Development, Characterisation and Implementation of Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry for the Measurement of Atmospheric Volatile Organic Compounds

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by

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Statement of Originality

The work described in this thesis was conducted by the author in the Department of Chemistry at the University of Leicester mainly during the period between October 2004 and September 2007. All the work in this thesis is original unless otherwise acknowledged in the text or by references.

Kevin Paul Wyche

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Volatile organic compounds (VOCs) are ubiquitous within the Earth's troposphere, being released both locally and globally from anthropogenic and biogenic sources. VOCs constitute an important class of reactive trace species responsible for the production and exacerbation of numerous documented atmospheric issues, including photochemical production of ozone and formation of secondary organic aerosol (SOA). Consequently, measurement of VOCs under both ambient and laboratory conditions is crucial, such that emissions controls may be affected, environment response may be monitored and scientific understanding of the atmosphere may be advanced. This thesis describes the development, characterisation and application of a novel technique for '*real-time*' detection of atmospheric VOCs. Termed Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS), analyte ionisation by ion-molecule interaction is employed under defined reaction conditions, followed by TOF mass spectrometric analysis.

Within this work CIR-TOF-MS is comprehensively characterised for the detection of a wide range of atmospheric VOCs using the chemical ionisation reagent ions H_3O^+ , NH_4^+ , NO^+ and O_2^{++} . Reaction products and species-specific markers are identified for future use and ionisation mechanisms are explained. Detailed investigations into instrument performance and optimisation are described, and compound specific sensitivities and detection limits are determined. The technique is validated for quantitative atmospheric monitoring using findings from a multi-institution measurement intercomparison. It is shown that VOC measurements are made by CIR-TOF-MS with a high level of accuracy and precision. CIR-TOF-MS is also applied for the first time to urban air monitoring, where typical 'city' VOC pollutants are measured in high detail.

The work presented culminates with a comprehensive description of the first major application of CIR-TOF-MS to the scientific exploration of a contemporary atmospheric issue: SOA formation. CIR-TOF-MS measurements provide key insight into the identity of potential SOA contributing compounds, including a number of previously unobserved molecules. Findings also provide support to current understanding of gas phase VOC degradation mechanisms.

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Introduction

1.1 Summary

The first chapter of this thesis begins with an overview of tropospheric composition and chemistry, with particular emphasis placed upon volatile organic compounds (VOCs) and their importance within a number of different atmospheric processes and phenomena. The chapter continues with a review of the most common types of instrumentation currently employed to monitor atmospheric VOCs, before concluding with an overview of the Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry technique.

1.2 The Earth's Atmosphere

The thin envelope of gas that surrounds a planetary body is known as an '*atmosphere*'. The term originates from the Greek words '*atmos*', meaning 'vapour' and '*sphaira*', meaning 'ball' (Wayne, 2002). The atmosphere of a planet is held in place by the fundamental force of gravity, exerted by the planet on account of its mass. The atmospheres possessed by the various planets and extraterrestrial bodies of the known solar system are hugely diverse in terms of composition, depth, temperature and physical properties; however, the Earth's atmosphere is unique, in that it is able to support life (Monks, 2005).

The Earth's atmosphere weighs approximately 5×10^{18} kg (Monks, 2005) and primarily comprises N₂ (78.1 %), O₂ (20.9 %) and Ar (0.9 %) (Brimblecombe, 1996), having evolved to its present day form mainly due to the existence of living organisms (Seinfeld and Pandis, 2006). As they essentially constitute the vast majority of the atmosphere, N₂, O₂ and Ar are often referred to as the 'bulk gases'. The remaining constituents of the atmosphere are known as the 'trace gases', and they include for example, water vapour, CO₂, CO, O₃, inorganic nitrogen oxides, sulphur compounds and organic compounds. Despite existing at relatively low concentrations, it is these 'reactive' species that drive the chemistry of the Earth's atmosphere.

As shown in **Figure 1**, the atmosphere can be divided into five distinct regions by virtue of its vertical temperature profile (Finlayson-Pitts and Pitts Jr., 2000). From the surface upwards these are the troposphere, stratosphere, mesosphere, thermosphere and ionosphere (Finlayson-Pitts and Pitts Jr., 2000). The boundary between Earth and space is generally considered to lie at a distance of approximately 100 km from the surface. Owing to the relationship which exists between gravitational force and distance, the bulk of the Earth's atmosphere (\sim 90 %) exists within the confines of the troposphere (Monks, 2005), with pressure decreasing exponentially with vertical height from the surface (Seinfeld and Pandis, 2006).



Figure 1: Vertical temperature profile and subdivisions of the Earths atmosphere (www.windows.ucar.edu)

With a latitude and seasonally dependent depth of 10 - 18 km, the troposphere is characterised by a temperature profile that decreases with altitude up to the tropopause, the temperature inversion which marks the beginnings of the stratosphere. The troposphere can be further subdivided into the boundary layer (*i.e.* < 0.5 - 1 km, where the atmosphere interacts with the surface) and the free troposphere (~ 1 km – tropopause) (McIlveen, 1998). It is within the troposphere that life resides and into which all natural and the majority of manmade reactive trace gases are emitted (Monks, 2005). Consequently, the troposphere plays host to a multitude of chemical processes.

1.3 Atmospheric Volatile Organic Compounds

Volatile organic compounds (VOCs) constitute a major branch of atmospheric reactive trace species. The term VOC is used to collectively describe all gaseous organic compounds which are emitted into the atmosphere by both biogenic and anthropogenic processes. Important subdivisions of the VOC family include methane, hydrocarbon compounds (sometimes

grouped into the category of non-methane hydrocarbons (NMHCs)) and oxygenated and nitrated VOCs (OVOCs and NVOCs, respectively). OVOCs and NVOCs may be emitted directly into the atmosphere or they may be formed from the atmospheric oxidation of parent The most abundant VOC within the atmosphere is methane (CH₄), present at VOCs. concentrations of approximately 2 parts per million by volume (ppmV). Other species of VOCs reside within the atmosphere at a range of concentrations, from several pptV to tens of ppbV (Blake et al., 2008). Non-methane VOCs are relatively reactive within the atmosphere and consequently they may perturb its chemistry such that various environmentally More specifically, VOC chemistry is responsible for the detrimental impacts result. photochemical production of excess ozone within the troposphere (Jenkin and Clemitshaw, 2000a), the formation of secondary organic aerosols (SOA) (Kanakidou et al., 2005) and perturbations to climate (Monks, 2005). Ozone and SOA are major constituents of modern, urban photochemical smogs, which have a range of well documented consequences in terms of air quality and human health (Mulcahy, 1981; Brimblecombe, 1996; Boadway et al., 1998). Certain VOCs (e.g. benzene) may also have a direct effect on human health, being carcinogenic and/or toxic (Sudnick and Corwin, 1994; Blake et al., 2008).

The biosphere constitutes by far the largest global source of VOCs, emitting an estimated 1150 Tg C Yr⁻¹ (of non-methane VOCs) to the atmosphere (Guenther *et al.*, 1995). The most abundant biogenic non-methane VOCs are the C5-hemiterpene, isoprene, and collectively the C10-monoterpenes (*e.g.* α - and β -pinene). The global emission rates for isoprene and C10-monoterpenes have been estimated to be 503 and 127 Tg C Yr⁻¹, respectively (Guenther *et al.*, 1995). In strong contrast, the total annual emission rate of anthropogenic VOCs is estimated to be of the order 98 Tg C Yr⁻¹ (Finlayson-Pitts and Pitts Jr., 2000). The principle sources of anthropogenic VOCs include use of solvents, fossil fuel extraction and use (including transport related activities) and various industrial processes (Hewitt, 1999). Atmospheres influenced by anthropogenic VOC emissions are generally characterised by the presence of simple alkanes such as ethane (C₂H₆) and propane (C₃H₈), and aromatic compounds such as benzene (C₆H₆) and alkyl substituted benzenes (Calvert *et al.*, 1995; Hester, 1995; Hewitt, 1999).

1.4 Chemistry of the Troposphere

Owing to the presence of the tropopause, very little mixing occurs between the troposphere and the upper atmosphere on short timescales (*i.e.* months (Minschwaner *et al.*, 1996)). Consequently most reactive trace gases such as VOCs, which are emitted from the Earth's surface, remain within the relatively well mixed and turbulent troposphere. Certain exceptions exist however, for example compounds such as methane and chlorofluorocarbons (CFCs) are sufficiently long lived that they will ultimately be able to reach the stratosphere.

Tropospheric chemistry may be summarised as a simple low temperature combustion mechanism, in which gaseous hydrocarbons are ultimately oxidised to CO_2 and H_2 (Monks, 2005):

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{R1.1}$$

Under the influence of actinic flux (that light available to molecules at a particular altitude with energy sufficient to initiate photochemistry) the primary tropospheric oxidant is the hydroxyl radical (OH), an extremely short lived species which reacts with organic compounds at rates of the order $4 \times 10^{-9} - 6 \times 10^{-15}$ cm⁻³ molecule⁻¹ s⁻¹ (Finlayson-Pitts and Pitts Jr., 2000). The OH radical resides within the atmosphere at average concentrations of ~ 2 × 10⁶ molecules cm⁻³ and has an estimated lifetime of ~ 1 s (Hewitt and Harrison, 1985; Monks, 2005). Other tropospheric oxidants include ozone (O₃) and, in the absence of light, the nitrate radical (NO₃).

1.4.1 The Hydroxyl Radical

A simplified mechanism describing the production and cycling of the OH radical within the troposphere is shown in **Figure 2**. In brief, OH production is initiated by the photolysis of ozone and the generation of atomic oxygen in the excited (¹D) state. Once formed the O(¹D) atom may undergo deactivation to O(³P) before reacting with oxygen to regenerate O₃, or it may react with water vapour to produce OH. At 50 % relative humidity, 1 Atm pressure and 300 K, ~ 90 % of all O(¹D) atoms formed from the photolysis of O₃ undergo deactivation and thus only ~ 10 % proceed to form OH (Finlayson-Pitts and Pitts Jr., 2000; Monks, 2005).



Figure 2: Simplified mechanism describing the atmospheric hydroxyl radical (OH) cycle (note, RO₂ represents a generic organic peroxy radical)

As shown in **Figure 2**, the OH radical may react *via* a number of different pathways. In a 'clean', remote atmosphere, the most likely fate of the OH radical is reaction with CO to produce the hydroperoxy radical (HO₂), or with methane (CH₄) to produce the methyl peroxy radical (CH₃O₂). In clean air, approximately 70 % of OH radicals proceed to produce HO₂ and approximately 30 % proceed to produce CH₃O₂ (Monks, 2005). If the concentration of nitrogen dioxide (NO₂) is sufficiently high, the OH radical may also undergo reaction with NO₂ to form nitric acid (HONO₂). Being liable to both wet and dry deposition from the gas phase, nitric acid effectively constitutes an OH and NO₂ sink.

1.4.2 Chemistry of Clean, Remote Air (low NO_x)

Within the atmosphere HO₂ and CH₃O₂ radicals may react with nitrogen oxide (NO) to regenerate OH (see **Figure 2**), or to produce the CH₃O alkoxy radical, respectively. However, within 'clean', remote boundary layer air, ambient levels of NO and nitrogen dioxide (NO₂) (the sum of which is referred to as NO_x) are relatively low, being of the order 20 - 40 pptV (Seinfeld and Pandis, 2006). Consequently, under such conditions other reaction routes become competitive, *i.e.* an appreciable fraction of all HO₂ and CH₃O₂ radicals will alternatively undergo *self-reactions* to produce hydrogen peroxide (H₂O₂) or methyl hydroperoxide (CH₃OOH) (Finlayson-Pitts and Pitts Jr., 2000):

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R1.2}$$

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$$
 (R1.3)

Under low NO_x conditions methyl peroxy radicals may also proceed to react with other methyl peroxy radicals (*i.e.* $CH_3O_2 + CH_3O_2$) to form either (i) a pair of methoxy radicals

(CH₃O), (ii) formaldehyde (HCHO) and methanol (CH₃OH), or (iii) dimethyl peroxide (CH₃OOCH₃) (Jenkin *et al.*, 1988). It must be noted, however, that the CH₃O₂ + CH₃O₂ reaction generally occurs more slowly than either reaction (R1.2) or (R1.3) and hence it tends to be of less importance under atmospheric conditions (see Section 1.4.4.3 for further details).

Constituting a peroxy radical sink and reservoir, peroxide compounds effectively act to terminate the OH radical cycle, however, under sufficient actinic flux, OH may be liberated by photolysis. Peroxides have low vapour pressures and are extremely soluble; hence they may condense out of the gas phase or dissolve into cloud droplets. Hydrogen peroxide is particularly soluble and constitutes a key oxidant within the aerosol phase (Brimblecombe, 1996).

One further fate for the HO_2 radical in the absence of NO_x is reaction with O_3 , leading to the regeneration OH:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{R1.4}$$

On account of the chemistry described here, remote atmospheres are often characterised by net ozone destruction and peroxide formation during day light hours (Ayers *et al.*, 1992).

1.4.3 Chemistry of Polluted, Urban Air (high NO_x)

The trace gas composition of urban air is characterised by relatively high concentrations of nitrogen oxide species, NO and NO₂. The NO_x concentration of a typical urban air mass is \sim 10 – 1000 ppbV, compared to \sim 0.2 – 10 ppbV in rural air (Seinfeld and Pandis, 2006). Nitrogen oxides primarily originate from high temperature combustion processes, such as the burning of fossil fuels in transport related activities and power generation (Brimblecombe, 1996). NO is emitted to the atmosphere as a primary pollutant, where it may react readily with O₃ to produce NO₂:

$$NO + O_3 \xrightarrow{k_1} NO_2 + O_2$$
(R1.5)

One potential fate for NO₂ during daylight hours is photolysis, producing atomic oxygen in the ground (^{3}P) state. The photolysis of NO₂ is highly significant in that it constitutes the sole route to the formation of tropospheric ozone (Finlayson-Pitts and Pitts Jr., 2000):

NO₂ +
$$h \nu (\lambda < 410 \text{ nm}) \xrightarrow{j} \text{NO} + \text{O}(^{3}\text{P})$$
 (R1.6)

$$O(^{3}P) + O_{2} + B \xrightarrow{k_{2}} O_{3} + B$$
(R1.7)

where B denotes a third body. In the absence of other trace species which may perturb the system (see Section 1.4.4), the molecule of NO produced in reaction (R1.6) will react with O_3 to regenerate NO₂ and O₂, as in reaction (R1.5). Consequently, reactions (R1.5) – (R1.7)

constitute a 'null cycle' and there is not net production of ozone. If the system described by equations (R1.5) - (R1.7) remains unperturbed, the chemistry will achieve a steady (or *photostationary*) state, and hence an expression may be derived to describe the net ozone concentration and the pseudo equilibrium constant for the process (Jenkin and Clemitshaw, 2000a):

$$[O_3] = \frac{j[NO_2]}{k_1[NO]}$$
(E1.1) $\frac{j}{k_1} = \frac{[NO][O_3]}{[NO_2]}$ (E1.2)

From measurements made of the polluted urban boundary layer, it is well known that ozone levels rise during daylight hours (Finlayson-Pitts and Pitts Jr., 2000). For this to occur there would need to be a decrease in the ratio of [NO]/[NO₂] in equation (E1.2), however this is not observed (Brimblecombe, 1996; Seinfeld and Pandis, 2006). Consequently, an alternative mechanism must exist for the oxidation of NO to NO₂, which does not require the destruction of O₃. This mechanism, proposed following seminal work by Haagen-Smitt in the 1950s to explain heavy smog pollution in Los Angeles (Haagen-Smit, 1952), involves the atmospheric chemistry of the peroxy radicals and volatile organic compounds (Haagen-Smit and Fox, 1954; Weinstock, 1969).

1.4.4 Tropospheric VOC Chemistry

1.4.4.1 The High NO_x Limit

Depending on its chemical structure, a VOC may undergo oxidation within the atmosphere by reaction with OH, NO₃ or O₃. Simple alkanes (which comprise $\sim 36 - 42$ % of total VOCs within polluted urban air (Calvert *et al.*, 2000)) will react only with OH and NO₃ and only by hydrogen abstraction (Atkinson, 2000). The abstraction of a hydrogen atom from an alkane molecule (RH) will result in the production of a highly reactive alkly radical (R), for example:

$$RH + OH \xrightarrow{k} R + H_2O \tag{R1.8}$$

For the simplest alkane, ethane, the recommended rate constant for reaction (R1.8) is 0.25×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K (Finlayson-Pitts and Pitts Jr., 2000). The reaction of alkanes with NO₃ is only significant at night and occurs much more slowly than with OH (*e.g.* see lifetime comparisons made by (Atkinson, 2000)). In the NO₃ + alkane reaction, a molecule of HNO₃ is produced in place of water. For both oxidants, the hydrogen abstraction rate constant increases with hydrocarbon chain length and addition of pendant alkyl groups (for a review of alkane chemistry and a list of recommended rate constants, see (Atkinson, 2000; Finlayson-Pitts and Pitts Jr., 2000; Wayne, 2002)).

Following its generation, the alkyl radical will react rapidly with oxygen to produce an equivalent organic peroxy radical (RO₂):

$$\mathbf{R} + \mathbf{O}_2 + \mathbf{B} \xrightarrow{k} \mathbf{R} \mathbf{O}_2 + \mathbf{B} \tag{R1.9}$$

where B denotes a third body. A simplified mechanism summarising the atmospheric oxidation of volatile organic compounds from the first initial steps of reactions (R1.8) and (R1.9), is given in **Figure 3**. It is clear from this mechanism that once formed the peroxy radical may proceed *via* a number of different routes depending on the composition of the gas phase matrix in which it resides.



Figure 3: The atmospheric VOC oxidation cycle (redrawn from (Kroll and Seinfeld, 2008))

Under high NO_x conditions the RO_2 radical will primarily react with NO to produce an alkoxy radical (RO) and a molecule of NO_2 :

$$RO_2 + NO \rightarrow RO + NO_2$$
 (R1.10)

By reaction (R1.10) the VOC has brought about the oxidation of NO to NO₂ without the destruction of O₃. As a result of this chemistry, the photostationary state described by equation (E1.1) is shifted towards net O₃ production. Under certain meteorological conditions (*i.e.* warm temperatures, sunlight, little turbulence *etc*), primary NO_x and VOC pollutants are able to build to sufficiently high levels, such that the ensuing photochemical reactions lead to the production of photochemical smogs containing up to hundreds of ppbV of ozone.

