous olivine (MgFeSiO₄), fayalite (Fe₂SiO₄) and forsterite (Mg₂SiO₄). These analogues of MSP, in the form of amorphous compounds with olivine compositions MgₓFe₂-xSiO₄, were provided by Professor Plane’s group. They were produced by mixing stoichiometric quantities of magnesium chloride (Aldrich), ferrous (II) ammonium sulphate (Sigma-Aldrich) and sodium orthosilicate (Alfa Aesar) in an aqueous solution for seven days at room temperature and any by-products were removed from products via repeated dialysis 164.
Measurements of $\gamma$(HO$_2$) were made at the lowest RH possible within the experimental setup (~ 10%) which is the most representative achievable RH for the mesosphere, although $\gamma$(HO$_2$) on olivine was also measured at a higher RH (20%) in order to shed possible light on the reaction mechanism. The anti-correlation experimental methodology (i.e. measurement of the anti-correlation between HO$_2$ concentrations and aerosol number density, see section 2.4.5) was utilised for measurements of $\gamma$(HO$_2$) onto MSP as the other experimental methodologies require the use of the atomiser to produce a constant output of aerosols. The atomiser requires the particles to be suspended within water which could potentially alter the chemical composition of particles. Entrainment of MSP was achieved using the magnetic stirrer method and later with the Acoustic Particle Disperser (APD, described in Chapter 2). An initial HO$_2$ concentration of $1.6 \times 10^9$ molecule cm$^{-3}$ was used within this study. The size distribution of the MSP analogues was measured 10 times to obtain the mean surface area of each particle.

Figure 5.1 shows some variability in aerosol concentration generated by the dust disperser, however averaging size distributions did produce a well-characterised lognormal distribution from which the average size of a particle could be calculated. The size distribution of MSP analogues shown in Figure 5.1 suggests some aerosols that entered the aerosol flow tube might be outside the detection range of the SMPS (i.e. particle diameter > 730 nm), however for the purposes of these experiments the lognormal fit to the SMPS data was used to calculate the average surface area which accounted for aerosols outside of this range.

![Figure 5.1](image.jpg)

**Figure 5.1:** Measured size distribution of fayalite at 9.9% RH, normalized to the peak of a lognormal fit to the distribution. Ten individual measurements are shown in grey with the mean in black and a lognormal fit to the size distribution in red. Mean mid-point diameter = 368 ± 0.7 nm and mean particle surface area = $4.25 \times 10^{-9}$ cm$^2$.

It should be noted that SEM images of the analogues of MSP have revealed their shape to be fractal-like in character. It is therefore likely that the spherical assumption used to calculate
the surface area is not wholly valid and would also ignore likely surface roughness leading to an underestimate of the surface area and an overestimation $\gamma(\text{HO}_2)$.

Figure 5.2 shows the clear anti-correlation of the HO$_2$ signal and aerosol number density measured with the CPC clearly indicating HO$_2$ uptake on airborne fayalite particles, which was observed for all MSP experiments.

![Figure 5.2: Example of the anti-correlation of HO$_2$ signal to number concentration of fayalite MSP analogue particles. HO$_2$ Signal shown in black and aerosol number density in red. RH = 9.9% RH and contact time = 20.6 s.](image)

Figure 5.3 shows typical plots of the HO$_2$ signal against aerosol number density for HO$_2$ uptake experiments on fayalite for different contact times used to calculate $0.25\gamma_{obs}\langle \omega \rangle A dt$. Longer contact times resulted in more HO$_2$ uptake hence a steeper gradient on this plot.

![Figure 5.3: The change in HO$_2$ signal with fayalite aerosol number density at RH =9.9% RH for three fixed contact times (Red = 8.8 s, Green = 14.7 s and Blue = 20.6 s).](image)
Figure 5.4 shows plots of $0.25\gamma_{\text{obs}}\omega\mathcal{A}_d t$ against $t$ used to calculate $\gamma(\text{HO}_2)$ for MSP.

![Graph showing plots of $0.25\gamma_{\text{obs}}\omega\mathcal{A}_d t$ against $t$]  

**Figure 5.4**: Plot of $0.25\gamma_{\text{obs}}\omega\mathcal{A}_d t$ as a function of reaction time, $t$, for uptake of HO$_2$ onto olivine at RH = 20.0% (black squares), fayalite at RH = 9.9% (red circles) and forsterite (green triangles) at RH 11.6%. The linear least squares fit to these points yields $0.25\gamma_{\text{obs}}\omega\mathcal{A}_d$ as the gradient (olivine = $(1.4\pm0.2)\times10^{-5}$, fayalite = $(6.3\pm1.4)\times10^{-6}$ and forsterite = $(1.2\pm0.1)\times10^{-6}$) from which $\gamma_{\text{obs}}$ was calculated (see Table 5.2). The intercept for olivine = $(4.2\pm1.6)\times10^{-5}$, fayalite = $(2.3\pm1.8)\times10^{-5}$ and forsterite = $(3.9\pm1.6)\times10^{-6}$. The error bars represent 2σ in the individual exponential fits shown in Figure 5.3.