When NO_x levels are high, the RO₂ radical may also undergo addition of NO (branching ratio typically < 25 %) to produce an organic nitrate compound (RONO₂), or the addition of NO₂ to produce a peroxynitrate compound (ROONO₂):

Chapter 1		Introduction
	$RO_2 + NO + B \rightarrow RONO_2 + B$	(R1.11)
	$\mathrm{RO}_2 + \mathrm{NO}_2 + \mathrm{B} \rightarrow \mathrm{RO}_2\mathrm{NO}_2 + \mathrm{B}$	(R1.12)

where B denotes a third body.

Depending on its structure, the alkoxy radical will either react with O_2 , to produce a carbonyl compound (R'CHO) and HO₂ (R1.13), undergo dissociation to produce a carbonyl compound and an alkyl radical (R1.14), or it will undergo isomerisation to yield a hydroxyalkyl radical (R'OH) (R1.15) (Kroll and Seinfeld, 2008):

$$RO + O_2 \rightarrow R'CHO + HO_2$$
 (R1.13)

$$RO \rightarrow R'CHO + R''$$
 (R1.14)

$$RO \rightarrow R'OH$$
 (R1.15)

In general, the larger and more substituted the alkoxy radical the more likely it is to undergo dissociation or isomerisation (Kroll and Seinfeld, 2008). The species of carbonyl (R'CHO) formed in reaction (R1.13) is determined by the point of initial OH attack, and hence the location of the radical site, *i.e.* terminal attack will generate an aldehyde (RCHO), while central attack will generate a ketone (R(CO)R') (the basic atmospheric oxidation mechanisms underlying the generation of aldehydes and ketones are given in **Figure A1.1** of Section A1 of the Appendix). It is important to note that the hydroperoxy radical formed in reaction (R1.13) may proceed to react with NO to form NO₂:

$$HO_2 + NO \rightarrow NO_2 + OH$$
 (R1.16)

The production of HO_2 will therefore help to facilitate an increase in the rate of turn over of the system and may result in the production of O_3 . For a full and more detailed review of alkoxy radical chemistry the reader is referred to work by Atkinson (Atkinson, 2000).

1.4.4.2 Tropospheric Chemistry of Carbonyl Compounds

Once formed a carbonyl compound is liable to undergo further oxidation following the mechanism outlined above in **Figure 3**. Oxidation may occur at various points on the carbonyl molecule, potentially resulting in the production of various multifunction organic peroxy radicals. Subsequent chemistry of the RO₂ radicals will again facilitate the production of HO₂, NO₂ and O₃ as well as various multifunction organic compounds, which may potentially contribute to SOA formation and growth (see Section 1.5.1). It is not within the scope of this introduction to describe in detail the various carbonyl oxidation processes; for further information the reader is referred to reviews by Atkinson (Atkinson, 2000). One particularly noteworthy process however, involves abstraction of the functional group hydrogen atom from aldehyde compounds. Abstraction of the aldehydic hydrogen will

generally occur in preference to abstraction at other sites, resulting ultimately in the production of an acyl peroxy radical (RCOO₂):

$$RCHO + OH \rightarrow RCO + H_2O$$
 (R1.17a)

$$RCO + O_2 \xrightarrow{B} RCOO_2$$
(R1.17b)

Within the atmosphere, the $RCOO_2$ radical may proceed along one of two different routes, *i.e.* reaction with NO to produce an RCOO radical, which will ultimately decompose to give an alkyl radical and CO_2 (R1.18a and R1.18b), or addition of NO₂ to form a peroxyacyl nitrate (PAN) compound (R(CO)O₂NO₂) (R1.19):

$$RCOO_2 + NO \rightarrow RCOO + NO_2 \tag{R1.18a}$$

$$RCOO \rightarrow R + CO_2 \tag{R1.18b}$$

$$RCOO_2 + NO_2 \rightarrow RCOO_2 NO_2 \tag{R1.19}$$

Being thermally unstable, PAN type compounds are liable to undergo decomposition to give NO_2 and organic radicals, which will ultimately yield OH. Consequently, the various species of PAN constitute a NO_x reservoir and a radical source, which is of particular importance at night.

1.4.4.3 The Low NO_x Limit

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Under conditions of sufficiently low $[NO_x]$, the RO₂ radical is liable to react with HO₂ to form an organic hydroperoxide compound (ROOH):

$$RCH_2O_2 + HO_2 \rightarrow RCH_2OOH + O_2$$
(R1.20)

or with other RO_2 radicals, of the same or different structure (R'O₂), to form either the equivalent alkoxy radical pair (R1.21a), a carbonyl compound and an alcohol (R1.21b), or an organic peroxide (ROOR) (R1.21c) (Jenkin *et al.*, 1988), *e.g.*:

$$RCH_2O_2 + RCH_2O_2 \rightarrow 2RCH_2O + O_2$$
 (R1.21a)

$$RCH_2O_2 + RCH_2O_2 \rightarrow RCHO + RCH_2OH + O_2$$
 (R1.21b)

$$RCH_2O_2 + RCH_2O_2 \rightarrow RCH_2OOCH_2R + O_2$$
 (R1.21c)

The relative importance of each of the three different $RO_2 + RO_2$ self-reaction pathways is highly dependent upon the structure of the RO₂ radicals taking part in the reaction. In general, the branching ratio for reaction (R1.21c) is minor for small RO₂, but it is known to increase in magnitude with alkyl chain length (Finlayson-Pitts and Pitts Jr., 2000). The branching ratios for reactions (R1.21a) and (R1.21b) are often of similar size, however, alkoxy radical formation appears to be less favourable for small R, *e.g.* for CH₃O₂, (R1.21a)/[(R1.21a)+(R1.21b)+(R1.21c)] \approx 30 % and (R1.21b)/[(R1.21a)+(R1.21b)+(R1.21c)] \approx 70 % (Finlayson-Pitts and Pitts Jr., 2000). Also, there exists evidence to suggest that tertiary RO₂ radicals react only *via* pathways (R1.21a) and (R1.21c) (Seinfeld and Pandis, 2006). For most RO₂ radicals reaction (R1.21) is generally at least one order of magnitude slower than reaction (R1.20), with structurally dependent rates ranging from ~ $10^{-13} - 10^{-17}$ cm³ molecule⁻¹ s⁻¹ (Finlayson-Pitts and Pitts Jr., 2000).

The formation and fate of organic peroxides has recently received much renewed attention owing to their low volatility and potential to form SOA (Kroll and Seinfeld, 2008). It should be noted that besides homogeneous polymerisation, reaction (R1.21c) constitutes the sole mechanism by which the carbon number of an atmospheric volatile organic compound may be increased. As, the branching ratio to ROOR formation increases in magnitude with the structure of the reacting RO_2 radicals, it is possible that reaction (R1.21c) could be significant in the initiation of homogeneous nucleation (see Section 1.5.2). As will be discussed in Section 1.4.4.4, peroxide species also constitute an alternative source of radicals (Monks, 2005).

1.4.4.4 Alternative Radical Sources

One particularly important OVOC in the context of atmospheric chemistry is formaldehyde, which may be formed as both a primary and a secondary product of gas phase VOC oxidation. One major pathway to formaldehyde formation is the reaction of the methyoxy radical (CH_3O) with O_2 , *i.e.*:

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
 (R1.22)

With an average atmospheric mixing ratio of nearly 2 ppmV, methane constitutes the most major source of the methoxy radical (Wayne, 2002); however, it may potentially be generated from many hydrocarbon compounds following several oxidative iterations around the 'atmospheric oxidation loop' described by **Figure 3**. Thus for many species of VOC, formaldehyde constitutes an 'end stage' oxidation product.

Within the atmosphere formaldehyde may either react with OH (R1.23), or undergo photolysis, *e.g.* (R1.24) and (R1.25). Both decomposition mechanisms are liable to lead to the production of HO_x radicals, thus causing the significance of formaldehyde in tropospheric chemistry:

$$HCHO + OH \xrightarrow{O_2} HO_2 + CO + H_2O$$
(R1.23)

$$\text{HCHO} + h\nu (\lambda < 334 \text{ nm}) \xrightarrow{O_2} 2\text{HO}_2 + \text{CO}$$
(R1.24)

$$\text{HCHO} + h\nu (\lambda < 360 \,\text{nm}) \rightarrow \text{H}_2 + \text{CO}$$
(R1.25)

It is important to note that although reactions (R1.23) and (R1.25) lead to the production of HO_x , reaction (R1.24) constitutes a chain termination step (Troe, 2007). The significance of

pathways (R1.24) and (R1.25) are similar, giving HCHO lifetimes of 9 and 7 hours, respectively. The average lifetime of HCHO with regard to reaction with OH, is approximately 31 hours (Seinfeld and Pandis, 2006).

Other significant radical sources within the troposphere include (i) the photolysis of HONO:

$$HONO + h\nu (\lambda < 400 \text{ nm}) \rightarrow OH + NO$$
 (R1.26)

(ii) the photolysis of carbonyl compounds, for example acetone:

$$CH_3COCH_3 + h\nu (\lambda < 338 \text{ nm}) \rightarrow CH_3CO + CH_3$$
 (R1.27)

(iii) the photolysis of peroxide compounds, for example hydrogen peroxide:

$$H_2O_2 + h\nu (\lambda < 350 \text{ nm}) \rightarrow 2\text{OH}$$
 (R1.28)

Clearly, the fraction of such compounds undergoing photolysis will increase with altitude within the troposphere. A further alternative route to radical production within the troposphere, which is becoming increasingly recognised, is the ozonolysis of alkenes (Monks, 2005; Johnson and Marston, 2008).

1.4.4.5 Tropospheric Chemistry of Alkenes

Alkenes constitute an important subdivision of the VOC category; they are emitted by both anthropogenic and biogenic sources and are highly reactive within the atmosphere. Alkenes react considerably faster than alkanes and have lifetimes of the order of hours to days (Calvert *et al.*, 2000). Unlike alkanes, alkenes are able to react with all three major atmospheric oxidants, OH, NO₃ and O₃. Reaction with OH primarily occurs *via* addition of the OH radical to the C=C double bond, but may also occur by hydrogen abstraction (as detailed above) from elsewhere on the carbon chain. The reactions of alkenes with NO₃ and O₃ occur solely by addition and at a slower rate than with OH (Seinfeld and Pandis, 2006; Johnson and Marston, 2008). For a review of recommended rate constants for various atmospheric alkene reactions the reader is referred to work by Calvert *et al.* (Calvert *et al.*, 2000). Example mechanisms describing the atmospheric oxidation of alkenes are given in **Figure A1.2** of Section A1 of the Appendix, and in the case of isoprene and α -pinene (the most abundant biogenic alkenes within the atmosphere), in Section 7.4.3 of Chapter 7.

Briefly, in the case of OH addition to the generic alkene RCH=CH₂, a β -hydroxyalkyl radical (RCHCH₂OH) is formed following addition of the OH radical, which will proceed *via* reaction with O₂ to form a β -hydroxyalkyl peroxy radical (RCH(OO)CH₂OH). The β -hydroxyalkyl peroxy radical is analogous to the RO₂ peroxy radical described above and will thus react following the mechanism outlined in **Figure 3**. Reactions with NO₃ follow this

same mechanism; however an alkene-NO₃ adduct is formed in place of the β -hydroxyalkyl radical.

The O₃-alkene reaction mechanism is significantly different to those detailed above. First proposed by Criegee in 1960, alkene ozonolysis proceeds by addition of the O₃ molecule across the C=C double bond to produce an energy rich primary ozonide (Calvert *et al.*, 2000). The primary ozonide undergoes rapid decomposition to give a carbonyl compound and a highly unstable *Criegee intermediate* (*e.g.* $[R_1R_2C^{\bullet}OO^{\bullet}]^*$). Alkene ozonolysis mechanisms are treated in further detail in **Figure A1.3** of Section A1 of the Appendix and in Section 7.4.3 of Chapter 7. In brief, the Creigee intermediate will either decompose or react further (following stabilisation) to yield OH and various species of OVOC (Johnson and Marston, 2008).

On account of their high reactivities and complex atmospheric degradation processes, alkenes have high photochemical ozone creation potentials (*i.e.* the degradation of one alkene molecule will facilitate the oxidation of many molecules of NO to NO₂) (Derwent *et al.*, 2007). For example, although alkenes constitute only ~ 10 % of all NMHCs in a typical modern city atmosphere, they account for ~ 25 % of OH reactivity and ~ 18 % of photochemical ozone production (Calvert *et al.*, 2000). Also, alkene oxidation constitutes a significant radical source (OH yields \approx 7 – 100% (Calvert *et al.*, 2000; Monks, 2005)), and it results in the formation of highly oxidised and hence low volatility organic species which will contribute readily to SOA formation and growth. For further details regarding atmospheric alkene chemistry the reader is referred to work by Calvert and colleagues (Calvert *et al.*, 2000) and Johnson and Marston (Johnson and Marston, 2008).

1.4.4.6 Tropospheric Chemistry of Aromatic Compounds

Aromatic VOCs are anthropogenic pollutants, emitted primarily from the use of petroleum based fuels (Calvert *et al.*, 2002). In the atmosphere aromatic compounds react mainly with OH and by addition to the aromatic ring to form a range of highly reactive products. Hydrogen abstraction (from the aromatic ring or from a pendant alkyl group) is also possible, but with a typical branching ratio of ≤ 10 % it constitutes a minor oxidation route (Seinfeld and Pandis, 2006). A detailed investigation of the atmospheric oxidation of aromatic compounds is reserved for Chapter 6, hence only a brief description is given here.

Following OH addition to the aromatic ring, the subsequent OH-aromatic radical adduct (a hydroxycyclohexadienyl radical) will react with O_2 to form an equivalent aromatic

hydroxyperoxy radical, which will cyclicize to yield an aromatic hydroxyperoxide bicyclic radical. The aromatic hydroxyperoxide bicyclic radical will proceed *via* various mechanisms to a number of different fates (*e.g.* see **Figure A1.4** of Section A1 of the Appendix) (Atkinson, 2000; Seinfeld and Pandis, 2006). Products of hydrogen abstraction from the aromatic ring include phenol compounds and products of abstraction from a pendant alkyl group include aromatic aldehydes (see **Figures A1.5** and **A.16** of Section A1 of the Appendix for example mechanism).

As with alkenes, aromatics have high photochemical ozone creation potentials (Derwent *et al.*, 2007). Using the same example as given above, in polluted urban air aromatic compounds constitute ~ 10 % of all NMHCs, yet they account for ~ 25 % of OH reactivity and ~ 18 % of photochemical ozone production (Calvert *et al.*, 2000). Aromatic VOCs are also known to generate SOA in high yields (Stern *et al.*, 1987). Comprehensive reviews describing the detailed oxidation of aromatic VOCs have been given by a number of different authors, to which the reader is referred for further information (Yu *et al.*, 1997; Calvert *et al.*, 2000; Finlayson-Pitts and Pitts Jr., 2000; Calvert *et al.*, 2002; Seinfeld and Pandis, 2006).

For further information and more general reading on the atmospheric oxidation of volatile organic compounds in the atmosphere, the reader is referred to the many comprehensive summary reviews given within the literature (*e.g.* (Atkinson, 2000; Finlayson-Pitts and Pitts Jr., 2000; Seinfeld and Pandis, 2006)).

1.5 Atmospheric Particulate Matter

The existence of particulate matter (PM) within the atmosphere has an array of well documented consequences (*e.g.* see (Czoschke *et al.*, 2003; Kanakidou *et al.*, 2005) and references therein). In brief, the negative effects associated with PM range from visibility impairment on the local scale to climate change, with PM being able to perturb the Earth's radiative budget *via* both direct and indirect mechanisms (IUPAC, 2006). Additionally, fine airborne particles have been shown to have numerous detrimental effects on human health, particularly in vulnerable members of the population (*e.g.* the young, the elderly and those individuals with respiratory problems) (Grosjean, 1992).

Atmospheric PM can be classified according to its various different compositional and physical properties and its formation routes. Initially, on the most basic level PM can be classified as being either inorganic or organic. Inorganic PM typically comprises inorganic salts and crustal material, including silicon and various species of transition metals. The

organic (carbonaceous) component of PM can be subdivided into three distinct categories, *i.e.* it may comprise (i) organic carbon (OC), (ii) carbonate carbon (CC) or (iii) elemental carbon (EC) (Seinfeld and Pankow, 2003). PM can be classified yet further according to physical size. A cluster of molecules is generally defined as a particle if it possesses a 'diameter' of approximately 0.002 to > 50 μ m (Finlayson-Pitts and Pitts Jr., 2000). Within this size band PM is generally subdivided into one of a number of different overlapping size 'modes', which are (i) the Nucleation mode (new particles, d < 10 nm) and (ii) the Aitken mode ($d \sim 10 - 100$ nm) for 'ultrafine' particles, and (iii) the Accumulation mode ($d \sim 0.1 - 2 \mu m$) and (iv) the Coarse mode (d $\sim 2 - 50 \mu m$) for 'fine' and 'coarse' particles, respectively (Seinfeld and Pandis, 2006). Nucleation and Aitken mode particles (which are known to contribute most significantly to the negative atmospheric effects of PM), have the largest number density within the atmosphere (Finlayson-Pitts and Pitts Jr., 2000). Another important PM classification system often employed defines the origin of the particle. Those particles emitted directly to the atmosphere are referred to as *primary particles*, while those formed within the atmosphere are referred to as secondary particles.

The exact chemical make-up of PM is highly complex and not well characterised; it varies both spatially and temporally and with size mode. Often the three composition categories of PM overlap and the 'real' atmospheric particle contains both organic and inorganic matter. In general fine particles are composed primarily of nitrate, sulphate, ammonium, metals, OC and EC. Coarse particles typically comprise crustal and biological matter, such as silicon, calcium and magnesium, pollen, spores, viruses and bacteria (Seinfeld and Pankow, 2003; Seinfeld and Pandis, 2006).

An airborne particle is often referred to as an *aerosol*, the definition of which is "a relatively stable suspension of solid or liquid particles in a gas" (Finlayson-Pitts and Pitts Jr., 2000). By this definition the term aerosol includes both the particulate matter and the medium in which it is carried. For clarity, the term aerosol shall be used throughout the remainder of this work when referring to atmospheric PM.

Organic aerosol (*i.e.* OC) comprises a significant fraction of total suspended particulate mass, *i.e.* 20 – 50 % in boundary layer air over continental mid-latitude regions and as much as 90 % over tropical forests (Kanakidou *et al.*, 2005). Using the same classifications defined above, organic aerosol can be divided into the categories of *Primary Organic Aerosol* (POA) and *Secondary Organic Aerosol* (SOA). The primary contribution to organic aerosol originates mainly from combustion processes such as vegetation fires, burning of biofuels and burning of fossil fuels. The emission rates for these processes have been estimated to be 34.6, 9.1 and 3.2 Tg C Yr⁻¹, respectively, which, in total is almost six times greater than annual emissions of elemental black carbon from such sources (Kanakidou *et al.*, 2005).

1.5.1 Secondary Organic Aerosol (SOA)

Secondary organic aerosol is formed within the atmosphere from the semi- and non-volatile oxidation products of a precursor VOC, which is generally emitted to the atmosphere by primary routes. Of all VOCs emitted to the atmosphere, it is believed that aromatic and terpene species possess the largest SOA forming potential (Kanakidou *et al.*, 2005).

When an SOA precursor VOC enters the atmospheric oxidation cycle (described in Section 1.4.4), it will react to form products containing a variety of different oxygen and nitrogen bearing functionalities. The addition of oxygen and/or nitrogen to the base structure will act to increase the size and polarity of the compound and hence decrease its vapour pressure. If the subsequent oxidised reaction product is sufficiently non-volatile it is liable to partition to the aerosol phase (see **Figure 4**). Modelling studies suggest that the addition of carboxylic acid (C(O)OH) and nitrate (ONO₂) groups have the greatest effect in reducing the volatility of the parent compound (Pankow and Asher, 2008).

SOA mass constitutes a major fraction of the total atmospheric loading of organic aerosol and indeed of all atmospheric particulate matter, on both the local (Baltensperger *et al.*, 2005) and the global (Kanakidou *et al.*, 2005) scale. Under certain scenarios atmospheric SOA can comprise as much as 90 % of organic aerosol mass (Kalberer *et al.*, 2004) and 50 % of the total mass of atmospheric aerosol (Kleindienst *et al.*, 1999). As SOA particles generally occupy the smaller size modes, they hold significant roles in all forms of negative atmospheric and climate impacts attributed to atmospheric PM.

1.5.2 Nucleation

The process by which a semi-volatile organic compound undergoes transition from the gas to the aerosol phase is known as *nucleation*, which may be either *homogeneous* or *heterogeneous* in nature (Seinfeld and Pandis, 2006; Holmes, 2007). Homogeneous nucleation is defined as the process by which a semi-volatile gas undergoes transfer to the particle phase to make new aerosol, *i.e.* the nucleating particle simply forms from the clustering of low volatility vapour molecules. Heterogeneous nucleation describes the partitioning process of a semi-volatile gas onto pre-existing particulate matter. During heterogeneous nucleation total suspended mass will increase, but no new particles are formed (Jenkin *et al.*, 2000b). Homogeneous and heterogeneous nucleation may involve only one species of gas, in which case the processes is termed *homomolecular*, or as is most likely within the real atmosphere, may involve more than one species of gas, in which case the processes is termed *heteromolecular* (Seinfeld and Pandis, 2006). The nucleation concept described here is shown diagrammatically in **Figure 4**.



Figure 4: Atmospheric evolution of VOCs to secondary organic aerosol (redrawn from (Seinfeld and Pankow, 2003))

In order for a gaseous compound to undergo partitioning to the aerosol phase, it must first accumulate to a sufficiently high concentration that is in excess of its saturation vapour concentration, *i.e.* the vapour phase must become supersaturated with respect to the nucleating compound (Stern *et al.*, 1987). This concept may be defined most clearly as a *saturation ratio*, *S* (Seinfeld and Pandis, 2006):

$$S = \frac{N_C}{N_C^s(T)} \tag{E1.3}$$

where N_C = number concentration within the gas phase and $N_C^S(T)$ = equilibrium saturated number concentration at a given temperature, *T*. Using equation (E1.3), supersaturation occurs when *S* exceeds a value of 1 (Seinfeld and Pandis, 2006).

1.5.3 Gas-Particle Partitioning

Under the nucleation theory described above, it would seem that only the less volatile oxidation products of a VOC SOA precursor are liable to take part in the production and/or growth of aerosol mass (Pandis *et al.*, 1992). However, a range of more volatile, low molecular weight compounds have been identified in SOA, which from the conventional view point would not be expected to exist outside of the gas phase (Jang *et al.*, 2003; Kalberer *et al.*, 2004; Tolocka *et al.*, 2004; Kanakidou *et al.*, 2005). Such findings can be explained by the pioneering theoretical work of Pankow and colleagues (*e.g.* (Pankow, 1994)). Pankow used a gas-aerosol partitioning model to describe SOA formation and growth, in which gaseous semi-volatile organic compounds would undergo *absorption* to a preformed organic surface. The crucial factor here is the presence of an organic surface, which allows partitioning of gas phase organic species to the aerosol even if they exist at concentrations below their atmospheric saturation limit. The equilibrium coefficient derived by Pankow to describe absorptive partitioning between the gas and aerosol phase, is given in equation (E1.4).

$$K_{p,i} = \frac{F_i}{A_i TSP} \tag{E1.4}$$

where $K_{p,i}$ = the partitioning coefficient for semi-volatile gas *i*, F_i = the mass concentration of semi-volatile, *i*, within the condensed phase, A_i = the mass concentration of semi-volatile, *i*, within the gas phase and *TSP* = the total mass of suspended matter.

It is not within the scope of this work to discuss the complexities of gas-particle partitioning theory further; for additional information the reader is referred work by Pankow, and reviews by Seinfeld and Pankow and Kanakidou (Pankow, 1994; Seinfeld and Pankow, 2003; Kanakidou *et al.*, 2005).

1.5.4 Heterogeneous Aerosol Chemistry

In general, until recently, only a small portion (typically 10 % or less) of collected SOA mass could be identified. Of those molecules qualified within the aerosol phase, a number of low molecular weight and relatively volatile species were found, which on vapour pressure grounds alone would not be expected to reside within the particle phase (Kanakidou *et al.*, 2005). Using state-of-the-art measurement techniques, it has now become apparent that such low molecular weight compounds undergo heterogeneous, or *accretion* reactions within the

aerosol to form large, non-volatile oligomeric^a compounds with masses up to 1000 Da (Baltensperger *et al.*, 2005). Much recent research has been invested into the investigation of SOA oligomers, which can comprise as much as 50 % of the total aerosol mass (Havers *et al.*, 1998; Kalberer *et al.*, 2004; Surratt *et al.*, 2006). To date oligomer compounds have been observed in SOA formed from various precursors, include α -pinene (Tolocka *et al.*, 2004), 1,3,5-trimethylbenzene (1,3,5-TMB) (Kalberer *et al.*, 2004) and isoprene (Surratt *et al.*, 2006).

It is not within the scope of this introductory material to discuss (non-oxidative) SOA heterogeneous chemistry in any depth, which is in any case not fully understood at present. However, in brief, the typical accretion reaction products expected to form within the aerosol include: peroxyhemiacetals (hydroperoxide + aldehyde), hemiacetals (alcohol + aldehyde), aldol addition products (carbonyl + carbonyl), esters (carboxylic acid + alcohol/carboxylic acid), sulphate esters (sulphuric acid + alcohol) and Criegee intermediate adducts (stabilised Creigee + various other compounds) ((Kroll and Seinfeld, 2008), see **Figure A1.7** of Section A1 of the Appendix).

The atmospheric aerosol may also undergo oxidative heterogeneous chemistry, *i.e.* the aerosol surface may react with gaseous atmospheric oxidants such as OH, NO₃ and O₃. Oxidative heterogeneous chemistry, also referred to as *aerosol aging*, can occur over a range of timescales and may effectively alter the chemical composition of the aerosol (Sax *et al.*, 2005).

1.6 Measurement of Atmospheric Volatile Organic Compounds

From the brief overview provided above, it is clear that VOCs play a major role in many tropospheric processes, from radical recycling to the photochemical production of tropospheric ozone and secondary organic aerosol. In order to understand and ultimately manage such phenomenon, it is crucial that we are able to: (i) measure VOCs under ambient conditions, such that emissions controls may be affected and environment response may be monitored, and (ii) measure VOCs under simulated/laboratory conditions such that we may advance our understanding of the role which they hold in our environment. However, VOC monitoring presents a number of unique challenges and is far from trivial. For instance the various species of VOC that reside within our atmosphere are many and diverse, they often

^a A relatively large ($\sim < 1000$ amu), low volatility molecule formed from the reaction of multiple smaller, more volatile molecules. Consequently, an oligomer is characterised by a structure comprising repetitive monomer units (similar to a polymer). The properties of an oligomer are known to vary appreciably with the addition or removal of one or more constituent units (Baltensperger *et al.*, 2005).

exist at low concentrations and their presence can be transient. For an instrument to be capable of monitoring such trace level species, a number of important criteria must be satisfied. As concisely stated in a seminal publication by Ulrich Platt (Platt, 1999), these criteria state that an instrument must have:

- 1. **Sensitivity**: the instrument must be sufficiently sensitive and have a sufficiently low detection limit, such that the target species may be identified above all background and ambient influences.
- 2. **Specificity**: the instrument must be able to differentiate between the target and other components of the sample matrix.
- 3. **High time resolution**: measurements should be made with a high repetition rate in order to capture rapidly fluctuating events.
- 4. **Precision and accuracy**: measurements should be reproducible and be made with little error.

Other important criteria include simplicity of design, portability and the ability to be operated remotely.

A number of different instruments possessing such important features have been developed in an attempt to provide accurate and precise measurements of atmospheric trace VOCs. The following sections provide a review of the most common and successful devices utilised today.

1.6.1 Gas Chromatography

Historically, the most common technique employed to monitor VOCs within the atmosphere has been *Gas Chromatography* (GC) coupled to either *Flame Ionisation Detection* (FID) or *Mass Spectrometry* (MS) (Hamilton and Lewis, 2006). First conceptualised in the 1920's, the GC technique has undergone significant development to reach its present day form. A typical modern GC instrument comprises of four separate components: (i) a sample acquisition/inlet system, (ii) a sample preparation system, (iii) a chromatographic column and (iv) a mass analyser/detector. The principle behind the GC technique is relatively simple, *i.e.* sample separation and identification according to species characteristic *retention time* upon a chromatographic *stationary phase* (Hamilton and Lewis, 2006). More specifically, following various stages of preparation (*i.e.* pre-concentration, water removal *etc*), the sample gas mixture is carried through a chromatographic column by a *mobile phase* (*i.e.* some carrier gas). As the sample gas progresses through the column, its constituent molecules will adsorb to and desorb from the stationary phase (*e.g.* the column wall coating) at some given,

compound-characteristic rate, or *retention time*, which is employed for identification purposes.

There are many advantages to using GC for the monitoring of atmospheric VOCs, particularly when coupled to MS (GC-MS). Perhaps the most significant advantage offered by GC-MS is its low detection limit; typically VOCs can be measured down to mixing ratios of a few pptV. As each VOC has a characteristic retention time, the GC technique also provides a high level of speciation. However, the technique is fundamentally slow, *i.e.* time is required to preconcentrate and dry the sample before column injection and depending on the species and number of VOCs present, elution time can be as long as tens of minutes. Consequently, GC-MS has poor measurement repetition rate and low temporal resolution, which can result in the rapid changes that occur in atmospheric composition being overlooked.

Other disadvantages of GC-MS include sensitivity to other trace gases (such as water vapour and O₃), the requirement for known standard gases for calibration purposes, poor measurement capability for oxygenated compounds (*i.e.* OVOCs are difficult to separate on the GC column) and the potential loss of compounds during sample pre-treatment. Also, as the GC-MS is not always deployed within the field, canister samples are often taken, which present a further potential loss source for compounds prior to measurement.

1.6.2 The Development of Chemical Ionisation and Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)

Until the 1970's few techniques with high time resolution existed to complement GC-MS, and those techniques which were available did not lend themselves readily to atmospheric monitoring. For example, the electron impact ionisation mass spectrometer (EI-MS), widely used as an analytical tool in other branches of science, causes extensive fragmentation of atmospheric samples and compound identification is at best, highly complex (Mark, 1984; Blake *et al.*, 2008). In the 1960's a new, much 'softer' ionisation method was developed (Munson and Field, 1966). Known as '*Chemical Ionisation*' (CI), the technique employs a reagent ion (*e.g.* CH_5^+) to confer charge to the analyte (M) in place of electron bombardment, for example:

$$CH_5^+ + M \rightarrow MH^+ + CH_4 \tag{R1.29}$$

CI and its development are discussed in detail in Chapters 2 and 3, hence only a brief description is given here. In the *Chemical Ionisation Mass Spectrometry* (CI-MS) technique, a reagent ion is generated in an ion source chamber, into which the analyte is injected.

Analyte ionisation takes place *in situ* within the ion source chamber, before unreacted reagent and charged analyte ions are extracted for mass spectrometric analysis. This CI technique coupled to mass spectrometry would eventually lead to the successful development of a range of *real-time* atmospheric VOC monitoring instruments.

One particularly significant development in CI instrumentation came in 1976 with the inception of the *Selected Ion Flow Tube Mass Spectrometer* (SIFT-MS) by Adams and Smith (Adams and Smith, 1976). SIFT-MS (an extension of the 'flowing afterglow' technique (Fehsenfeld *et al.*, 1966)) was originally employed to investigate ion-molecule chemistry, but after much early success it was developed into an analytical tool for fast VOC measurement (Smith and Spanel, 2005). The SIFT-MS (shown diagrammatically in **Figure 5**) essentially comprises four main components (i) a CI reagent ion source, (ii) a reagent ion filter, (iii) a flow tube and (iv) a mass analyser/detection system. Unlike original CI-MS instrumentation, in SIFT-MS the ion source and reaction chamber (*i.e.* the *flow tube*) are separate components, such that ion-molecule reactions take place in isolation of reagent ion generation. A brief description of SIFT methodology is given below.



Figure 5: Diagram of the Selected Ion Flow Tube Mass Spectrometer (SIFT-MS) (Schoon et al., 2003)

In the SIFT technique a continuous reagent ion stream is produced in the ion source before being drawn into a quadrupole mass filter. The mass filter ensures that only a predetermined species of reagent ion is transferred to the flow tube to take part in any subsequent ionisation processes. Typical reagent ions employed include H_3O^+ , NO^+ and O_2^{++} . Having traversed the mass filter the reagent ion stream enters a large, low pressure (~ 1 Torr) flow tube (typically 30 - 100 cm in length), which is constantly flushed at a high flow rate with an inert carrier gas (typically He). The sample air is injected in a continuous flow at the upstream end of the flow tube in a thermalised '*swarm*' cloud, in which the sample VOCs are ionised by ion-molecule reaction with reagent ions. At the downstream end of the flow tube, the unreacted reagent ions and ionised VOCs are analysed by a quadrupole mass spectrometer. Owing to the use of
a separate reaction vessel, ion-molecule interaction takes place under well defined reaction conditions (*e.g.* temperature, reaction time *etc.*). Consequently following detection, various properties of the reaction system may be determined (*e.g.* reaction rate constants or analyte concentrations) using well known physical and kinetic theory (Smith and Spanel, 2005).

The SIFT-MS has proven highly successful in the monitoring of atmospheric trace VOCs, with quantitative ppbV level detection achieved on time scales of the order minutes to seconds. Further to this, SIFT-MS has provided an extensive set of kinetic data for ion-molecule chemistry, which is employed in various branches of modern science (*e.g.* (Spanel and Smith, 1997a)). SIFT-MS does, however, suffer from several drawbacks; primarily it is rarely able to achieve sub-ppbV detection. Also, the SITF-MS is rather large and has substantial gas, pumping and power requirements, as such it becomes somewhat difficult to deploy in the field.

1.6.3 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

Developed in the mid 1990s by Werner Lindinger and colleagues, *Proton Transfer Reaction Mass Spectrometry* (PTR-MS) is an evolution of the SIFT-MS technique (Lagg *et al.*, 1994; Hansel *et al.*, 1995), and a further subdivision of CI-MS instrumentation. PTR-MS is similar to SIFT-MS except the ion-molecule interaction between reagent and analyte takes place inside of a much smaller *drift tube* (typically \sim 10 cm in length), rather than the large flow tube. Also the PTR-MS incorporates a carefully designed and highly characterised hollow cathode discharge ion source, which provides an extremely 'clean' reagent ion pool containing few impurity ions. Consequently, the PTR-MS does not require a reagent ion mass selection stage.

With the PTR-MS technique the sample air is injected continuously into the drift tube, inside of which the reagent and analyte ions are transported by an electric field instead of a bulk carrier gas (de Gouw and Warneke, 2007). Therefore as the sample does not undergo dilution, the sensitivity achieved by PTR-MS is much greater (roughly two fold) than that achieved by SIFT-MS (Hansel *et al.*, 1995). The fixed length of the drift tube provides a fixed ion-molecule reaction time (Blake *et al.*, 2008). Thus, if the proton donor is present in large excess over the analyte molecules, simple kinetic theory can be employed to convert measured donor and analyte ion signals into absolute concentration (as will be discussed in Chapter 3). Hence, as with SIFT-MS, analyte quantification may be achieved using PTR-MS without the need for experimental calibration.

The proton transfer chemical ionisation process at the heart of the PTR-MS technique essentially constitutes the transfer of a single proton from a donor reagent ion, typically hydronium (H₃O⁺), to an analyte molecule (M), in order to generate its protonated counterpart (MH⁺), *i.e.*:

$$H_{3}O^{+} + M \rightarrow MH^{+} + H_{2}O \qquad (R1.30)$$

Introduction

However, the proton transfer reaction shown in reaction (R1.30) will proceed only if the proton affinity of the analyte is greater than that of the reagent. In the case of hydronium this excludes the bulk components of air, such as nitrogen and oxygen, but includes the majority of VOCs (Williams, 2006) (with the exception of short chain alkanes, see **Table 1**). Consequently, one major advantage of hydronium as an ionisation reagent for atmospheric VOC monitoring, is a lack of spectral congestion from unwanted inorganic species.

Classification	Molecule	PA / kJ mol ⁻¹	Classification	Molecule	PA / kJ mol ⁻¹
Inorganics	O_2	421	Alkynes	acetylene	641
	N_2	494		propyne	748
	CO_2	541			
	O_3	626	Aromatics	benzene	750
	H ₂ O	691		toluene	784
	NH_3	854		phenol	817
				aniline	883
Alkanes	methane	544			
	ethane	596	Others	chloromethane	647
	propane	629		formaldehyde	713
	<i>i</i> -butane	678		acetaldehyde	769
				ethanol	776
Alkenes	ethene	641		acetone	812
	propene	752		acetonitrile	839

 Table 1: Example proton affinities for a range of atmospherically significant compounds

Another important feature of PTR-MS is that under thermal conditions the ionisation process tends to be rather soft; in general, only a protonated parent ion is formed with few fragmentation products. Consequently, spectral interpretation and analyte identification is made easier, particularly in the analysis of complex mixtures. Furthermore, exothermic proton transfer is relatively rapid, typically occurring at the collision limited rate, hence reaction efficiency is high.