Table 5.1 presents the values of $\gamma(\text{HO}_2)$ measured on MSP in this work. The measurements clearly show that the presence of Fe is important for the mechanism of HO$_2$ uptake onto MSP, unlike C$_2$H$_2$ uptake onto MSP. The measurements also suggest that $\gamma(\text{HO}_2)$ on MSP is strongly dependent on RH, however, as conditions are dry in the mesosphere and RH does not exceed 20% in the WACCM model simulations used to evaluate the impact of HO$_2$ impact within the mesosphere, further investigation of this dependence was not conducted.

**Table 5.1**: Values of $\gamma(\text{HO}_2)$ measured on MSP in this work

<table>
<thead>
<tr>
<th>MSP Analogue</th>
<th>RH / %</th>
<th>$\gamma(\text{HO}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
<td>11.6</td>
<td>$(4.3 \pm 0.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>Olivine (MgFeSiO$_4$)</td>
<td>10.0</td>
<td>$(6.9 \pm 1.2) \times 10^{-2}$</td>
</tr>
<tr>
<td>Olivine (MgFeSiO$_4$)</td>
<td>20.0</td>
<td>$(1.9 \pm 0.2) \times 10^{-1}$</td>
</tr>
<tr>
<td>Fayalite (Fe$_2$SiO$_4$)</td>
<td>9.9</td>
<td>$(7.3 \pm 0.4) \times 10^{-2}$</td>
</tr>
</tbody>
</table>
5.3 Mechanism of HO$_2$ Uptake onto analogues of MSP

Inspection of Table 5.1 clearly shows that the presence of Fe in the MSP analogue increases its reactivity with HO$_2$, thus this finding suggests Fe drives the uptake of HO$_2$ on MSP. Indeed, $\gamma$(HO$_2$) measured on Forsterite (Mg$_2$SiO$_4$) is comparable to effloresced inorganic salt aerosols. Measurements of $\gamma$(HO$_2$) onto deliquesced inorganic salt aerosols doped with Fe(II) ions in this work has shown that Fe acts as a catalyst for HO$_2$ uptake (see section 3.3). However, this reaction occurs once HO$_2$ is accommodated and diffused into the aerosol and involves homogeneous aqueous-phase catalytic chemistry. Measurement of $\gamma$(HO$_2$) on Arizona Test Dust (ATD), mineral dust containing Fe (Fe$_2$O$_3$, 2 – 5%), at similar RH and initial [HO$_2$] was $0.01 \pm 0.01$ $^{66}$. This measurement is consistent with measurements made in this work as ATD contains a lower amount of Fe than olivine or fayalite, although direct comparison should be made with caution as ATD is composed of a complex mixture of other metal oxides too.

Electronic structure calculations were conducted by Professor Plane who studied HO$_2$ binding to either the Fe or Mg end of an olivine (FeMgSiO$_4$) unit $^{51}$. These calculations show that a Fe atom exposed on the surface may indeed be able to catalyse the destruction of HO$_2$ via self-reaction producing H$_2$O$_2$ and O$_2$. The calculation suggests HO$_2$ can diffuse to the surface exposed Fe atom and chemisorb to it with a considerable binding energy ($225$ kJ mol$^{-1}$). Then, via the Eley-Rideal mechanism, another HO$_2$ radical can abstract the hydrogen atom from the adsorbed HO$_2$ resulting in the formation of H$_2$O$_2$ and O$_2$ still bound to the Fe atom. A third HO$_2$ can displace the bound O$_2$ and the reaction starts over again. The calculation also reveals that when HO$_2$ adsorbs onto an Mg atom the H atom from HO$_2$ migrates onto an O atom within the silicate group resulting in a very strongly bound O$_2$ on the Mg atom which cannot be displaced effectively deactivating the Mg site and thus explaining the low reactivity of Forsterite.

Whilst this mechanism is plausible, the mechanism suggests that $\gamma$(HO$_2$) measured on fayalite should be greater than $\gamma$(HO$_2$) measured on olivine as fayalite contains stoichiometrically twice as many Fe atoms than olivine, and hence, it should have twice as many active sites, however, measurements of $\gamma$(HO$_2$) for both MSP were broadly similar suggesting that the number of active sites are identical. This could only be possible if the surface exposed FeMgSiO$_4$ (olivine) unit is always orientated so that the Mg atom is contained within the bulk of the particle and the Fe atom is exposed on the surface. This would the same number of active sites as fayalite, otherwise it could be possible that Fe is not the active site for this reaction.