Thanks to the many benefits offered by PTR-MS, the technique has become widely used for the monitoring and measurement of trace VOCs in the gas-phase (Blake *et al.*, 2008). Today, PTR-MS has applications in areas as diverse as atmospheric composition and pollution monitoring (*e.g.* (de Gouw and Warneke, 2007) and references therein), aroma analysis and

Chapter 1

food science (Yeretzian *et al.*, 2003), and medical diagnostics (Yeretzian *et al.*, 2003) including breath analysis (Amann *et al.*, 2004). The lack of reagent ion filtration, flow tube and extensive pumping, means that the PTR-MS instrument is far more portable than the SIFT-MS and as such it has been successfully deployed upon various platforms (de Gouw *et al.*, 2003; Galbally *et al.*, 2007) and to the most remote of field sites (Karl *et al.*, 2007).

1.6.4 Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry

(CIR-TOF-MS)

This thesis details the development and application of a new on-line method for the monitoring of trace level VOCs within the atmosphere. Termed *Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry* (CIR-TOF-MS), the technique constitutes an extension of PTR-MS, in which a novel, high pressure radioactive ion source is used in place of the standard hollow cathode hydronium generator. As will be shown in the following chapters, the radioactive ion source offers many benefits including enhanced sensitivity and the ability to generate a range of different CI reagent ions, not just hydronium. Also, with CIR-TOF-MS a time-of-flight mass spectrometer is employed as the mass analyser rather than a simple quadrupole device. TOF-MS comes into its own when complex mixtures must be analysed in *real-time*, since the entire mass spectrum is captured at any given instant. Consequently, CIR-TOF-MS provides a comprehensive picture of the sample matrix, being able to monitor even the most complex and transient events in high detail.

1.7 Thesis Structure

The work detailed within this document is divided into a number of different chapters which collectively chart the development of the CIR-TOF-MS technique from early stage laboratory testing, through detailed characterisation, to application in a series of field studies. This thesis provides findings which illuminate and support current theories regarding the gas phase oxidation mechanisms of a number of atmospherically important VOCs and investigates their role in SOA formation; it also ultimately heralds the advancement of technology for future monitoring of atmospheric organic trace species.

Initially the CIR-TOF-MS was characterised for the detection of a range of atmospherically significant VOCs using a number of different CI reagents (H_3O^+ , NH_4^+ , NO^+ and O_2^{++}), these first findings are reported in **Chapter 3**. Reaction products and common species-specific markers are identified and their formation mechanisms are explained, thus, *qualitatively* the foundations are laid for all future work with the chemical ionisation reaction mass

spectrometry technique (CIR-MS). Having proven the CIR-TOF-MS capable of *qualitatively* detecting a comprehensive range of VOCs, the technique was established as a fully *quantitative* monitoring method. This was done as part of a 'refereed' intercomparison campaign for the measurement of atmospheric OVOCs. **Chapter 4** describes the results from this intercomparision experiment, which prove the CIR-TOF-MS fully able to provide 'accurate' and 'precise', *quantitative* measurements.

In order apply the CIR-TOF-MS technique to the task of VOC monitoring in the 'real' atmosphere, further, more detailed characterisation was required, this is collectively described in **Chapter 5**. As part of this work instrument sensitivities were determined for a range of VOCs, as were the effects of ambient water vapour concentration and reaction energy on detection capability. Detection limits were also established as was response linearity. **Chapter 5** concludes with a description of the first application of the CIR-TOF-MS to VOC monitoring in the 'real' atmosphere. VOC measurements during an urban air monitoring campaign are presented, the goals of which were to determine the present state of air quality in Leicester, as an example of a typical UK city. This initial application of the CIR-TOF-MS to VOC monitoring in the real atmosphere proved highly successful, with measurements achieved for a range of compounds. The VOCs observed with greatest abundance included methanol, acetaldehyde, acetone and various aromatic species. All VOCs were observed with classic diurnal profiles.

Chapters 6 and 7 collectively describe the first major application of the CIR-TOF-MS to the scientific exploration of a contemporary atmospheric issue, *i.e.* the formation of secondary organic aerosol. The mechanisms of SOA formation are at present not well understood, nor are the detailed oxidation pathways of many SOA precursor VOCs. In order to elucidate these matters, a series of comprehensive VOC oxidation/aerosol formation experiments were conducted for the known SOA precursors 1,3,5-trimethylbenzene (**Chapter 6**), isoprene and α -pinene (**Chapter 7**).

Experiments were conducted within an atmospheric simulation chamber under various NO_x , oxidant and seeding conditions and at various precursor concentrations. The evolution of the chamber matrix was monitored by the CIR-TOF-MS and a suite of gas and aerosol phase monitoring instruments. The CIR-TOF-MS technique excelled by providing crucial compositional and behavioural measurements of an array of gas phase organic oxidation products, including a number of previously unobserved, high mass compounds. Certain gas phase data presented here are compared with the output of a box model employing data

extracted from the Master Chemical Mechanism (http://www.mcm.leeds.ac.uk/MCM, see Chapter 6). The combined analysis performed provides insight into the identity of species that may potentially contribute to SOA formation and growth, and provides findings to support our current understanding of the gas phase degradation mechanisms of organic compounds.

However, before this work is presented, this thesis will continue with **Chapter 2** which provides a detailed description of the CIR-TOF-MS instrumentation central to this thesis.

Chapter 2

Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry: Instrumentation

2.1 Summary and Introduction

This chapter provides a detailed description of the University of Leicester Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS), the development, characterisation and application of which is reported within this thesis. As was described in Chapter 1, analytical mass spectrometric instrumentation utilising chemical ionisation (CI) has proved highly successful in the field of atmospheric monitoring, for the detection and quantification of trace level volatile organic compounds (VOCs) (Hewitt *et al.*, 2003). Such instruments offer many benefits over their competitor techniques; these benefits include rapid data acquisition and pptV – ppbV detection capability (de Gouw and Warneke, 2007).

The CIR-TOF-MS technique constitutes an extension of Proton Transfer Reaction Mass Spectrometry (PTR-MS), which in itself was born out of Selected Ion Flow Tube Mass Spectrometry (SIFT-MS). The common feature which links these techniques is the use of chemical ionisation under defined reaction conditions such that chemical kinetics can be employed to determine analyte concentrations. Thus, collectively CIR-TOF-MS, PTR-MS and SIFT-MS instruments may be categorised as 'chemical ionisation *reaction* mass spectrometers' (CIR-MS). A typical CIR-MS type instrument is composed of six distinct components: (i) an ion source, (ii) a reactor, (iii) an inlet system, (iv) a mass analyser, (v) a detection system and (vi) a vacuum generator. The design and function of each of these components within the University of Leicester CIR-TOF-MS system is discussed here, as are some key theoretical principles upon which the technique is based. However, before a full description of the CIR-TOF-MS is presented, this introduction continues with a review of some of the more common variants of the three most critical components employed by CIR-MS type instrumentation: (i) the ion source, (ii) the reactor and (iii) the mass analyser.

2.1.1 The Ion Source

In order to accomplish the ionisation of a neutral analyte *via* ion-molecule reaction, a 'pool' of reagent ions must first be generated. Reagent ion production takes place within the ion source. One of the most common types of ion source employed to generate a CI reagent (particularly in PTR-MS), is the hollow cathode discharge (HCD) source (Lindinger, 1973; Lindinger and Hansel, 1997; Ennis et al., 2005). In a HCD source, reagent ions are generated in a strong electrical discharge, which is produced by the application of a large electrical potential difference between two electrodes located inside a partially evacuated chamber (Lindinger, 1973; Ennis et al., 2005; Inomata et al., 2006). The ions produced are drawn out of the source chamber by an electric field into a *source drift* region, before being injected into a reaction vessel (Hansel et al., 1995). Despite not always being stable in the long term, HCD sources have been proven to be extremely effective CI reagent generators that are capable of producing strong ion currents. For example, the commercially available HCD source designed by Lindinger, Hansel and co-workers, is reported to produce an ion current equivalent to ~ 10^6 (hydronium) ions s⁻¹ measured at the mass spectrometer (Hansel *et al.*, 1995; Hansel et al., 1998).

The strength of the electrical discharge in a hollow cathode ion source is generally sufficient to cause extensive ionisation of molecules present within the source chamber, and hence it often results in the production of a range of different ions (Ennis *et al.*, 2005). As only one species of reagent ion is desired for chemical ionisation, this is somewhat problematic. One method to ensure a 'clean' source of reagent is to introduce some form of ion 'pre-selection' before entry to the reactor, as is the case in the SIFT-MS technique (Smith and Spanel, 2005). However, this requires the incorporation of a mass filter into the ion source, which adds cost and complexity to the instrument. Also, due to poor ion transmission through the quadrupole type mass filters employed, some proportion of the reagent ions will be lost prior to application. In the PTR-MS technique no mass filter is required, as the ion source chemistry of hydronium (the CI reagent employed almost exclusively in the technique), will conveniently recycle all other species produced rapidly back to H_3O^+ (see Section 2.2.1.2 and (Kebarle *et al.*, 1967; Hansel *et al.*, 1998)).

To ensure that the electrical discharge does not become quenched, the hollow cathode source, and the reactor coupled to it, must be operated at relatively low pressures (< 2 - 3 mbar) (de Gouw and Warneke, 2007). The low pressure requirement brings about the second major disadvantage associated with the technique, *i.e.* as the efficiency of ion-molecule chemistry

and hence ultimate instrument sensitivity is proportional to reactor pressure, a pressure limited ion source can restrict detection capability (Hanson *et al.*, 2003).

Various other types of ion source have been employed as CI reagent generators, in brief these include electron impact (Munson and Field, 1966), microwave discharge (Spanel *et al.*, 2007), plane electrode discharge (Inomata *et al.*, 2006) and radioactive (using either ²⁴¹Am, (Hanson *et al.*, 2003), or ²¹⁰Po, (Tanimoto *et al.*, 2007)) variants.

2.1.2 The Drift Cell Reactor

The key defining feature of CIR-MS type instrumentation is the use of a separate reaction vessel to contain the analyte ionisation process. In the SIFT-MS this reaction vessel is the flow tube, whereas in PTR-MS and CIR-TOF-MS a *drift cell* or *drift tube* reactor is employed. Drift cell reactors were first introduced in the 1960's in so called '*swarm*' type experiments for the study of ion-molecule kinetics (Lindinger, 1986); however, they have been employed in various types of mass spectrometric instruments since, *e.g.* ion mobility (IMS) (Kanu *et al.*, 2008), proton transfer reaction (de Gouw and Warneke, 2007) and selected ion flow drift tube (SIFDT) (Fairley *et al.*, 1999) mass spectrometers.

A drift cell reactor essentially comprises a pumped reaction vessel composed of alternately sited insulating spacers and guide electrodes. The analyte molecules are bled into the reactor in a buffer gas matrix at a fixed flow rate in order to maintain a constant cell pressure, typically of the order 2 - 15 mbar (Blake *et al.*, 2008). Once present within the reactor, the analyte molecules can undergo chemical ionisation *via* ion-molecule reaction with the reagent ions, which are drawn into the cell from the ion source. All ions produced are transported to an exit aperture at the base of the reactor by an electric field established by the guide electrodes. After traversing the exit aperture, the ions are passed to a mass spectrometer for analysis.

As the length, electric field strength and gas number density of a drift cell reactor can be accurately defined, ion transit, and therefore reaction time can easily be determined (Blake *et al.*, 2008). Thus, if the reagent ion is present in excess of the analyte, analyte quantification may be facilitated through application of simple kinetic theory (see Chapter 3).

2.1.3 The Mass Analyser

In order to measure the composition of the analyte matrix, the ions are separated according to their mass-to-charge (m/z) ratio using mass spectrometry. The most common mass spectrometer employed in CIR-MS type instrumentation is the quadrupole analyser (de Gouw and Warneke, 2007). The quadrupole mass spectrometer (QMS), invented in 1953 (Paul and Steinwedel, 1953; de Hoffman and Stroobant, 2007), primarily comprises two pairs of metallic rods, orientated parallel to each other and the z-axis of the instrument. During operation a combination of dc and rf voltages are applied to the rods, one pair of which resides at positive potential, the other at negative. A specific combination of dc and rf fields allows the transit of an ion of specific m/z ratio through the analyser, with all other ions having unstable flight paths which result in termination on the rods (de Hoffman and Stroobant, 2007). Quadrupole analysers are able to operate in one of two modes: (i) scanning *mode*, in which the dc and rf fields are progressively modulated to allow ions with a range of m/z ratios through to detection, or (ii) selected ion mode, during which the fields are set to allow transmission of only a specific, predetermined set of ions with specific m/z. Quadrupole mass spectrometers can acquire high counting rates and detection sensitivities by observing only those specific mass channels of interest.

The QMS suffers, however, from several drawbacks, such as relatively low mass resolution $(m/\Delta m \sim 100)$ and limited mass range (generally transmission is poor above 1000 Da). Perhaps the most notable weakness of the QMS ironically originates from its greatest strength, *i.e.* it essentially acts as mass filter, and hence at any one instant all sample ions, except those in the mass channel of interest, will be discarded and therefore, potentially important information may be lost (de Hoffman and Stroobant, 2007).

Recently, other types of mass analyser have been coupled to CI ion sources in an attempt to counter some of the problems associated with the QMS, including the quadrupole ion trap (IT) (Prazeller *et al.*, 2003; Warneke *et al.*, 2005) and the time-of-flight (TOF) (Blake *et al.*, 2004; Ennis *et al.*, 2005; Tanimoto *et al.*, 2007) mass spectrometer.

2.1.4 The University of Leicester Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer

The University of Leicester *Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer* (CIR-TOF-MS) comprises of a radioactive ion source/drift cell assembly coupled to a time-

of-flight mass analyser (mass analyser supplied by Kore Technology, Ely, UK). The instrument is shown in the photograph given in **Figure 1** and in the diagram of **Figure 2**.



Figure 1: The University of Leicester Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer



Figure 2: Diagram of the University of Leicester CIR-TOF-MS. All major components labelled.

Radioactive ion source/drift cell assemblies of the type employed here, are able to operate at significantly higher pressures than most other CI ion generators, and hence they offer an ultimate improvement in detection sensitivity (Hanson *et al.*, 2003; Tanimoto *et al.*, 2007;

Blake *et al.*, 2008). Indeed, being able to operate with reactor pressures as high as 13 mbar, radioactive ion source instruments have been shown to achieve sensitivities in excess of those obtained by instruments equipped with standard HCD sources (Hanson *et al.*, 2003).

Also, radioactive ion sources tend to produce a cleaner reagent ion pool than the more common HCD devices, with few impurity species (Hanson *et al.*, 2003). A further advantage associated with radioactive ion sources is the lack of any substantial settling time required after a change in source operating conditions, such as the change in identity of the CI reagent gas (Wyche *et al.*, 2005).

The TOF-MS is an ideal tool for compositional monitoring of complex analyte matrices such as the Earth's atmosphere, as unlike the more common QMS, the TOF-MS captures the entire mass spectrum at any given instant (de Gouw and Warneke, 2007). TOF-MS is also a very rapid analysis technique, being able to record a single scan on the μ s time scale (Cotter, 1999). Coupled to a highly efficient radioactive ion source, sufficient signal-to-noise statistics can be achieved with relatively little repetitive scan integration. Typically, detailed and meaningful information on the analyte matrix can therefore be obtained on time scales of ~ 1 second or less. The TOF-MS also offers none mass discriminatory transmission and a high mass resolution ($m/\Delta m > 1000$).

The following sections give an in depth description of the University of Leicester CIR-TOF-MS system, focusing on each of the key components. A summary of ion kinetics in drift tube type instruments is also given and the principles of the TOF-MS technique are explored.

2.2 The Ion Source/Drift Cell Assembly

The first major component of the CIR-TOF-MS system is the *ion source/drift cell assembly*. It is in this section of the instrument that the reagent ions are generated and reacted with the sample in an uninterrupted process to produce a continuous 'ion beam'. It is also the role of the drift assembly to ensure efficient focusing of the ion beam into the mass spectrometer. The CIR-TOF-MS ion source/drift cell assembly is composed of three distinct sections (i) an ion source chamber, (ii) a drift cell reactor and (iii) an exit/collision cell. The entire assembly, shown diagrammatically in **Figure 3**, was constructed 'in-house' at the University of Leicester using designs published by Hanson *et al.* (Hanson *et al.*, 2003).



Figure 3: Diagram of the radioactive ion source/drift cell assembly, with major sections labelled

2.2.1 The Radioactive Ion Source

2.2.1.1 Design of the Radioactive Ion Source

Reagent ion generation within the CIR-TOF-MS is achieved by passing the neutral reagent molecules in gaseous form through a chamber containing a static alpha particle emitter. In this instance alpha particles with energies of the order 5 MeV are released from a sealed foil containing a small quantity of americium-241 (half-life 432 years), in the form of americium oxide (~ 1.2 mCi, NRD Inc.Grand Island, New York, USA).

In design the radioactive foil constitutes a quantity of americium oxide powder embedded in a matrix of silver subsequently overlaid with three separate layers of gold, each approximately 1.5 μ m in thickness. Overall the radioactive foil has dimensions 8.3 × 1.4 cm. Following designs by Hanson *et al.* (2003), the radioactive foil is mounted upon the inner surface of a stainless steel cylinder to compose the *Ion Source Chamber* (see **Figure 4**).



Figure 4: (a) Mounting of the ²⁴¹Am foil within the ion source chamber and **(b)** diagram of radio active ion source (dimensions given in cm)

As shown in **Figure 4**, the ion source chamber is held within a second stainless steel cylinder and between two stainless steel plates, each of which has a diameter of 6.2 cm and depth of 0.4 cm. The upper plate is fitted with a 0.48 cm internal diameter stainless steel gas inlet tube, orientated such that the neutral reagent gas enters the ion source chamber perpendicularly to the radioactive foil. The second plate, referred to hereafter as the *Source Exit Plate* (SEP), constitutes the first of a series of guide electrodes equally spaced throughout the reactor cell region to an exit aperture before the mass spectrometer. The reagent ions generated within the ion source chamber are expelled *via* a 2 cm wide circular aperture situated in the SEP concentric to the chamber itself. The ion source chamber is made vacuum tight with the use of Viton o-rings (Leicester Bearings Ltd., UK) situated between the plates and the central chamber cylinder.

2.2.1.2 Ion Generation within the Radioactive Ion Source

Reagent ions are produced within the ion source chamber following bombardment of neutral source gas molecules by α -particles emitted from the americium foil. In the case of hydronium generation (the main CI reagent employed in the CIR-MS technique), neutral water molecules are first converted to either H₂O^{+•} or OH⁺ (Kebarle *et al.*, 1967). It has been shown in various studies that following their production both of these ions will then react rapidly with H₂O to form the H₃O⁺ ion (Mann *et al.*, 1940; Lampe *et al.*, 1957):

$$H_2O + \alpha \rightarrow H_2O^{+\bullet}/OH^+$$
 (R2.1)

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + OH^{\bullet}$$
 (R2.2)

$$OH^+ + H_2O \rightarrow H_3O^+ + O^{\bullet}$$
 (R2.3)

Efficient hydronium production is ensured by maintaining the ion source chamber at high relative humidity (see Section 2.3.1). It should be noted here that the hydronium ion is also liable to form cluster complexes with the neutral water present within the ion source, forming ions of the type H_3O^+ .(H_2O)_n.

Using an identical α -particle emitter to that employed here, Hanson *et al.* (Hanson *et al.*, 2003) predicted a hydronium generation rate of roughly 10¹⁰ ions s⁻¹ from their ion source, which gave measured ion currents on the drift cell exit plate of 300 - 900 pA. Comparing these ultimate ion currents with those obtained by Blake *et al.* (Blake *et al.*, 2004) for the assembly described here (*i.e.* ~ 500 pA on the drift cell exit plate); a similar hydronium generation rate is likely.

In the case of other CI reagents, NH_4^+ ions are formed from neutral, gaseous ammonia in a similar manner to that described here for hydronium from water vapour, whereas, NO^+ and $O_2^{+\bullet}$ ions are most likely first generation ionisation products, formed following removal of an outer shell electron during collision with an α -particle.

2.2.2 The Drift Cell Reactor

The CIR-TOF-MS radioactive ion source is coupled directly to a *Drift Cell Reactor*, in which a proportion of the analyte molecules are converted to ionic form through reaction with the CI reagent. The CIR-TOF-MS drift cell reactor is composed of a series of five guide electrode plates and spacers. As with the SEP, each guide plate is constructed from stainless steel and has an external diameter of 6.2 cm and thickness of 0.4 cm. Each plate has an internal diameter of 5.4 cm and an electrode thickness of 0.2 cm (see **Figure 5(a)**). The electrodes are constructed with a central circular aperture through which the ions are channelled. All plate apertures are concentric with one another and the SEP of the radioactive ion source. As will be discussed below the electrode apertures have various sizes.



Figure 5: Drift cell reactor guide electrodes (a) and spacers (b) (dimensions given in cm)

The guide electrodes within the drift cell assembly are separated from each other by a series of five spacers constructed from Semitron ESD 500 (Quadrant Engineering Plastics, USA), a static dissipative material with a volume resistivity of the order $10^{11} \Omega$. Each of the Semitron spacers has an outer diameter of 5.4 cm, a depth of 2 cm and an internal diameter of 3.6 cm (see **Figure 5(b)**). Consequently there exists an internal volume of approximately 20.4 cm³ between each electrode. As within the ion source, vacuum seal is achieved in the drift cell with the use of Viton o-rings situated between each spacer and electrode. A diagram of the drift cell reactor is given below in **Figure 6**.



Figure 6: Diagram of the CIR-TOF-MS drift cell reactor and source drift region (dimensions given in cm)

The SEP of the radioactive ion source and the first guide electrode of the reactor cell (referred to hereafter as the *Reactor Entry Plate*- REnP) are separated from each other by a *Source Drift Region* of length 2 cm (*i.e.* the first of the Semitron spacers). As will be discussed in detail below (Sections 2.4 and 2.5), an electric field is generated within the source drift region by the application of a potential difference between the SEP and the REnP. The electric field acts to accelerate the reagent ions out of the ion source and to focus them into an ion beam. The reagent ions exit the source drift region and enter the drift cell reactor *via* a 1 cm aperture situated in the REnP. In concert, the relatively narrow aperture of the REnP and the source drift region help to limit the back streaming of gas resident within the reactor back towards the ion source. Should any gas molecules 'leak' from the reactor back into the ion source they may become ionised by direct interaction with the α -particles, and hence may ultimately proceed to perturb the chemistry of the reactor and invalidate the CIR-MS technique. Clearly

then, it is crucial that within a CIR-MS ion source/drift cell assembly, no gas molecules are allowed to enter the ion source region from the direction of the reactor.

Following exit from the source drift region, the ion beam is channelled through the reactor by an electric field generated by three identical *Guide Electrode Plates* (referred to hereafter as GEP1, GEP2 and GEP3). Each GEP has a circular aperture of diameter 2 cm machined into the centre of the plate to allow transit and focusing of the ion beam. The aperture of each GEP is concentric with the aperture of the SEP and the REnP. Each GEP is separated by a Semitron spacer such that the drift cell reactor has a total length of 10.75 cm and a reaction length of 8.45 cm. The total internal volume of the reactor assembly is roughly 81.4 cm³.

The sample gas is introduced into the drift cell reactor *via* a 0.48 cm internal diameter PTFE (polytetrafluoroethylene) inlet (Entergris, De.). The sample inlet is mounted centrally in the second Semitron spacer of the reactor assembly separating the REnP and GEP1, such that the sample gas enters the cell perpendicularly to the flow of the primary reagent ions. Once resident within the reactor, the sample gas is pulled along a pumping gradient to the base of the cell, where any neutral gas molecules are expelled *via* a 0.76 cm internal diameter PTFE outlet connected to a dry *Scroll pump* (Varian Ltd., It., model: SH-01001). Similar to the sample inlet, the drift cell exhaust outlet is mounted directly into the fifth Semitron spacer and oriented such that the gas glow out of the cell is perpendicular to the direction of the ion beam.

As the primary reagent ions are guided through the drift cell reactor they will encounter buffer gas molecules in collisional events, which result in an equilibrium becoming established within the energy distribution of the reagent ion pool, or 'swarm'. Subsequent collisions with analyte molecules may occur as the reagent swarm continues to be drawn along the reactor, and chemical ionisation may result providing specific kinematics are obeyed (see Chapter 3). Once ionised the target species within the sample will move along the potential gradient of the electric field to the drift cell *Reactor Exit Plate* (RExP).

The gas pressure within the ion source/reactor assembly is measured at the centre of the cell by a Baratron dual capacitance manometer (MKS Ltd., USA, model: 750B) and a Pirani pressure gauge (Leybold Ltd., UK). Both pressure gauges are coupled to the drift cell *via* a 0.48 cm internal diameter PTFE fitting coupled directly to a Semitron spacer. Pressure measurements from the Baratron are read by a PDR 2000 digital readout (MKS Ltd., USA) and are subsequently recorded by an NI-DAQ mx data logging device (National Instruments,

USA) on a 1 second time scale. *Real-time* pressure measurements from the Pirani pressure gauge are displayed by a second digital readout.

2.2.3 The Exit Collision Cell

At the base of the drift cell the ion beam will traverse the final electrode of the reactor, designated the *Reactor Exit Plate* (RExP), before entering an *Exit/Collision Cell* (ECC). The reactor exit plate additionally constitutes the first electrode of the ECC. The RExP is similar in design to those electrodes previously described, with the exception of a smaller central aperture of diameter 0.6 cm. Reducing the size of the aperture at his point facilitates focusing of the ion beam and helps to limit gas pressure near the entry to the high vacuum region of the mass spectrometer (Blake, 2005).

The exit/collision cell fulfils several crucial roles within the CIR-TOF-MS. Primarily the ECC acts to accelerate the ions generated within the reactor to their final exit velocity and helps to focus the ion beam into the transfer optics of the mass spectrometer. Additionally, the ECC provides the reactor with a tuneable region within which the ions may be collisionally dissociated (Warneke *et al.*, 2001). As well as providing structural information regarding the analyte, collision-induced dissociation of the ions at this stage can be employed to limit or remove any unwanted ion-neutral clustering (Hanson *et al.*, 2003).

Throughout this thesis two variants of the CIR-TOF-MS radioactive ion source/drift cell assembly have been employed, which differ only in the design of the ECC and in the coupling of the entire assembly to the mass spectrometer. The two variants of the ion source/drift cell assembly and ECC shall be referred to as designs Mk.1 and Mk.2.

2.2.3.1 Drift Cell Design Mk.1- Exit Collision Cell

The Mk.1 ECC is composed of two electrodes, the RExP and a *Final Exit Plate* (FExP), separated by a 0.42 mm thick wafer of PTFE. The ECC plates are fixed together with three 6 mm nylon screws. As within the drift cell, vacuum seal is ensured within the ECC by the appropriate use of Viton o-rings located between each component.

Having traversed the ECC, the ion beam encounters a *transfer aperture* (Micrometrics, UK) mounted on the upper surface of the FExP. An aperture is required here in order to facilitate separation of the 'high' pressure region of the reactor from the low pressure region of the mass spectrometer. The transfer aperture of the ECC is a precise laser drilled pin hole in a small stainless steel disc of diameter 2.5 cm and depth 0.4 mm. It has been noted by various

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workers that it is imperative to keep the transfer aperture as thin as possible; an overly deep aperture has been noted to have a severely detrimental effect on the transmission of the ion beam (Reich, 2005).

Selecting the correct size of pinhole to act as the exit aperture of the drift cell assembly is a compromise between ion transmission and achieving the required vacuum within the mass spectrometer. It has been previously determined that in order to achieve the optimum gas pressure within the transfer region of the Kore MS-200 time-of-flight mass spectrometer, the diameter for the exit aperture must be no more than 200 μ m (Blake, 2005). Increasing the aperture diameter above this to 300 μ m will allow more gas to enter the mass spectrometer, which will result in signal loss due to scattering of the ion beam prior to detection. Despite providing favourable pressures, a decrease in aperture diameter to 100 μ m has also been shown to reduce detected yields (by a factor of 4), by impairing the transmission of the ion beam into the mass spectrometer (Blake, 2005).

Once the ion beam exits the pin hole transfer aperture, it passes through a 0.68 cm deep skimmer cone arrangement machined within the FExP. Conical lenses are often used at transition points between low and high pressure as they counter focusing problems that result from super sonic expansion of the ion beam (Whyte, 2003).

2.2.3.2 Design Mk.1- Coupling to the Mass Spectrometer

The radioactive ion source, the drift cell reactor and the Mk.1 variant of the ECC are held together by three threaded insulating rods, which in turn are fixed to a Conflat (CF) iso-160 stainless steel flange. The entire assembly is compressed by three 6 mm nuts applied to the rods at the uppermost plate of the ion source, as shown in the photograph of **Figure 7**. A 1.7 mm thick Tufnell spacer is employed at the base of the assembly in order to separate the FExP from the mounting flange.

As was described in Section 2.1, in order to maximise overall instrument sensitivity the drift cell should be operated at as high a pressure as possible. However, an increase in the drift cell pressure will cause a corresponding increase in pressure within the mass spectrometer, which will cause a decrease in sensitivity through scattering of the ion beam. To overcome this problem, a differential pumping regime is established within the CIR-TOF-MS with the use of an intermediate pumping chamber located within the Mk.1 variant mounting flange. The intermediate chamber is evacuated by a turbo molecular pump, of pumping speed 70 litres per second (Varian Ltd., It., model: V-70). A dual stage rotary vane pump, of pumping speed 8

 m^3 per hour (Varian Ltd., It., model: DS-102) is employed to provide the requisite backing pressure for the turbo pump. When pressures within the Mk.1 drift cell are of the order 10 – 12 mbar (*i.e.* standard operating conditions), pressures within the intermediate pumping chamber and the transfer region of the mass spectrometer are roughly 10⁻⁴ and 10⁻⁶ mbar, respectively. The Mk.1 variant of the ECC and the intermediate pumping chamber are shown diagrammatically in **Figure 8**.



Figure 7: The Mk.1 variant of the radioactive ion source/drift cell assembly



Figure 8: The Mk.1 variant of the ECC and the intermediate pumping chamber.

Having traversed the intermediate pumping chamber within the Conflat mounting flange (path length ~ 2.2 cm), the ion beam passes through a 5 mm aperture before entering the *Transfer Lenses* of the mass spectrometer.

2.2.3.3 Drift Cell Design Mk.2- Exit Collision Cell and Coupling to the Mass Spectrometer

Results obtained from modelling simulations suggest that the ion beam emerging from the FExP takes the form of a cone (Blake, 2006), with the apex centred on the transfer aperture located in the FExP (shown in the diagram of **Figure 8**). Clearly, as the distance between the apex of the cone and the entrance aperture of the transfer optics increases, so will the percentage of ions lost to the walls of the first transfer lens. The Mk.2 ECC was developed to remedy this problem by increasing the fraction of ions passed from the reactor to the mass spectrometer. Consequently, an improvement is conferred to detection capability under the premise that increasing the percentage of the ion beam passed through to the mass analyser increases signal strength.

In essence an improvement is achieved in ion beam transmission by moving the entire ion source, drift cell and ECC assembly closer to the transfer optics of the mass spectrometer. To facilitate this rearrangement, the transfer aperture was moved from the FExP to the underside of the mounting flange, reducing the path length of the ion beam between the exit of the collision cell and the mass spectrometer to only ~ 0.5 cm. In order to accommodate this rearrangement the intermediate pumping chamber, the FExP and PTFE wafer were removed from the system and a second mounting flange containing a 1.5 cm deep stepped well was employed (see **Figure 9** and main diagram in **Figure 3**). Consequently, the collision region of the Mk.2 ECC constitutes the 0.83 cm deep region situated between the RExP and the transfer aperture plate.



Figure 9: The Mk. 2 variant of the exit/collision cell

The RExP, the drift cell and ion source are fixed together, as well as to the mounting flange, by three 6 mm diameter threaded rods, as in design Mk.1. The RExP is separated both physically and electrically from the Conflat mounting flange by a 1.7 mm deep Tufnell spacer, while Viton o-rings provide vacuum seal.

With no intermediate pumping chamber to limit the gas load at the entry of the mass spectrometer, the Mk.2 drift cell is operated at lower pressures than its predecessor. Gas loading and resultant pressures are discussed below in Section 2.3.3.

Despite imposing the requirement for a lower reactor pressure, use of the Mk.2 design ECC substantially increases the magnitude of the measured primary reagent ion signal. For example, the H_3O^+ count measured using the Mk.1 and Mk.2 ECC variants are of the order 3000 and 7000 counts s⁻¹, respectively. Increased ion transmission also results in an improvement in the ultimate instrument detection limit for any given analyte.

2.3 Gas Delivery

2.3.1 Reagent Gas Delivery

Neutral reagent molecules are delivered to the ion source chamber for ionisation, in gaseous form. The reagent gas is injected into the ion source chamber at a flow rate of 30 - 52 sccm (standard cubic centimetres per minute), which is maintained at a constant value by a mass flow controller (Celerity, CA, model: Tylan FC260) situated between the neutral reagent gas source, which resides at atmospheric pressure, and the vacuum of the reactor. The reagent gas is delivered from the mass flow controller to the ion source chamber *via* a heated 1/8" Teflon tube held at 40 °C (\pm 1 °C). Maintaining a relatively high flow rate of source gas into the ion source chamber further helps to prevent sample and buffer gas molecules back diffusing from the reactor into the ion source, and hence ensures that all analyte ions are formed solely within the reactor *via* ion-molecule reactions involving the primary reagent ion (Hanson *et al.*, 2003).

In the case of hydronium generation, water vapour is supplied to the ion source by passing a pure nitrogen carrier gas (BOC Special Gases, 99.9999 % purity) through a glass vessel containing high purity deionised water (15 M Ω). All other reagent gases are typically delivered from cylinder. The use of high concentration or pure source gases has been shown to suppress formation of 'background' ions and thus helps ensure purity of the ion generation.

2.3.2 Sample Gas Delivery

The sample gas is delivered to the reactor in a continuous flow *via* a second mass flow controller (Celerity, CA, model: Tylan FC260) and a second 1/8" Teflon tube, also heated to 40 °C (\pm 1 °C). Typically the flow rate of sample gas into the reactor is of the order 230 – 260 sccm. In order to prevent wall losses when the sample gas is known to contain particularly condensable material, the mass flow controller is substituted for a simple PTFE critical orifice.

2.3.3 Gas Load and Gas Behaviour within the CIR-TOF-MS Drift Cell

As the pumping speed of the entire instrument is fixed, the combined flow rates of both input gases will determine the pressure in both the reactor and the mass spectrometer. **Table 1**, shown below, gives typical pressures recorded in the reactor and mass spectrometer at various flow rates of reagent and sample gases (note: pressures given in **Table 1** were obtained when the reactor was fitted with the Mk.2 variant of the ECC).

Table 1:	Drift cell	(Mk.2) and	transfer c	hamber	pressures	for a n	umber o	of example	gas loads	s (i.e.	the sum	of the
reagent ar	nd sample	gas flows).										

Gas Load / sccm	Drift Cell Pressure	Transfer Chamber Pressure		
(reagent gas / sample gas)	/ mbar	/ mbar		
10 / 100	3.2	5.9×10^{-7}		
15 / 150	4.1	$7.9 imes 10^{-7}$		
20 / 200	4.9	9.9×10^{-7}		
25 / 250	5.7	$1.2 imes 10^{-6}$		
30 / 300	6.6	1.3×10^{-6}		

The CIR-TOF-MS is typically operated at reactor pressures of 7.0 - 12.0 mbar when equipped with the Mk.1 variant of the ECC, and 5.0 - 6.5 mbar with the Mk. 2 variant. These pressures represent a compromise between maximising pressure within the reactor to achieve large ion-molecule reaction yields, and minimising pressure within the mass spectrometer in order to prevent scattering of the ion beam (Chambers *et al.*, 1998).

At typical operating pressures, the gas within the CIR-TOF-MS reactor approximates a 'perfect gas' hence it obeys the Maxwell-Boltzmann kinetic model, in which all molecules can be approximated as hard, elastic spheres which are small in comparison to their separation (Chambers *et al.*, 1998). Consequently, prior to the application of the electric field the molecules within the drift cell have a Maxwellian energy distribution, with average kinetic energy and speed defined by equations (E2.1) and (E2.2), respectively.

$$\frac{1}{2}m\bar{v}^{2} = \frac{3}{2}k_{B}T \qquad (E2.1) \qquad \bar{v} = \sqrt{\frac{8k_{B}T}{\pi m}} \qquad (E2.2)$$

where, m = molecular mass of the gas molecules, k_B = Boltzmann's constant and T = temperature. Using equation (E2.1), the average kinetic energy of neutral molecules within the reactor maintained at 40 °C is 6.49×10^{-21} J (*i.e.* 0.04 eV). The kinetic energies of ions within the reactor are substantially different to this as will be shown in Section 2.6.