The mechanism also does not explain the significant rise in $\gamma$(HO$_2$) observed as RH was nominally increased by 10%. This work suggests water molecules act as a promotor of reactive HO$_2$ uptake on the surface of MSP rather than an inhibitor that may bound to active
sites and block adsorption of HO. It is likely that as HO could also chemisorb to surface exposed Fe atoms so could H₂O, however, similar calculations of binding energies would be required in order to understand whether H₂O could be an effective inhibitor. The rate of the self-reaction of HO in the gas-phase has been shown to be enhanced linearly as a function of the partial pressure of water vapour, attributed to the formation of a HO₂.H₂O complexes. However, the preferred mechanism of that study for this reaction is that a vibrationally relaxed H₂O intermediate is produced, removing the need for collisional deactivation. As third body reactions are more applicable to gas-phase reactions rather than heterogeneous reactions this mechanism is not likely. The magnitude of the enhancement of the bi-molecular rate coefficient at atmospheric pressure with [H₂O] (a four-fold increase in [H₂O] results in a 50% increase of the bi-molecular rate coefficient) is not great enough to explain an increase in γ(HO₂) with RH shown in this work. We would also expect to see the same large increase of γ(HO₂) with RH due to this mechanism for studies of HO₂ uptake onto other mineral dusts (i.e. TiO₂ and ATD), however, this is not the case. Another possible reason might be the dissolution of Fe, however, this may only occur when multiple layers of water surround the particle and the water binding structure tend to that found in bulk water. Although these experiments were conducted at relatively low RH two monolayers of water does surround ATD at a RH of ~ 30% and γ(HO₂) measured on olivine at 20% RH is comparable to deliquesced inorganic salt aerosols doped with a high concentration of Fe (see Chapter 3). This work (Chapter 4) has shown that γ(HO₂) on TiO₂, and likely on ATD, is dependent on the wetting properties of the particle surface. In the case of TiO₂, this property is dependent on bridging OH groups formed from the dissociation of water at oxygen vacancy defects which act as anchoring sites for uptake of water on to the surface. As more water is adsorbed onto the surface, the hydrogen-bonding network increases stabilising HO₂ and also allowing more HO₂ to adsorb on the surface as the number of water molecules to complex with increases. A similar mechanism could be at play in this system. If the ability of olivine and fayalite to form OH groups in greater quantities than TiO₂ or ATD and the enthalpy of adsorption of water with the OH groups is great enough these particles may well uptake larger quantities of water onto their surface within this range of RH, so much so, that enough water is adsorbed onto the particle at 20% for dissolution of Fe to occur. This would both explain the large values of γ(HO₂) measured on olivine and fayalite than TiO₂ and ATD and the dramatic increase of γ(HO₂) observed as RH was increase from 10 to 20%. A computational study has previously been carried out demonstrating olivines can contain considerable amounts of water in the form of OH defects. These calculations predict that the pathway for incorporation of OH defects into olivines is reaction with water accompanied by the reduction of ferric iron, therefore it is likely that forsterite contains very little OH defects in comparison with olivine and fayalite. Indeed, it has been shown that little or no water adsorbs to forsterite with water coverage
unlikely to exceed 10% of a monolayer\textsuperscript{168} which could explain why $\gamma$(HO\textsubscript{2}) for this MSP is low, similar to dry effloresced inorganic salt aerosols. If the ability to uptake water onto the surface of olivine is comparable to fayalite it would also explain the similarity in the measurement of $\gamma$(HO\textsubscript{2}). If dissolution of Fe does occur then we might expect $\gamma$(HO\textsubscript{2}) to decrease as RH is increased above 20% as the concentration of Fe would decrease within this layer of water and then possibly increase at an RH where the amount of water can support the formation of O\textsubscript{2}⁻, the conjugate base of HO\textsubscript{2}, which reacts up to two orders of magnitude faster with Fe. Although no measurements of $\gamma$(HO\textsubscript{2}) exist across a wide range of RH for MSP, measurements of $\gamma$(HO\textsubscript{2}) onto ATD across a wide range of RH have been previously conducted\textsuperscript{66}, which does show this relationship. If future studies do show that the wetting properties of these particles are such that the surface is particularly hydrophilic then this may account for a missing sink for water in the mesosphere and the low concentrations of OH observed.

### 5.4 HO\textsubscript{2} Uptake onto analogues of MSP as a Function of Time

As shown by Figure 5.4, with the exception of forsterite, the plots used to calculate $0.25\gamma_{obs}\omega A_d t$ in this work showed a positive y-intercept (i.e. at $t = 0$), which suggests that $\gamma$(HO\textsubscript{2}) is strongly time dependent. It has been suggested this is the result of measurements at contact times too short for HO\textsubscript{2} to reach equilibrium with the particle surface\textsuperscript{66}. At short contact times, before the equilibrium has been reached, a large number of active sites are unoccupied meaning the probability of reactive uptake is high. As the contact time increases the number of available sites decreases exponentially as more HO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} occupy them. Once equilibrium has been reached the number of available active sites should be constant resulting in $\gamma$(HO\textsubscript{2}) becoming independent of time.

In order to investigate the effect, the raw data were treated much in the same way as data in the fixed injector experiments (section 2.4.4) to yield a calculated value of $\gamma$(HO\textsubscript{2}), where the observed pseudo-first order rate coefficient ($k'$), calculated by subtracting the natural log of the HO\textsubscript{2} signal with no aerosols present away from the natural log of the HO\textsubscript{2} signal with aerosols present and dividing by the contact time corresponding to the injector position, here for 10.3 s, was plotted against the surface area density of particles within the aerosol flow tube, as shown in Figure 5.5.
Figure 5.5: The pseudo-first order rate coefficient plotted as a function of surface area density, $S_a$, used to determine $\gamma$(HO$_2$) on fayalite at 10.3 s. The linear least squares fit to these points yields $0.25\gamma_{\text{ads},0}$ as the gradient = 981.5 $\pm$ 20.8, from which $\gamma$(HO$_2$) = (8.8$\pm$0.1) $\times$ 10$^{-2}$ was calculated.

Figure 5.6 shows the time dependence of $\gamma$(HO$_2$) for both fayalite and forsterite. The values of $\gamma$(HO$_2$) were fitted with the following exponential decay functions:

$$\gamma$(HO$_2$) = 0.046 e^{(-t/2.99)} + 0.0026 \quad \text{Forsterite} \quad (E5.1)$$

$$\gamma$(HO$_2$) = 6.529 e^{(-t/1.84)} + 0.0643 \quad \text{Fayalite} \quad (E5.2)$$

The uptake coefficient at long contact times approaches that calculated from the fit to the entire dataset shown in Figure 5.4. These values should be taken as the true atmospherically relevant uptake values, since they correspond to HO$_2$ in equilibrium with the particle surface. The strong time dependence of $\gamma$(HO$_2$) with contact time suggests measurements taken at contact times less than the time taken for HO$_2$ to reach equilibrium with the particle surface are not valid and inclusion of these points when determining $\gamma$(HO$_2$) from plots such as Figure 5.4 results in a deviation from linearity. Exclusion of measurements at injector positions that correspond to contact times less than the time taken for HO$_2$ to be in equilibrium with the particle surface is applicable to all experiments within this work. Figure 5.6 also shows that forsterite takes longer than fayalite to reach equilibrium, which may suggest that the adsorption lifetime and adsorption enthalpy of HO$_2$ on the surface of forsterite is lower than on fayalite or that the number of active sites on the surface of the particle meaning diffusion of
HO₂ to the active site would take longer and the site remains unoccupied for a much longer time. A combination of these properties mean that the rate of adsorption is much slower than the rate of desorption resulting in longer contact times before equilibrium is reached and hence lower values of $\gamma$(HO₂). It is likely that the contact time at which equilibrium is reached is strongly dependent on the initial concentration of HO₂ emitted from the injector.

![Graph showing time dependence of $\gamma$(HO₂) for Fayalite (black) and Forsterite (red) at RH of 9.9% and 11.6% respectively. The solid lines represent the exponential fits given in E5.1 and E5.2. The error bars represent 2σ.](image)

Surface coverage of HO₂ was investigated further by estimating the average distance between HO₂ molecules on the particle surface at the longest contact time (20.6 s), assuming all HO₂ taken up remains on the particle surface. By integrating the loss of HO₂ with respect to time the total HO₂ adsorbed on a particle of known surface area was calculated, assuming that the HO₂ molecules are dispersed isotropically over the surface. The smallest distance calculated was 1 nm, inferring that a substantial fraction of the surface sites might have become occupied. However, as the linearity of plots such as Figure 5.4 suggests that there was no deviation from pseudo first-order uptake kinetics (i.e. number of active sites $\gg$ [HO₂]), available surface sites must be reactivated after HO₂ reacted and H₂O₂ desorbs from the surface.