At a given temperature (*T*) and pressure (*p*), the number density (*N*) of gas molecules within the CIR-MS reactor is given by equation (E2.3):

$$N = \frac{N_A T_0 p}{T p_0 V_{mol}}$$
(E2.3)

where N_A = Avogadros number (*i.e.* 6.02×10^{23} mole⁻¹), T_0 and p_0 = standard temperature and pressure (*i.e.* 273.16 K and 1000 mbar, respectively) and V_{mol} = the volume of one mole (*i.e.* 22400 cm³ mole⁻¹) (Blake, 2005). Under typical operating conditions of 6 mbar pressure and 40 °C, the gas number density within the reactor is $\approx 1.41 \times 10^{17}$ cm⁻³. With knowledge of *N* it is possible to determine the distance travelled by each molecule (of diameter, *d*) within the reactor between collisions, *i.e.* the mean free path (λ), using equation (E2.4):

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 N} \tag{E2.4}$$

Assuming the reactor to be populated primarily with nitrogen molecules (d = 3.7 Å), $\lambda = 1.2 \times 10^{-5}$ m at 6 mbar and 40°C.

2.4 Generation of the Electric Field

An electric field is employed within the reactor assembly to constrain the ions into a coherent beam and to guide them towards the transfer optics of the mass spectrometer. For the flow of positive ions away from the ion source, the source itself and the first guide electrode (*i.e.* the SEP) are held at a high, positive electrical potential relative to earth. In order to generate an electric field such that the ions are subsequently drawn along the drift cell, away from the ion source, each successive guide plate is held at a progressively lower positive potential relative to earth. To ensure the electric field gradient has a constant slope throughout the reactor, the potential difference between each plate is held constant. In order to facilitate the required energy 'ramp' before drift cell exit, the electric field strength is increased over the ECC.

The voltage required by the ion source/drift cell assembly is supplied by a Stanford Research Systems PS350 power supply unit (PSU). A simple resistor chain is employed to distribute the total output voltage of the PSU amongst the various electrodes of the ion source, reactor

and ECC, in which five 1 M Ω resistors are coupled in series. During typical operation, input potentials of the order 500 – 3000 V are employed to generate electric fields of ~ 45 – 280 V cm⁻¹. To allow variable control of the energy ramp over the ECC, two further variable resistors are included at the end of the chain. For the Mk.1 variant of the ECC the electrical potential difference is varied in two stages; first by roughly 0 – 100 V prior to the transfer aperture and then by 0 – 50 V over the 1.7 mm Tufnell spacer (Blake, 2005). The potential difference across the Mk.2 variant of the ECC is varied in one single stage, between ~ 30 and 280 V. **Figure 10** shows the circuit diagram for voltage supply to the Mk.2 variant of the ion/source drift cell assembly.



Figure 10: Circuit diagram showing the resistor chain employed to facilitate voltage division amongst the electrodes of the ion source, reactor and ECC (note, R6 represents two variable resistors)

It has become convention to describe the energy within a drift tube type device in terms of the electric field strength per gas number density, or an E/N ratio (McFarland *et al.*, 1973a). The gas number density, N, has been defined above in equation (E2.3) and the value of E (the magnitude of the electric field) is simply the potential difference between two points (V) divided by their separation distance (l), *i.e.*:

$$E = \frac{V}{l} \tag{E2.5}$$

The *E/N* value is often quoted following multiplication by a factor of 1×10^{17} , to give the result in *Townsend* (Td) units (Lindinger and Hansel, 1997). The *E/N* convention described here is used throughout this thesis to describe the energy imparted to the ions during their transit through the reactor.

2.5 Ion Optics in Mass Spectrometry

As electric fields and the electrodes, or 'ion optics', which generate them play such a major role in the CIR-TOF-MS system, a brief overview of their basic underlying physics is provided in the following sections.

2.5.1 The Principles of Ion Optics

An electric field (*E*) will exert some quantity of force (*F*) on a discrete particle carrying some quantity of charge (q_{θ}), equal to the vector product of the field and the charge (Tipler, 1999), *i.e.*:

$$\boldsymbol{F} = \boldsymbol{q}_0 \boldsymbol{E} \tag{E2.6}$$

Note, vectors are denoted by bold symbols.

It is because of this force that an electric field exerts upon a charged particle, that they can be used within a mass spectrometry system to move, guide, constrain or accelerate the ions produced (Wollnik, 1999). Electric fields are generated within a mass spectrometer by the application of an electrical potential to *electrode plates* or *guide rings*, which may be analogously thought of as the lenses and mirrors of an optical system employed to move a beam of light. Because of this analogy, all components of the mass spectrometer that employ electric fields to influence the ion beam are referred to as *ion optics*.

When an ion carrying charge, q_0 , resides within an external electric field, E, generated by certain ion optics within the mass spectrometer, it will possess a quantity of electrical potential energy, U, which is a function of q_0 , E and position, r_1 , of the ion within the electric field (Tipler, 1999). The electrical potential of the stationary ion at position r_1 is defined as the electrical potential energy per unit charge, *i.e.*:

$$V = \frac{U}{q_0} \tag{E2.7}$$

The force exerted by the electric field on the ion may be sufficient to cause the ion to move some distance ds. When a charge carrying particle moves within an electric field, its electrostatic potential energy, U, will be changed by a quantity equal to the negative of the work done by the electric field in moving the ion the defined distance, *i.e.*:

$$dU = -q_0 \boldsymbol{E}.d\boldsymbol{s} \tag{E2.8}$$

If equation (E2.8) is divided by q_0 , the result is the potential energy change per unit charge, or the electrical potential difference (dV):

$$\frac{dU}{q_0} = -\boldsymbol{E}.d\boldsymbol{s} = dV \tag{E2.9}$$

Consequently, the change in electrical potential between points r_1 and r_2 , is given by:

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$$\Delta V = V_{r2} - V_{r1} = \frac{\Delta U}{q_0} = -\int_{r1}^{r_2} E.ds$$
 (E2.10)

In moving the ion from point r_1 to r_2 the electric field will have imparted some quantity of velocity to the ion, and in doing so will have increased its kinetic energy (*KE*). The kinetic energy gained by the ion moving from one potential to another is equivalent to the work done on the ion by the electric field (Tipler, 1999), *i.e.*:

$$KE = \Delta U = -q_0 \int_{r_I}^{r_2} E.ds$$
 (E2.11)

2.5.2 Plain Electrostatic Plates

The simplest form of electrostatic lens employed within the CIR-TOF-MS system essentially comprises a flat metal electrode electrically biased by an external power supply. Lenses of this type include the x and y 'steering' plates and the back plate of the 'pulser' unit of the TOF-MS (see Section 2.9). When an ion crosses the equipotential field lines established between two plain electrodes (of potential difference ΔV), work will be done on the ion as described above and it will undergo acceleration or deceleration accordingly.

2.5.3 Aperture Lenses

The electric field employed within the ion source/drift cell assembly of the CIR-TOF-MS is established by the application of an electrical bias to the guide electrodes. Each of the guide electrodes described above essentially constitutes a simple *aperture*, or *Calbick* lens (Moore *et al.*, 1991). As well as causing the charged particles to accelerate to a given velocity as they traverse the equipotential surfaces established within the drift cell, the electric field produced by each aperture lens acts to focus the ion beam to a certain 'focal point'. This focusing effect arises from the equipotential surfaces breaking into the region of the aperture, as shown in **Figure 11** (Moore *et al.*, 1991). In the reactor the focal point of the ion beam is the aperture of the RExP plate and the ECC. Increasing the magnitude of the electric field will increase the focusing effect of the lens, hence the requirement for a large potential difference across the ECC in order to focus the ion beam onto the transfer aperture to the mass spectrometer.



Figure 11: Diagram depicting the equipotential lines generated around an aperture lens arrangement with finite separation (a and b). Voltages V_1 , V_2 and V_3 represent a potential gradient (adapted from (Moore *et al.*, 1991)).

2.6 Ion-Molecule Kinetics within the CIR-TOF-MS Reactor

Under the influence of the applied electric field, those ions generated within the ion source and within the reactor are accelerated along the length of the drift cell until they ultimately reach their terminal drift velocity (v_d , which for simplicity shall be referred to as a scalar quantity for the purpose of this work). Ion drift velocity is determined not only by the magnitude of the electric field (*E*), but also by the number of collisional encounters an ion makes with those molecules comprising the buffer gas. Consequently, the ion drift velocity can be determined from the product of the electric field and the *ion mobility* (μ) (Fairley *et al.*, 1999):

$$v_d = \mu E \tag{E2.12}$$

Ion mobility is a pressure and temperature dependent parameter describing the transit of a given ion through a specific buffer gas (Dotan *et al.*, 1976). The value of μ for a specific set of conditions can be determined through knowledge of the experimentally derived *reduced mobility* (μ_0) using equation (E2.13) (Dotan *et al.*, 1976; Viehland and Mason, 1995):

$$\mu = \frac{760}{P} \frac{T}{273.16} \mu_0 \tag{E2.13}$$

where, *P* and *T* are the pressure and temperature of the buffer gas in units of Torr and Kelvin, respectively (McFarland *et al.*, 1973a). Substituting for μ in equation (E2.12) the expression for *v_d* becomes:

$$v_d = \frac{760}{P} \frac{T}{273.16} \mu_0 E \tag{E2.14}$$

If we now define the parameter N_0 to be the gas number density under standard temperature and pressure (*i.e.* 273.16 K and 760 Torr), equation (E2.14) may be rewritten as follows:

$$v_d = \mu_0 N_0 \frac{E}{N} \tag{E2.15}$$

Equation (E2.15) now clearly demonstrates that the drift velocity of a given ion is directly proportional to the applied electric field and inversely proportional to the number density of the prevailing buffer gas, *i.e.* that the ion drift velocity is proportional to the E/N ratio of the drift cell reactor (de Gouw and Warneke, 2007).

If the length (L) of the drift cell reactor is known, then equation (E2.15) can be employed to calculate the transit time of a given ion through the cell:

$$t = \frac{L}{\mu_0 N_0} \frac{N}{E} \tag{E2.16}$$

As will be discussed further in Chapter 3, reactor transit time can be used as an approximation of ion-molecule reaction time. This is turn can be employed along with the appropriate reaction rate constant (k), in order to determine the absolute concentration of a given analyte without the requirement for experimentally derived calibration factors.

By accelerating an ion to its terminal drift velocity, the applied electric field facilitates an increase in its overall kinetic energy. The kinetic energy of an ion (KE_{ion}) travelling at its terminal drift velocity in a buffer gas can be obtained using the Wannier equation:

$$KE_{ion} = \frac{3}{2}k_BT + \frac{m_i v_d^2}{2} + \frac{m_b v_d^2}{2}$$
(E2.17)

where k_B is Boltzmann's constant, m_i is the mass of the ion and m_b is the average mass of the buffer gas molecules (Wannier, 1953; McFarland *et al.*, 1973b).

The first term on the right hand side of equation (E2.17) (*i.e.* $3/2 k_BT$) gives the *thermal energy* of the ion, which is clearly dependent solely on the temperature of the gas mixture. The second term of equation (E2.17) (*i.e.* $m_i v_d^2/2$) constitutes the *drift energy* component of the ion's kinetic energy, which arises simply from the terminal drift velocity of the ion moving under the influence of the electric field. Finally, the third term of equation (E2.17) (*i.e.* $m_b v_d^2/2$) constitutes the *random field energy* component, which accounts for the random collisions of the ion with the neutral molecules of the buffer gas (Fairley *et al.*, 1999).

For a collision involving the same test ion with a neutral analyte molecule of molecular mass, m_a , the total collision energy in a reference frame central to the collision event (KE_{cm}), can be determined from the kinetic energy of the ion (KE_{ion}) and the thermal energy of the system (McFarland *et al.*, 1973b; Blake *et al.*, 2006)

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$$KE_{cm} = \frac{3}{2}k_{B}T + \frac{m_{a}}{m_{a} + m_{i}}\left(KE_{ion} - \frac{3}{2}k_{B}T\right)$$
(E2.18)

The mean ion-molecule centre of mass kinetic energy resulting from collision of the reactant ion with a molecule of the buffer gas, can be obtained simply through substitution of m_b into equation (E2.18) in place of m_a (Fairley *et al.*, 1999).

Clearly, an increase in the magnitude of the electric field will result in an increase in the kinetic energy of the ion pool and thus collision events of enhanced energy. As the collision energy (*i.e.* KE_{cm}) is increased, so is the possibility that bonds will be dissociated within the colliding molecules. Bond cleavage in an ion-molecule collision event is known as *collision-induced dissociation* (CID) (de Hoffman and Stroobant, 2007). CID is highly useful in limiting unwanted ion-neutral clustering (McLafferty and Turecek, 1993), which can cause a decrease in sensitivity if the primary reagent ion is involved (see Chapter 5). Also, should the ionised analyte undergo ion-neutral clustering, problems associated with spectral congestion may also arise and interpretation of the resultant data may be somewhat difficult.

2.7 Simulations of the CIR-TOF-MS Ion Source/Drift Cell Assembly

In order to aid early design and development work of the CIR-TOF-MS system, the ion trajectory program SIMION (Bechtel BWXT, USA) was employed to simulate the evolution of the ion beam in the ion source drift/cell assembly. SIMION has been successfully employed by various workers in the design of similar mass spectrometry systems; see for example Hanson *et al.* (2003), Ennis *et al.* (2005) and Blake (2005). The SIMION program simulates the electric fields generated by user defined electrodes and predicts their subsequent impact upon a test ion packet. The basic SIMION package does not consider the presence of a gas load, but for the work presented here the effect of neutral gas molecules was accounted for by the inclusion of the custom parameter driven code published by Gillig and colleagues (Gillig *et al.*, 2004). **Figure 12** shows the results obtained from a simulation of the CIR-TOF-MS ion source/drift cell assembly, coupled to the Mk.2 variant of the ECC. The model was run at a temperature of 40 °C and with a typical 6 mbar operating pressure. The reactor and ECC electric fields were 155 and 245 Vcm⁻¹, respectively, giving *E/N* values of 110 and 170 Td. The simulated ion packet comprised 20 hydronium ions (H₃O⁺, *m/z* = 19) and the buffer gas was nitrogen (molecular mass = 28 g mol⁻¹).



Figure 12: SIMION simulation of the CIR-TOF-MS radioactive ion source/drift cell assembly equipped with the Mk.2 variant of the ECC

In Figure 12 the white grids represent the guide plate electrodes and the green lines depict the equipotential surfaces of the electric field generated once the plates are electrically biased. The black lines map the calculated ion trajectory. Figure 12 shows how the ion packet is constrained into a relatively coherent beam by the electric field as it travels along the length of the drift cell. Results obtained from the model simulation suggest that roughly 75 - 85 % of the ions generated successfully reach the end of the cell, and impinge upon the aperture plate situated in the mounting flange. Figure 12 also constitutes a prime example of how the electric field produced by an aperture lens style guide plate, protrudes into the aperture region to generate focusing of the ion beam.

2.8 Time-of-Flight Mass Spectrometry

Following its generation within the drift cell, the ion beam is passed into the Kore MS-200 Time-of-Flight mass spectrometer for mass analysis. In this section the basic principles and components of TOF-MS are discussed, before a specific overview of the MS-200 system is given in Section 2.9.

2.8.1 The Basic Principles of Time-of-Flight Mass Spectrometry

Time-of-Flight mass analysers were first introduced in 1946 by Stephenson (Stephenson, 1946) for use in experiments in nuclear physics. Almost a decade later the first commercial instruments were made available and publications were presented by Wiley and McLaren (Wiley and McLaren, 1955). The main principle at the heart of the TOF-MS technique is the separation of ions in time rather than in space, as is the norm for most mass spectrometers.

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For example, consider a distribution of ions covering a range of masses. If each ion within this pool is given an equal amount of kinetic energy by accelerating the ion pool over a finite distance, the ions will travel through a field free region with a terminal velocity proportional to their mass-to-charge ratio (m/z). This is demonstrated in **Figure 13**, where ions A and B of equal charge and masses m_A and m_B , respectively ($m_B > m_A$), are accelerated over a distance P_L ; ion A of lower mass will acquire a greater velocity hence will have the shorter time-of-flight. If the distance that the ions travel in the field free region, F_L , is fixed and well known, each mass-to-charge ratio will have its own characteristic *time-of-flight* (TOF). Consequently, the measurement of an ion's TOF can be employed to determine its m/z.



Figure 13: Diagram to show the basic components and principles of a linear TOF-MS system (adapted from Whyte (2003))

A TOF-MS instrument is composed of four distinct components, these are, (i) an ion extraction/acceleration region (or *Pulser*), (ii) x and y steering plates, (iii) a field free flight tube and (iv) a detector. All components of the TOF-MS reside under high vacuum ($< 10^{-6}$ Torr), as collisions with gas molecules will cause scattering of the ion beam and perturbation of the ion flight. The coupling of some of these components in a TOF-MS system is shown diagrammatically in **Figure 13**.

2.8.2 Time-of-Flight Mass Spectrometry: Theoretical Principles

Many substantial reviews on the TOF-MS technique and its underlying theoretical principles have been conducted (Guilhaus, 1995; Cotter, 1999), hence only a basic overview is provided here.

In continuous beam systems, once the ion beam exits the ion source it often undergoes some form of focusing in a *Transfer Region* within the TOF-MS before being passed to the *pulsed ion extraction region*. In its most simple form, the pulse extraction region, or the *pulser*, consists of two electrodes separated by a distance, P_L , over which a pulsed potential

$$E = Ze\Delta V = z\Delta V = zEP_L = \frac{mv_d^2}{2} = KE$$
 (E2.19)

Rearranging equation (E2.19), an expression may be derived for the terminal drift velocity of the ions:

$$v_d = \sqrt{\frac{2zEP_L}{m}} \tag{E2.20}$$

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Having acquired their terminal velocity, the ions enter a field free *flight tube*, in which they are isolated from any external forces. The ions will travel the length of the flight tube (F_L) at their constant, terminal drift velocity in a time (t_F) given by:

$$t_F = \frac{F_L}{v_d} \tag{E2.21}$$

Substituting equation (E2.20) into (E2.21), we obtain the flight time for the ions in the field free region:

$$t_F = \sqrt{\frac{m}{2zEP_L}}F_L \tag{E2.22}$$

If there were no other factors to consider, equation (E2.22) would give the final flight time of the ions. However, it might also be necessary to consider their response time (t_0), following application of electric field. Other factors that might also require consideration are the response time of the detector (t_d), and the time taken for the ions to undergo acceleration within the pulser. The ion acceleration time can be determined trivially by equating F = Ez with F = ma and solving for acceleration (a):

$$a = \frac{Ez}{m} \tag{E2.23}$$

From a = dv/dt it follows that, the terminal velocity achieved by the ions is:

$$v_d = v_0 + \left[\frac{Ez}{m}\right]t \tag{E2.24}$$

where, v_0 = the initial component of velocity of the ions in the direction of the electric field. Thus the time spent by the ions undergoing acceleration within the pulser is given by $t_a = dv/a$, *i.e.*:

$$t_a = \frac{v_d - v_0}{E} \frac{m}{z} \tag{E2.25}$$

Taking into account these additional factors, the total ion time-of-flight is given thus:

$$TOF = t_0 + \left[\frac{v_d - v_0}{E}\frac{m}{z}\right] + \left[\sqrt{\frac{m}{2zEP_L}}F_L\right] + t_d$$
(E2.26)

Generally, $t_F \gg t_0 + t_a + t_d$ (Guilhaus, 1995), hence from equation (E2.26) it becomes clear that the ion TOF is proportional to $\sqrt{(m/z)}$.