### 5.5 Atmospheric Implications of HO₂ Uptake onto MSP

Professor Plane’s group investigated the possible impact that HO₂ uptake by MSP could have to HO₂ concentrations within the middle atmosphere through a modelling study involving WACCM coupled with the Community Aerosol and Radiation Model for Atmospheres (CARMA) \(^{51}\). Two simulations were conducted within the modelling study; a control
simulation with no HO$_2$ heterogeneous chemistry and another where heterogeneous removal of HO$_2$ by MSP was considered. A value for $\gamma$(HO$_2$) for MSP of 0.2 was used within the modelling study which took into consideration the laboratory measurements within this work and the likely temperature and RH dependencies of $\gamma$(HO$_2$). The modelling study considers a total atmospheric input of 44 t day$^{-1}$ of cosmic dust, all of which is assumed to ablate into MSP with a radius of 0.2 nm over a range of altitudes from 75 – 110 km. Figure 5.7 shows the percentage decrease in HO$_2$ volume mixing ratios due to HO$_2$ uptake onto MSP as a function of latitude predicted during June 2009. It shows that impact is strongly dependent to latitude with a significant impact on the HO$_2$ budget predicted within the polar vortex, with decreases in the HO$_2$ volume mixing ratio of up to 40%. This result is consistent with the presence of MSP in the polar night. A degree of caution should be made when taking any quantitative values from this assessment as there remains significant uncertainties with key parameters involved within this study. However, this figure is considered relatively conservative as some studies suggest that the meteoric input into the atmosphere could be up to three times greater than considered in this study\textsuperscript{169}, although other uncertainties such as MSP composition could offset this. Nevertheless, the study does suggest that HO$_2$ uptake by MSP has the potential to significantly affect the HO$_2$ budget within the middle atmosphere.

![Figure 5.7: Percentage difference in HO$_2$ volume mixing ratio between the control and HO$_2$ uptake model simulations as a function of latitude for June 2009, courtesy of Dr Sandy James.\textsuperscript{51}](image)

**5.6 Summary**

Measurements of $\gamma$(HO$_2$) onto analogues of MSP, forsterite, olivine and fayalite, were conducted at a RH of 10% following the anti-correlation methodology described in section 2.4.5. These experiments showed forsterite to have the lowest reactivity with HO$_2$, similar to that of effloresced inorganic aerosols, and olivine and fayalite to have a similar reactivity that
was more than an order of magnitude greater than that of forsterite, thus demonstrating that the presence of Fe within the MSP is required for significant reactivity with HO\textsubscript{2}. Electronic structure calculations predicts that difference in reactivity is associated mechanistic and energetic differences between the binding of HO\textsubscript{2} to Fe and Mg sites, however, the positive dependence of $\gamma$(HO\textsubscript{2}) with RH and similar values of $\gamma$(HO\textsubscript{2}) for olivine and fayalite suggests that OH bridging groups or water molecules adsorbed to such sites, as with TiO\textsubscript{2} nanoparticles, are adsorption sites for HO\textsubscript{2}.

Taking the measurements made in this work and the likely dependence of $\gamma$(HO\textsubscript{2}) on temperature and RH, a value of 0.2 for $\gamma$(HO\textsubscript{2}) was applied by Dr Sandy James in WACCM-CARMA. This modelling study predicted reductions in the HO\textsubscript{2} volume mixing ratio of up to 40% in the polar vortex. Impact to HO\textsubscript{2} budgets in the mesosphere was found to be dependent on latitude, giving agreement with the presence of MSPs in the polar night. However, this study cannot be considered quantitatively as uncertainties in the values of $\gamma$(HO\textsubscript{2}) and available surface area of MSP means the study is particularly simplistic in its approach and therefore caution should be taken when discussing whether such reactions can account for the discrepancies for the differences in modelled and measured HO\textsubscript{2}, known as the HO\textsubscript{x} dilemma. Although, this study does highlight that such reactions could well be important. The conservative and simplistic approach taken within this study means there is potential for the meteoric input to be higher and the temperature dependence of uptake could also be much more pronounced than estimated meaning that the impact predicted could be a lower limit of the impact this process has in the atmosphere. Other complications, such as MSP composition and humidity dependence, could offset the impact somewhat. In the future, reanalysis of Aura MLS HO\textsubscript{2} measurements may enable a more quantitative comparison by extending the latitude range of mesospheric HO\textsubscript{2} observations to ensure the areas highlighted in this study (i.e. polar regions) as receiving the largest impact to concentrations of HO\textsubscript{2} via heterogeneous reactions is covered.
Chapter 6 – Conclusions and Future Work

This chapter discusses the key findings within this work along with recommendations of future work.
6.1 Overview

The reactive uptake coefficients for the heterogeneous reaction of HO₂, γ(HO₂), onto airborne particles relevant to the troposphere, stratosphere and mesosphere were measured using an aerosol flow tube reactor coupled with a sensitive FAGE HO₂ detection system and an SMPS. The effect of parameters such as RH, pH, aerosol composition and time on γ(HO₂) has investigated and where possible an explanation for the dependence has been offered. Production of HO₂ on the surface of TiO₂ aerosols has also be investigated. Sections 6.2 – 6.4 offer a brief precis of the findings of these studies and section 6.5 offers some suggestions for possible future work.