2.8.3 The Duty Cycle

From the basic principles of TOF-MS described above, it is clear that only one 'packet' of ions may be extracted from the continuous source beam for analysis at any one instant. This means that whilst each ion packet is 'in flight' the continuous ion beam not under analysis is simply lost to exhaust. That fraction of ions which are extracted for analysis is known as the *duty cycle* of the instrument (D_C). The duty cycle of a TOF-MS is defined by three parameters: (i) the size of the extraction aperture in the extraction electrode (X_l), (ii) the speed of ions within the continuous ion beam (u_c) and (iii) the repetition frequency of the scan (f) (Inomata *et al.*, 2006):

$$D_C = \frac{X_I f}{u_c} \tag{E2.27}$$

In typical modern TOF mass spectrometers, the duty cycle rarely exceeds ~ 2 % (Blake *et al.*, 2008), meaning 98 % of the generated ion beam is simply lost. Consequently, the low instrument duty cycle of TOF-MS results in its major drawback, *i.e.* limited sensitivity.

2.8.4 Orthogonal Acceleration TOF Mass Spectrometers

Orthogonal acceleration TOF mass spectrometers were developed to counter some of the major problems associated with simple linear acceleration devices (Dawson and Guilhaus, 1989). In an orthogonal device the field free flight tube is situated in a roughly perpendicular orientation with respect to the ion source/drift cell assembly, the transfer optics and the pulsed extraction region (Guilhaus, 1995). The first major benefit of this design is that the ions to be analysed are extracted in a direction that is 90° to that of the flow of the continuous ion beam. Consequently, the ion packets produced are generally 'tighter' due to the ions having minimal velocity components in directions other than that of the continuous beam (Guilhaus, 1995). The production of tighter ion packets ultimately leads to enhanced instrument resolution (see Section 2.8.5). Secondly, as the extraction electrodes themselves are situated perpendicularly to the flight tube, the extraction region can be 'filled' with a new ion packet whilst the first is

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under analysis. This more efficient use of the pulser helps to improve the cycle time and hence increases the overall duty cycle (Guilhaus, 1995).

2.8.5 TOF-MS Resolution and the Reflectron

In mass spectrometry, the term *mass resolution* is used to defined the ability of the instrument to distinguish between two ions of similar mass (de Hoffman and Stroobant, 2007). Because of instrument limitations, ultimately there will always be some degree of 'spread' in the energy distribution of ions within a single ion packet. Due to this energy spread a peak in the TOF mass spectrum will not comprise a single discrete signal; instead it will be composed of a range of signals with a roughly Gaussian distribution. Hence, for a single peak with no spectral interference, the resolution of a mass spectrometer can be quantified by taking the ratio of the peak mass (*m*) to the peak width (Δm) at half the height of the peak, *i.e.* the *full width half maximum* (FWHM) mass:

$$R = \frac{m}{\Delta m} \tag{E2.28}$$

In the case of TOF-MS, equation (E2.28) can also be expressed in temporal terms. Using equations (E2.19) - (E2.25) from Section 2.8.2 above:

$$R = \frac{m}{\Delta m} = \frac{t_F}{2\Delta t_F} \approx \frac{F_L}{2\Delta x}$$
(E2.29)

where Δx is the width of the ion packet.

There exist several different definitions that may be employed to determine the resolving power of a mass spectrometer. A second definition redefines the terms in equation (E2.28) for two adjacent spectral peaks of masses m and $m+\Delta m$, where in this instance Δm is simply the mass difference between the two peaks (de Hoffman and Stroobant, 2007).

Along with application of orthogonal acceleration, mass resolution in TOF-MS may be improved by the implementation of a *reflectron array*. The reflectron, first introduced in 1957 by Alikanov (Alikanov, 1957), constitutes a series of 'mesh' style electrostatic lenses situated at the end of the field free flight path. The electric field generated by the reflectron acts to 'bend' the ion beam through almost 180° as shown diagrammatically in **Figure 14**.



Figure 14: Ion trajectory inside a TOF-MS equipped with reflectron array (adapted from Whyte (2003))

The reflectron array acts to enhance mass resolution in TOF-MS in two different ways. Most obviously, as the reflectron almost doubles the length of the field free flight path, the ions will have a greater flight time. Consequently, ions of different mass will arrive at the detector with larger temporal separation, and hence resolution will be increased.

The ions contained within in any single ion packet will have a range of different velocities in all directions; hence some ions will be slightly more energetic than their isobaric counterparts (Guilhaus, 1995). The result is a spatial spreading of the ion packet and therefore spectral peaks of poor resolution. Introduction of the orthogonal acceleration TOF helped to counter this issue somewhat, as was detailed above, but the use of a reflectron array can improve matters further. When an ion packet enters the reflectron, those ions of slightly greater energy, *e.g.* $KE(+\delta KE)$, will penetrate deeper than those of slightly less energy, *e.g.* KE. Consequently, the more energetic ions will spend longer within the reflectron, hence when they exit they will be both spatially and temporally closer to those slightly less energetic same mass ions. The result is a tightening of the ion packet and a further enhancement in resolution.

Typically the mass resolution $(m/\Delta m)$ achieved by reflectron TOF-MS is far higher than most other mass analysers employed for atmospheric monitoring (*e.g.* quadrupole spectrometers), being of the order 1000 – 3000 (Blake *et al.*, 2008).

2.9 The Kore MS-200 Time-of-Flight Mass Spectrometer

Mass analysis of ions produced within the University of Leicester CIR-MS drift cell assembly is performed using a Kore MS-200 time-of-flight mass spectrometer (Kore Technology, Ely, UK). The MS-200 is an orthogonal device equipped with a wide bore reflectron array, as

shown in the schematic given in **Figure 15** (see **Figure A2.1** of Section A2 of the Appendix for a larger image).



Figure 15: Schematic of the Kore MS-200 time-of-flight mass spectrometer

The CIR-MS ion source/drift cell assembly is coupled to the MS-200 TOF-MS by a Conflat mounting flange, as was described above in Section 2.2. A vacuum seal is ensured by use of a copper gasket situated between the mounting flange and the mass spectrometer. A photograph of the complete CIR-TOF-MS instrument was given in **Figure 1** and it was also shown diagrammatically in **Figure 2**.

2.9.1 Operation of the MS-200 CIR-TOF-MS

Upon leaving the ECC of the drift cell, the ion beam enters an *Einzel lens* array situated within the *transfer chamber* of the MS-200 TOF-MS. The Einzel, or 'unipotential' lens, is an electrostatic lens comprised of three cylindrical electrodes, which act to collimate and focus the ions into a tighter beam without perturbing their kinetic energy (Moore *et al.*, 1991). The first two elements of the Einzel lens are tuneable between 0 and -9.6 and -52 and -247 V, respectively. Following columnation by the Einzel lens, the ion beam is passed into the *pulsed extraction region*. The MS-200 pulsed extractor is comprised of a plain *back plate* electrode and three *extraction* grid electrodes. In order to inject a packet of positive ions into the *flight chamber*, the pulser unit generates a strong negative voltage pulse, the magnitude of which is tuneable to a maximum of -400 V. Application of the extraction potential is
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controlled by a trigger pulse sent from a *time-to-digital conversion unit* coupled to a controlling PC (see Section 2.9.2).

Before the extracted ion packet enters the flight chamber, it passes through two sets of *steering plates*, which allow steering of the ion packet in the x and y directions. The x and y steering optics comprise two simple plain electrode plates, which may be electrically biased by between -1826 and -1977 V. Having traversed the steering plates, the ion packet begins its journey through the field free *flight chamber* and the *reflection array*. In order to prevent perturbation of the ion energy by any form of external field, the flight chamber is maintained 'field free' by the application of a large voltage (approximately -2 kV) to an internal 'shield', which lines the inside of the chamber. Following their transit through the flight chamber (effective flight path 3.455 m) the ions are detected by a *Galileo 'long life' microchannel plate assembly (MCP)*. The microchannel plate detector essential comprises a series of closely packed continuous-dynode electron multiplier tubes, each of which has an operational diameter of roughly 10 μ m (Wiza, 1979). When an ion impacts upon a channel an electron cascade is generated and measured as a signal current. The ion current generated during a *signal amplification unit*.

The input voltage required for operation of all of the electrodes and the detector in the MS-200 is supplied by a second Stanford Research Systems PS350 PSU (typically operated at -2 kV). Voltage distribution amongst the various electrodes is facilitated by the use of a resistor chain containing variable resistors to allow tuning of the electric fields generated.

2.9.2 Ion Counting and Software

Measurement of ion flight time is performed by a time-to-digital conversion (TDC) unit (Kore Technology, UK, model: V2.2/B). The TDC provides the pulsed extractor with a start pulse signal and then subsequently registers the ion arrival time. Ions are counted by the TDC in (user selectable) time bins of 2 - 8 ns. The TDC is controlled by the *Grams AI* (Thermo Galactic Inc., USA) software package, which facilitates the conversion of flight times into m/z units by application of equation (E2.30):

$$\frac{m}{z} = \left(\frac{t - t_0}{C_b}\right) \tag{E2.30}$$

where t is the ion flight time and t_0 and C_b are calibration coefficients determined after measurement of an ion of known m/z ratio.

2.9.3 Generation of Vacuum within the CIR-TOF-MS

High vacuum is achieved in the CIR-TOF-MS by use of three turbo molecular pumps, two of pumping speed 70 litres per second (Varian, model: V-70, It.) and one of pumping speed 255 litres per second (Edwards, model: Ext 255, UK). The backing pressure required by the three turbo molecular pumps ($< 10^{-2}$ mbar) is supplied by three *dual stage rotary vane pumps*, each of pumping speed 8 m³ per hour (Edwards UK, model: E2M8, UK; Varian Ltd. It., model: DS-102). As has been described in Section 2.2.3.2, when the drift cell is operated with the Mk.1 variant of the ECC, the first V-70 turbo molecular pump is coupled to the intermediate pumping chamber. The second V-70 pump is situated below this, coupled directly to the transfer chamber of the MS-200, in a perpendicular orientation with respect to the vertical axis of the instrument. The second V-70 pump is mounted via a CF-iso 40 stainless steel flange. The Ext-255 turbo molecular (drag) pump is mounted below the pulsed extraction region of the MS-200 via a Conflat mounting flange, aligned along the vertical axis of the instrument (see Figure 15). When the Mk.2 variant of the ECC is employed, the first V-70 pump is relocated to a second mounting port of the transfer chamber, which is orientated perpendicularly to the second V-70 pump and the vertical axis of the instrument. Copper gaskets are employed throughout the MS-200 to supply vacuum seals. In the absence of gas load, the typical vacuum achieved in the CIR-TOF-MS is approximately 1×10^{-9} Torr. Pressure measurements are made in the TOF-MS by a cold cathode vacuum gauge (MKS, USA, series: 943), located in the transfer chamber.

2.10 The CIR-TOF-MS Mass Spectrum and Performance Criteria

Figure 16 given below shows a typical mass spectrum produced by the CIR-TOF-MS operating with the hydronium ion as the ionisation reagent. The sample gas in this instance was background urban air and the reactor and ECC were operated with E/N values of 110 and 170 Td, respectively. The mass spectrum was constructed by integrating over ten separate one minute scans, recorded over the mass range 0 - 200 amu.



Figure 16: Typical CIR-TOF-MS mass spectrum, using hydronium as the primary CI reagent. Data recorded during urban air sampling.

Figure 16 demonstrates that the CIR-TOF-MS is able to successfully generate a clean mass spectrum over a reasonable mass range with few impurity or artefact peaks. The ions present in Figure 16 include (1) the hydronium ion (m/z 19), (2) hydrated hydronium (m/z 37), (3) the nitric oxide cation (m/z 30), (4) the oxygen radical cation (m/z 32) and the protonated forms of the trace organic compounds acetone and xylene (59 and 107, respectively).

The performance capability of the CIR-(MS-200)-TOF-MS system shall be demonstrated throughout this thesis, particularly in Chapter 5 where various aspects of instrument characterisation will be discussed. However, to conclude this chapter, which has described the major features of CIR-TOF-MS system, a summary is given below detailing the major statistics that are employed to define instrument performance:

Chemical ionisation reagents employed:	$H_{3}O^{+}, NH_{4}^{+}, NO^{+}, O_{2}^{+\bullet}$
Sensitivity ^a :	$\sim 5-230 \text{ ncps}^{\text{b}} \text{ ppbV}^{-1}$
Detection limit ^a :	$\sim 1-10 \; ppbV^c$
Accuracy ^a :	~ 10 %
Precision ^a :	~ 10 %
Scan frequency:	10^4 Hz for $0 - 300$ amu scan
Mass resolution (m/ Δ m):	< 3000
Mass range:	Theoretically unlimited

All performance statistics derived from work conducted as part of this thesis.

^a Reagent and analyte dependent factor (see Chapters 4 - 7)

^b ncps = normalised counts per second (definition given in Chapter 3)

^c Detection limit quoted for 10 minute data acquisition (see Chapter 5)

Chapter 3

Chemical Ionisation Reaction Mass Spectrometry: Ion-Molecule Kinetics and Chemistry

3.1 Summary

The current chapter details the comprehensive characterisation of the Chemical Ionisation Reaction (CIR) technique for the use in a novel Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS). Detailed investigations are conducted into the type and variety of reaction products generated following the ionisation of a wide array of volatile organic compounds by four different CIR reagents. The ability to employ multiple CI reagents confers many benefits to an on-line mass spectrometric technique, as the ionisation method can be tailored to best suit the target. In this work, the four different reagents, H_3O^+ , NH_4^+ , NO^+ and $O_2^{+\bullet}$, were generated in a 'clean' source pool by the radioactive ion source of the CIR-TOF-MS without requirement for pre-selection. The four reagent ions underwent successful ion-molecule reaction with the test analytes *via* a number of different mechanisms, including proton transfer, charge transfer, hydride ion abstraction and adduct formation. Reaction products and common species-specific markers are identified here and their formation mechanisms are explained, thus qualitatively the foundations are laid for all future work with CIR-TOF-MS technique. It is also shown here that the different 'spectral fingerprints' produced by the various CI reagents can be employed to distinguish between nominally isobaric compounds, which is not usually possible with Proton Transfer Reaction Mass Spectrometry (PTR-MS) alone.

3.2 Introduction

Historically the conventional means of transferring charge to a target molecule for mass spectrometric analysis has been electron impact (EI) ionisation, *i.e.* the removal of an electron

from a neutral molecule by electron beam bombardment (Mark, 1984). In the EI technique the ionising electrons are typically generated by a hot filament (usually made from tungsten), before being accelerated by an applied electric field up to energies as high as 70 - 100 eV(McLafferty and Turecek, 1993). Following impact the significant products of ionisation are a singly charge radical cation and two free electrons (*e.g.* M + e⁻ \rightarrow M^{+•} + 2e⁻). As the energies involved are high, EI ionisation typically generates a significant amount of molecular ion fragmentation, especially for hydrocarbon species (Lagg *et al.*, 1994). Consequently, EI is generally considered a 'hard' ionisation technique often producing highly congested mass spectra that are difficult to interpret. Because of the low reactor pressures required (~ 10^{-5} Torr) EI ionisation is also somewhat inefficient, with only ~ 1 in 10^5 electron collisions resulting in ionisation (McLafferty and Turecek, 1993).

Between 1965 and 1966 a new and revolutionary ionisation technique was introduced by Munson and Field termed '*chemical ionisation*' (CI) (Munson and Field, 1966). With CI the target neutral is ionised in a rapid ion-molecule reaction with a reagent ion in a relatively high-pressure reactor (~ 1 Torr). At such high pressures the mean free path is sufficiently low that the analyte undergoes many collisions during its journey through the reactor (Munson and Field, 1966; McLafferty and Turecek, 1993). As the reagent ion is present in excess of the analyte and as ion-molecule reactions are typically very fast (~ 10^{-9} cm³ s⁻¹) (Lindinger *et al.*, 1993), ionisation is extremely efficient.

The first major species of reagent ion to be used were the CH_5^+ and $C_2H_5^+$ ions, generated from electron bombardment of methane, *in situ* within the reactor (Munson and Field, 1966). Munson and Field ably demonstrated that such reagent ions were capable of successfully ionising a number of large hydrocarbons. Their results showed the production of much more simple and "useful" spectra, containing product ions that were both more easily identifiable and more characteristic of the analyte than those obtained with EI ionisation.

Developments in ion source technology have subsequently led to separate reagent ion generators, separated from the reactor by small apertures through which the reagent ion beam is extracted (de Hoffman and Stroobant, 2007). The various types of modern ion source employed for reagent ion generation range from hollow cathode dc, glow and spark discharge sources, photoionisers and laser desorption ionisers, to microwave and radioactive type devices.

Following the successful application of CH_5^+ and $C_2H_5^+$ by Munson and Field, many different types of ions have also been employed as the reagent in the CI technique, including Kr⁺ and Xe⁺ (Lindinger *et al.*, 1993; Lagg *et al.*, 1994), isobutane (de Hoffman and Stroobant, 2007), NH₄⁺ (Lindinger *et al.*, 1998), H₃O⁺ (Hansel *et al.*, 1995), NO⁺ and O₂^{+•} (Smith and Spanel, 2005). The various CI reagents ionise the analyte *via* a number of species-specific mechanisms, the most common of which are *charge transfer*, *proton transfer*, *hydride abstraction* and *adduct formation*.

The energies involved in any CI reaction are relatively low, with reaction exothermicity constituting the dominant factor. As ion-molecule reactions are generally exothermic by only a few eV (Lagg *et al.*, 1994) and as collision energies are usually much less than one eV (Lindinger *et al.*, 1993), the CI process is a considerably 'soft' ionisation mechanism. Because of the low energies involved, CI will often yield a simple mass spectrum containing only the molecular ion (or a dominant product) and little in the way of fragmentation (McLafferty and Turecek, 1993).

Of the many different CI reagent species available for compound ionisation in mass spectrometry, it is the hydronium ion (H_3O^+) that has become most widely used, particularly in *proton transfer reaction mass spectrometry* (PTR-MS) and *selected ion flow tube mass spectrometry* (SIFT-MS). In the PTR-MS and SIFT-MS techniques the CI reactor is a defined length, and hence the ion-molecule reaction time is well known. As will be shown below, this means that an absolute analyte concentration can be determined simply through measured signals and knowledge of the reaction rate constant (Smith and Spanel, 2005; Blake *et al.*, 2006).