6.2 HO₂ uptake on aerosols relevant to the troposphere

The reactive uptake of HO₂ onto deliquesced inorganic salt aerosols doped with transition metal ions has been studied within this work. Measured values of γ(HO₂) onto deliquesced (NH₄)₂SO₄ aerosols doped with different concentrations of Cu(II) at a RH of 65% showed good agreement with calculated values of γ(HO₂) and that Cu ions are the most effective transition metal within this study to catalyse reactive uptake of HO₂. However, at a RH (43%) within proximity of the efflorescence point (37%), calculated values of γ(HO₂) agreed with measured values of γ(HO₂) onto such aerosols doped within the higher range of Cu(II) concentrations studied, however a continual worsening of the agreement was observed as the concentration of Cu(II) was lowered. This indicates a lowering of HO₂ solubility within the bulk of the aerosol. This study has shown RH to be an important environmental parameter when determining aerosol reactivity towards reactive uptake of trace atmospheric gas-phase species, not only because RH determines the phase of the aerosol but also determines the solubility of such species at a RH within proximity of the efflorescence point. It might be expected that γ(HO₂) onto deliquesced NaCl aerosols doped with different concentrations of Cu(II) at a RH of 65% to be larger than γ(HO₂) onto Cu(II)-doped (NH₄)₂SO₄ aerosols as NaCl aerosols are not acidic so HO₂ solubility should be enhanced due to near total dissociation of HO₂ to O₂⁻ and also O₂⁻ is a much more reactive species with TMI, but this was not the case. At higher Cu(II) concentrations γ(HO₂) values were comparable between the two inorganic salt aerosols, however at lower Cu(II) concentrations γ(HO₂) onto Cu-doped NaCl aerosols were depressed and reactive uptake was limited by diffusion processes at much higher concentrations of Cu(II) than for Cu-doped (NH₄)₂SO₄ aerosols. This is likely due to electrostatic repulsion of [CuCl₄]²⁻ ions into the aerosol bulk by enhanced concentrations of Cl⁻ ions within the interfacial layer of the aerosol. It is only until enough Cu(II) is present to overcome these repulsive forces that diffusion of HO₂ within the aerosol is no longer a limiting factor to HO₂ uptake. The effect of irradiating Cu(II)-doped deliquesced inorganic aerosols with UVA light to γ(HO₂) was also studied. No change in γ(HO₂) onto deliquesced Cu-doped
NaCl was measured upon irradiation, however irradiating deliquesced Cu(II)-doped (NH$_4$)$_2$SO$_4$ aerosols has a significantly depresses values of $\gamma$(HO$_2$). The magnitude of this effect is proportional to the concentration of Cu(II) within the aerosol. A possible cause for this effect could be that photochemistry involving Cu(II) within the aerosol generates radicals that cause Cu(II) to precipitate out of the aqueous phase reducing the number of Cu(II) ions available for reaction. When considering the implications of this study to atmospheric chemistry it is likely that consideration of Cu-doped aerosols as a sink for HO$_2$ is over stated with many processes depressing the catalysing effect Cu has to HO$_2$ destruction.

The presence of Fe ions within deliquesced inorganic aerosols has a much lower ability to act as sink for HO$_2$ than Cu ions, however Fe ions are present in more abundance within such aerosols in the atmosphere. Similar to deliquesced Cu(II)-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43%, calculated values of $\gamma$(HO$_2$) agreed with measured values of $\gamma$(HO$_2$) onto Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% within the higher range of Fe(II) concentrations studied, however a continual worsening of the agreement was observed as the concentration of Fe(II) was lowered. The effect of Fe(II) doping to HO$_2$ solubility within the bulk is greater than the effect Cu(II) has to HO$_2$ solubility. Measurements of $\gamma$(HO$_2$) onto Fe(II)-doped NaCl aerosols were larger than measurements of $\gamma$(HO$_2$) onto Fe-doped (NH$_4$)$_2$SO$_4$ aerosols across the entire range of Fe concentrations measured and Cu(II)-doped NaCl aerosols at a [TMI]$_{aerosol}$ of 0.04 M. This is likely caused by an increase of HO$_2$ solubility and full dissociation to O$_2$ within pH neutral NaCl aerosols and that Fe(II) ions are more likely to be attracted towards the interfacial layer enriched with Cl$^-$ ions, although it is unlikely that at higher [TMI]$_{aerosol}$ $\gamma$(HO$_2$) onto Fe-doped NaCl aerosols will be higher than Cu-doped NaCl aerosols as the reaction will be limited to how fast Fe(II) can react with HO$_2$. Measurements of $\gamma$(HO$_2$) onto deliquesced Fe(II)-doped LiNO$_3$ were low as Fe(II) seems to be oxidised to the more stable Fe(III) form by LiNO$_3$. When irradiated with UVA light, negative values of $k'$ (i.e. $k_{wall} > k_{wall} + k_{aerosol}$) were measured indicating the production of OH radicals likely from photo-Fenton chemistry.

Mn ions, like Cu and Fe ions have shown to catalyse the destruction of accommodated HO$_2$ in deliquesced inorganic aerosols. Whilst the rate for the reactions of HO$_2$ and Mn ions are faster than for Fe ions, measurements of $\gamma$(HO$_2$) onto Mn-doped aerosols were lower than onto Fe-doped aerosols. This was attributed to Mn enhancing salting out effects to HO$_2$ solubility in deliquesced aerosols just above their efflorescence point.

Measurements of $\gamma$(HO$_2$) onto mixed Cu(II) and Fe(II)-doped (NH$_4$)$_2$SO$_4$ aerosols at a RH of 43% could not determine whether the Mao hypothesis that an electron transfer reaction between Cu(I) and Fe(III) results in the conversion of HO$_2$ to H$_2$O, rather than H$_2$O$_2$. However, values of $\gamma$(HO$_2$) did not simply equal the sum of $\gamma$(HO$_2$) onto Cu or Fe-doped
aerosols individually, indicating that the presence of both TMI in the aerosol does alter the
chemistry of the aerosol in some way. Irradiation of Cu(II) and Fe(II)-doped aerosols resulted
in an enhancement of $\gamma$(HO$_2$), possibly indicating an alternative mechanism than that proposed
by Mao where HO$_2$ is converted to H$_2$O due to photochemical reactions within deliquesced
aerosols.

The presence of I$^-$ within NaCl aerosols does not result in any change of $\gamma$(HO$_2$), however the
when converted to I$_2$ by reaction with Cu(II) an enhancement of $\gamma$(HO$_2$) was observed.

6.3 HO$_2$ uptake on aerosols relevant to the stratosphere

HO$_2$ uptake coefficients on TiO$_2$ nanoparticles were measured to be from $\gamma$(HO$_2$) = 0.021 ±
0.001 to 0.036 ± 0.007 over a range of RH from 11% to 66% respectively. Measured HO$_2$
utake coefficient showed a positive dependence on RH which correlated with the number of
monolayers of water adsorbed onto the TiO$_2$ nanoparticle suggesting a mechanism by which
HO$_2$ adsorbs to the surface of the TiO$_2$ particle by forming complexes with water molecules
bound to bridging OH groups. As RH increases so does the number of water molecules
adsorbed to the surface of the TiO$_2$ nanoparticle. This increases the network of hydrogen
bonds that stabilises HO$_2$ leading to a longer adsorption lifetime and increased $\gamma$(HO$_2$). The
TOMCAT chemical transport model was used by Professor Chipperfield to predict the
possible effects of HO$_2$ uptake (using an upper limit of $\gamma$(HO$_2$) = 1) onto the surface of TiO$_2$
nanoparticles on the stratospheric concentrations of HO$_2$ and O$_3$. The amount of TiO$_2$ used was
chosen to achieve a similar cooling to that following the Mt. Pinatubo eruption, but the model
predicted a very small loss of both stratospheric HO$_2$ and O$_3$.

As TiO$_2$ possesses photocatalytic properties, water adsorbed onto its surface may dissociate
under stratospheric illumination providing a source of HO$_x$.$^{138,162}$ Production of HO$_x$ radicals
by irradiated airborne TiO$_2$ was therefore investigated. This work presents the first direct
observations of radicals emitted from the surface of airborne particles and provides an insight
into the photocatalytic reactions occurring on the surfaces of TiO$_2$. Upon illumination of
airborne TiO$_2$ nanoparticles with UV light, significant quantities of HO$_2$ was formed within the
gas-phase. The reaction is dependent on the presence of gas-phase O$_2$ within the system. The
production of HO$_2$ has shown to slow down as a function of irradiation pointing towards a
photochemical aging process occurring. The dependence of HO$_2$ production on O$_2$ and H$_2$O
concentrations has been determined which shows a typical Langmuir adsorption saturation
curve for O$_2$ suggesting it is the gas-phase reactant in this process. The addition of H$_2$O into
the system inhibits the reaction and reduces the adsorption equilibrium coefficient for both
species. Reduction of O$_2$ by photogenerated electrons is likely to be the initial step in this
process followed by reaction with a proton. Hydrogen extraction from OH$_{br}$ groups by O$_2$−
could explain the slow down observed in the rate of HO₂ production. Production of gas-phase OH radicals were investigated and showed OH was produced only when large concentrations of TiO₂ aerosols entered the aerosol flow tube, probably associated with the decomposition of H₂O₂ formed from reactive uptake. Although the production of HO₂ by TiO₂ aerosols initially would not be advantageous for its use within SRM schemes, the reaction ceases upon prolonged photocatalytic aging of the aerosol surface.

### 6.4 HO₂ uptake on aerosols relevant to the mesosphere

HO₂ uptake coefficients were measured onto three MSP analogues; forsterite, olivine, and fayalite. Such measurements showed that γ(HO₂) was dependent on RH and composition of the MSP analogue. Forsterite particles, Mg₂SiO₄, showed the lowest reactivity with HO₂ (γ(HO₂) = (4.3 ± 0.4) × 10⁻³), whilst γ(HO₂) onto olivine, FeMgSiO₄, and fayalite, Fe₂SiO₄, was an order of magnitude greater and broadly within error of each other (γ(HO₂) = (6.9 ± 1.2) × 10⁻² and (7.3 ± 0.4) × 10⁻² respectively). Electronic structure calculations suggest that the difference in reactivity is associated with mechanistic and energetic differences between the binding of HO₂ to Fe and Mg sites, however, the positive dependence of γ(HO₂) with RH and similar values of γ(HO₂) for olivine and fayalite suggests that OH bridging groups or water molecules adsorbed to such sites, as with TiO₂ nanoparticles, are adsorption sites for HO₂ uptake.

Taking the measurements made in this work and the likely dependence of γ(HO₂) on temperature and RH, a value of 0.2 for γ(HO₂) was applied by Dr Sandy James in WACCM-CARMA. This modelling study predicted reductions in the HO₂ volume mixing ratio of up to 40% in the polar vortex. Impact to HO₂ budgets in the mesosphere was found to be dependent on latitude, giving agreement with the presence of MSPs in the polar night.

### 6.5 Future Work

In the future, a number of studies could be conducted to better understand how aerosols affect the oxidising capacity of the atmosphere. Such work should include measurement of γ(HO₂) onto Fe-doped NaCl aerosols. This work has shown γ(HO₂) on Fe-doped NaCl aerosols to be relatively high, even at relatively low [Fe(II)]_aerosol, and as Fe ions are commonly found within deliquesced sea-salt aerosols these could potentially be a significant sink of HO₂ in coastal regions. The same can be said for sea-salt aerosols containing I₂, which could potentially react more rapidly with HO₂ within aerosols than Cu ions. Therefore studies that measure γ(HO₂) on NaCl aerosols at different [Fe(II)]_aerosol and [I₂]_aerosol should be conducted. As this work has shown a possible HO₂ solubility gradient in (NH₄)₂SO₄ aerosols dependent on the TMI, γ(HO₂) onto mixed Cu and Fe aerosols should be measured again but at a RH of 65%, as at this RH HO₂ solubility should remain constant. This would then eliminate possible effects to γ(HO₂)
caused by possible changes in HO$_2$ solubility making the verification of Mao’s hypothesis more likely. Further work should be done on irradiated Fe-doped aerosols and Cu and Fe doped aerosols. Experiments involving addition of CO, an OH scavenger which rapidly converts OH to HO$_2$, to an aerosol flow tube containing irradiated deliquesced Fe-doped aerosols should confirm whether emissions of OH from the aerosols was occurring as it is known OH will not survive within the flow tube do to rapid losses to the walls. HO$_2$ production from (NH$_4$)$_2$SO$_4$ aerosols containing imidazole-2-carboxaldehyde, a photosensitizer produced within aerosols by glyoxal chemistry, and citric acid, an organic proxy and H donor, in the presence of limonene should be investigated to confirm work by González Palacios et al. as they did not detect HO$_2$ directly and NO conversion could have been caused by a different species such as RO$_2$. Further measurements of $\gamma$(HO$_2$) onto irradiated Cu and Fe-doped (NH$_4$)$_2$SO$_4$ aerosols could be used to verify the proposed photochemical mechanism for the conversion of HO$_2$ to H$_2$O proposed within this work. The reactivity of TiO$_2$ aerosols with HO$_2$ was investigated in this work, however once irradiated HO$_2$ was produced at a rate which slowed over time. This was attributed to reactions between photogenerated O$_2^-$ reacting with bridging hydroxyl groups, essential for adsorption of gases onto their surface. Further work investigating HO$_2$ production from such aerosols over longer time periods and then measurements of $\gamma$(HO$_2$) onto such aged aerosols could verify this proposed mechanism. If the reactivity of these aerosols with trace gas-phase species was shown to be lower once aged in this way these aerosols could prove to be a better proposition for application in SRM schemes. Measurements of $\gamma$(HO$_2$) onto MSPs at different RH could also be conducted and correlated with the number of monolayers of later surrounding the particle in order to test the hypothesis presented in this work that hydroxyl groups could also be at play in this system too.

A study should also be carried out on the heterogeneous reactions between RO$_2$ and atmospherically relevant aerosols. RO$_2$ is a key intermediate within the HO$_x$ cycle and could enhance the solubility of organic species within the aqueous phase. This study could be carried out on the existing apparatus with a few modifications to the FAGE technique. Also, measurements of $\gamma$(HO$_2$) in the presence of RO$_2$ should be made as the reaction between these two species in the condensed phase could be atmospherically important.
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