Although as discussed in Chapter 1, the hydronium ion lends itself remarkably well to the analysis of reactive trace species found within the atmosphere, there are some circumstances that require the application of a different reagent ion. For example, although most air-borne organic compounds can easily be ionised by hydronium (and its water cluster complexes), certain key inorganic environmental pollutants such as nitric oxide (NO) and nitrogen dioxide (NO₂) and many chlorofluorocarbons (CFCs) cannot be (Spanel and Smith, 1997a). Other impetus for the use of alternative CI reagents comes from the inability of the PTR technique to distinguish between nominally isobaric species. As already discussed, PTR from hydronium is a relatively soft ionisation technique that produces little fragmentation. Often therefore ionisation will yield a dominant product, usually of the form MH^+ (*i.e.* the

protonated target). If two isobaric analytes are present in the same sample matrix, it is therefore impossible to distinguish between them. Such issues can be overcome by exploiting the different ion-molecule chemistry of the various types of reagent ions, as is done with SIFT-MS. By using an ion pre-selection system coupled to the ion source, the SIFT-MS technique is able to employ other CI reagents besides hydronium, *i.e.* with SIFT-MS it is possible to switch between reagent ions.

The Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS) at the heart of this thesis was initially demonstrated as a PTR-MS system (Blake *et al.*, 2004). Initial tests proved the instrument to be capable of successfully detecting a limited set of common volatile organic compounds (VOCs) in an urban air sample, utilising PTR from hydronium as the CI technique. The work presented within this chapter expands on those preliminary tests by investigating in detail the ion-molecule kinetics and chemistry of hydronium and three other species of CI reagent ion. Here the ion-molecule kinetics and chemistry of the CI reagents H_3O^+ , NH_4^+ , NO^+ and O_2^{++} are characterised within the CIR-TOF-MS for reaction with a comprehensive series of organic analytes. By detailing the behaviour of compounds across the functional group range, the findings presented provide a crucial base for future endeavour within this field. Significantly, this work shows for the first time that multiple species of CI reagent can be generated in what was originally designed to be a PTR-MS system. It is shown here that not only is the CIR-TOF-MS radioactive ion source capable of producing various species of reagent, but each reagent pool is 'clean' with few impurity ions, hence the requirement for ion pre-selection is dispensed with.

In the field of mass spectrometry, a common solution to the issue of isobaric analyte coincidence has been the introduction of *collision induced dissociation* (CID) to the ionisation regime, mainly through the application of a large electric field. However CID is not at all selective and will generally produce unwanted fragmentation across the entire mass spectrum. As a solution to this, it is also demonstrated here that the multiple CI reagent ions can be employed to produce unique 'spectral fingerprints' that allows speciation of same mass compounds.

3.3 Experimental

The Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer employed during the current exercise was as described in Chapter 2; hence only experiment specific details are presented here.

3.3.1 Reagent Ion Generation

The reagent ions employed during this work were generated from their neutral gaseous form. Each specific reagent gas was delivered to the ion source chamber at a rate of 52 sccm, as detailed below (and in Chapter 2). Subsequent reagent ion production was effected by bombardment of the neutral reagent gas by alpha particles emitted from the ²⁴¹Am foil.

Hydronium ions were generated from water vapour, which was delivered to the ion source by passing a nitrogen carrier gas (BOC 99.998 %) through a glass reservoir containing high purity deionised water (15 MΩ). The glass water reservoir and the Teflon delivery lines were maintained at a constant temperature of 40 (± 1) °C. In order to generate all other reagent ions, the reagent gases were delivered from cylinder to the ion source chamber *via* a stainless steel coil cooled by dry ice in order to remove potential water contamination. In order to produce O_2^{+} and NH_4^+ ions, cylinders of pure oxygen (BOC Special Gases 99.999 %) and ammonia (BOC Special Gases, MS grade) were employed. However in the case of NO⁺ generation the source gas was a 600 ppmV mixture of NO in nitrogen (BOC α -spectraseal). One of the advantages of using a radioactive ion source is that it requires little more than a gas toggle valve on the inlet line to switch between such reagents: all other experimental conditions remain the same and there is no significant settling time.

3.3.2 Sample Compound Delivery

Thirty five atmospherically significant VOCs were chosen as the test analytes, a full list of which can be found in **Table 1**. **Table 1** also lists all available proton affinity and ionisation energy data for the target compounds. Where possible these data were obtained from the National Instrument and Standards database (NIST, www.nistwebbook.com). **Table A3.1** in the Appendix supplies supplementary information including the source and purity of the test compounds.

Table 1: Analytes employed, grouped by functionality. Also given is the molecular weight of each analyte along with their structure, proton affinity and first ionisation energy.

Compound	MW	Functionality	Structure	PA / k.I. mol ⁻¹	IE / eV
acetaldehyde	44	aldehyde	CH ₃ CHO	769.0	10.2291 ± 0.0007
propanal	58	aldehyde	CH ₃ CH ₂ CHO	786.0	9.96 ± 0.01
methacrolein	70	aldehyde/ alkene	CH ₂ C(CH ₃)CHO	808.8	9.92
butanal	72	aldehyde	CH ₃ CH ₂ CH ₂ CHO	792.7	9.82 ± 0.04
hexanal	100	aldehyde	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CHO	794 - 797	9.72 ± 0.05
benzaldehyde	106	aldehyde/ aromatic	C ₆ H ₆ CHO	834.0	9.50 ± 0.08
acetone	58	ketone	CH ₃ COCH ₃	812.1	9.703 ± 0.006
methyl vinyl ketone	70	ketone/ alkene	CH ₂ CHCOCH ₃	834.7	9.65 ± 0.02
butan-2-one	72	ketone	CH ₃ COCH ₂ CH ₃	827.3	9.52 ± 0.04
hexan-2-one	100	ketone	CH ₃ COCH ₂ CH ₂ CH ₂ CH ₃	843.2*	9.35 ± 0.06
hexan-3-one	100	ketone	CH ₃ CH ₂ COCH ₂ CH ₂ CH ₃	843.2	9.12 ± 0.02
methanol	32	alcohol	CH₃OH	754.3	$\begin{array}{c} 10.84 \\ \pm \ 0.01 \end{array}$
ethanol	46	alcohol	CH ₃ CH ₂ OH	776.6	$\begin{array}{c} 10.48 \\ \pm \ 0.07 \end{array}$
1-propanol	60	alcohol	CH ₃ CH ₂ CH ₂ OH	786.5	10.22 ± 0.06
1-butanol	74	alcohol	CH ₃ CH ₂ CH ₂ CH ₂ OH	789.2	9.99 ± 0.05
hydroxy acetone	74	alcohol/ ketone	CH ₃ COCH ₂ OH		10.0 ± 0.1
2 methyl-3- buten-2-ol	86	alcohol/ alkene	CH ₂ CHC(CH ₃)(CH ₃)OH		9.90
cis-2-butene-1,4-diol	88	diol/ alkene	OHCH ₂ CHCHCH ₂ OH		

Comment	N/1887	F!	Stars stars	DA /	
Compound	IVI VV	Functionality	Structure	PA / kJ mol ⁻¹	IE / eV
1,3,5-trimethyl phenol	136	alcohol/ aromatic	C ₆ H ₆ (CH ₃) ₃ OH		
methyl acetate	74	ester	CH ₃ OCOCH ₃	821.6	$\begin{array}{c} 10.25 \\ \pm \ 0.02 \end{array}$
ethyl acetate	88	ester	CH ₃ C(O)OCH ₂ CH ₃	835.7	$\begin{array}{c} 10.01 \\ \pm \ 0.05 \end{array}$
methyl benzoate	136	ester/ aromatic	CH ₃ OCOC ₆ H ₅	850.5	9.32 ± 0.04
formic acid	46	acid	НСООН	742.0	11.33 ± 0.01
acetic acid	60	acid	CH ₃ COOH	783.7	$\begin{array}{c} 10.65 \\ \pm \ 0.02 \end{array}$
methacrylic acid	86	acid/ alkene	CH ₂ CCH ₃ COOH	816.7	10.15
pyruvic acid	88	acid/ ketone	CH ₃ COCOOH		9.9
lactic acid	90	acid/ alcohol	СН ₃ СОНСООН		
1-butene	56	alkene	CH ₂ CHCH ₂ CH ₃	746.8	9.55 ± 0.06
isoprene	68	dialkene	CH ₂ CCH ₃ CHCH ₂	826.4	$\begin{array}{c} 8.86 \\ \pm \ 0.02 \end{array}$
1-pentene	70	alkene	CH ₃ CH ₂ CH ₂ CHCH ₂		9.49 ± 0.03
benzene	78	aromatic	C_6H_6	750.4	9.2438 ± 0.0001
toluene	92	aromatic	$C_6H_6CH_3$	784.1	8.828 ± 0.001
1,3,5-trimethyl benzene	120	aromatic	C ₆ H ₆ (CH ₃) ₃	836.2	8.40 ± 0.001
α-pinene	136	terpene/ alkene	$C_{10}H_{16}$	< 854.0	8.07
acetonitrile	41	nitrile	CH ₃ CN	779.1	12.20 ± 0.01

* No PA available for hexan-2-one, value given is PA for hexan-3-one

As each of the test compounds employed here (with the exception of 1-butene) reside within the liquid phase at room temperature, a headspace extraction method was employed for their delivery into the sample inlet of the CIR-TOF-MS. The headspace extraction technique involved the transfer of 1 cm³ of the test compound to a 100 cm³ sealed glass sample vessel,

through which a stream of high purity nitrogen (BOC special gases, 99.998 %) was flowed in order to purge the head space gas into the instrument sample inlet. Before being allowed to enter the glass sample vessel, the nitrogen carrier gas was first passed through a stainless steel coil cooled by dry ice in order to aid removal of trace water contamination.

The delivery flow of the test compound from the glass sample vessel to the CIR-TOF-MS reactor was maintained at a constant rate of 275 sccm throughout all experiments. The glass sample vessel and the Teflon delivery lines were maintained at a constant temperature of 40 (± 1) °C in order to minimise wall loss of the test compounds.

3.3.3 CIR-TOF-MS Experiment Conditions

With combined reagent and analyte gas flows of 52 and 275 sccm, respectively, the drift cell operating pressure throughout all experiments was 7.4 mbar. In order to limit ion-neutral clustering and to guide the ions through the drift cell, a 2700 V electrical potential difference was applied along the ion source/drift cell assembly. For certain experiments involving hydronium as the CI reagent, the potential applied to the drift cell was lowered to 2300 V. Consequently, the electric field strength to gas number density ratio (E/N) within the drift cell reactor during this work was either 151 or 120 Td, respectively. In order to maintain constant reaction conditions within the reactor, the entire ion source/drift cell assembly was maintained at a constant temperature of 40 °C.

In order to focus the ion beam into the transfer optics of the mass spectrometer and to remove unwanted analyte-water cluster ions from the mass spectrum, a potential ramp was applied over the exit collision cell (ECC) for all experiments. For the majority of experiments the E/N ratio of the ECC was ~ 190 Td, which was lowered to 150 Td for certain experiments. In this instance the radioactive ion source drift assembly was operated with the Mk.1 variant of the ECC.

All mass spectra were recorded over an averaging period of 60 seconds and over the mass range 0 - 150 Da. In order to provide an instrument background, 'blank' scans were conducted of the N₂ carrier gas in the absence of sample, both before and after each sample run. Each mass spectrum was normalised to 10^6 primary CI reagent ion counts and in all cases the appropriate normalised background scan was subtracted. Consequently, all data presented here have been extracted from the residual spectrum trace that contains only those peaks produced by reaction of the CI reagent with analyte.

3.4 Ion-Molecule Chemistry: Theoretical Principles

3.4.1 Reaction Kinetics

Before the results of this study are presented and discussed, a review is given of the theoretical principles behind the ion-molecule chemistry employed in the CIR-TOF-MS technique.

In order for an ion-neutral collision to result in reaction, the reactants must collide in a specific orientation and usually with enough energy to overcome an activation energy barrier, the magnitude of which is related to the energy involved in the breaking and formation of intermolecular bonds within the reactants, *i.e.* a reaction will proceed only if the energy involved in the collision event is greater than that of the activation energy barrier (McMurry and Fey, 1998). In the case of proton transfer, the amount of energy required for reaction is related to the proton affinity of the neutral form of the reactants; often the process is exothermic and virtually barrierless. Similarly during charge transfer ionisation it is the relative first ionisation energies of the CI reagent and the analyte that determines the charge transfer thermodynamics.

The total energy involved in a given reaction can be determined by summing over all of the individual energy components pertaining to the ions and molecules taking part (Williams *et al.*, 2000):

$$E_{total} = RE_{ion} + KE_{cm} + E_{rot} + E_{vib} + E_{int}$$
(E3.1)

In equation (E3.1), E_{total} is the total energy of reaction and the terms RE_{ion} , E_{rot} , E_{vib} and E_{int} are the recombination energy of the product ion, the average rotational energy of the analyte, the average of the vibrational energy of the analyte and the average internal energy of the product ion, respectively. The term KE_{cm} is the centre of mass kinetic energy of the reaction as defined in Section 2.6 of Chapter 2.

Equation (E3.1) will therefore determine the overall exothermicity of a given reaction and will supply information on the extent of any excess energy available for fragmentation of the resultant reaction products. Considering all of the terms that comprise equation (E3.1), the easiest parameter to vary in the CIR-MS drift cell reactor in order to effect a change in the total energy of an ion-neutral collision, is the kinetic energy of the reactants. Consequently

either the electric field along the drift cell or gas number density is varied in order to encourage unfavourable reactions, or to induce fragmentation of the product ions.

3.4.2 Proton Transfer Reaction Ionisation

Proton transfer reaction ionisation constitutes one specific branch of the chemical ionisation technique, the *modus operandi* of which is the transfer of charge to a neutral target molecule by the addition of a proton from a proton donor reagent ion. The products of reaction are an *even electron cation with a bound proton* and a neutral, deprotonated reagent molecule, for example:

$$XH^{+}(g) + M(g) \rightarrow X(g) + MH^{+}(g)$$
(R3.1)

where XH⁺ is the proton donor and M is the target analyte to undergo ionisation.

Historically, several different cation species have been employed as proton transfer reagents, including the CH_5^+ ion (Munson and Field, 1966); NH_4^+ , the ammonium ion (Lindinger *et al.*, 1998) and more recently H_3O^+ , the hydronium ion (Hansel *et al.*, 1995).

As described in Chapter 1, in order for the neutral analyte molecule, M, to accept a proton from the reagent donor, X, and hence for reaction (R3.1) to occur spontaneously at some temperature, *T*, the standard Gibbs energy change (ΔG^{Θ}_{T}) for the reaction must be negative (Blake *et al.*, 2008). Conventionally ΔG^{Θ}_{T} is related to the standard enthalpy (ΔH^{Θ}_{T}) and entropy (ΔS^{Θ}_{T}) change of a system at a given temperature as follows:

$$\Delta G^{\Theta}{}_{T} = \Delta H^{\Theta}{}_{T} - T\Delta S^{\Theta}{}_{T}$$
(E3.2)

For a simple proton transfer reaction such as (R3.1) the difference in entropy between the reactants and products is negligible (Blake *et al.*, 2008), and hence it has become convention to use the *proton affinity* (PA) of the reacting molecules to determine whether or not a proton transfer reaction is thermodynamically feasible (Ennis *et al.*, 2005). The proton affinity of a neutral molecule is defined as the negative of the enthalpy change of the proton addition system given by reaction (R3.2):

$$M(g) + H^{+}(g) \rightarrow MH^{+}(g)$$
(R3.2)

i.e.

$$PA(M) = -\Delta H_T \approx -\Delta G_T \tag{E3.3}$$

Hence, a simple proton transfer reaction such as that shown in reaction (R3.1) will be thermodynamically spontaneous if the analyte, M, has a proton affinity greater than that of the neutral form of the reagent, X.

The proton affinities of neutral water and ammonia have been measured to be 691 (\pm 2) and 853.6 (\pm 8) kJ mol⁻¹, respectively (www.nistwebbook.com). Clearly this means that the ammonium ion constitutes a much more selective PTR reagent than the hydronium ion. Methane has been measured to possess a proton affinity of 544 (\pm 8) kJ mol⁻¹ (www.nistwebbook.com) and hence is be able to ionise a wider array of species.

In the work described here, both ammonium and hydronium ions were successfully generated within the radioactive ion source of the CIR-TOF-MS, and were subsequently employed as reagent ions for proton transfer to a range of organic species. Investigations were also conducted into the use of methane to produce CH_5^+ , however, owing to water contamination during the experiments, ion yields were low and as such those results are not reported.

3.4.3 Proton Transfer Reaction Ionisation from the Hydronium Ion

The majority of the work presented within this thesis was conducted utilising the hydronium ion as the primary CI reagent; hence the specific kinetics behind proton donation from H_3O^+ (and its water cluster adducts) shall form the focus of discussion for this and later chapters. The proton transfer ionisation kinetics of the ammonium ion are analogous however, and will be discussed where relevant in the sections to follow.

Reaction (R3.3) demonstrates the most common reaction pathway for the proton transfer reaction involving the hydronium ion and a typical analyte molecule, M:

$$H_3O^+(g) + M(g) \xrightarrow{k_{PTR}} MH^+(g) + H_2O(g)$$
 (R3.3)

Providing the neutral analyte molecule, M, has a sufficiently large proton affinity such that the subsequent reaction between it and the hydronium ion is exothermic, and assuming that there is no steric hindrance involved, the rate of reaction (R3.3) (k_{PTR}) is extremely rapid, *i.e.* reaction occurs at the collision-limited rate (one collision results in one reaction). The rapidity of the proton transfer reaction with a range of analytes has been demonstrated in the flowing afterglow experiments of Bohme and co-wokers (Bohme, 1975) and in the multitudinous SIFT-MS experiments of Smith and Spanel (Smith and Spanel, 2005). For most common organic molecules the rate of reaction (R3.3) is typically of the order $1 - 4 \times 10^{-9}$ cm³ molecules⁻¹ s⁻¹ (*e.g.* (Warneke *et al.*, 2001; Smith and Spanel, 2005) and references therein).

Proton transfer from the hydronium ion is a relatively 'soft' ionisation process, considerable less energetic than more conventional techniques such as electron impact ionisation for example. In a simple bi-molecular, ion-neutral proton transfer reaction that is uninfluenced by any form of external forcing, the excess energy released following reaction can be determined from the differences in proton affinity of the neutral forms of the reactants. As the proton affinities of most common organic molecules found within the atmosphere generally lie within the approximate range $700 - 1000 \text{ kJ mol}^{-1}$ (*e.g.* see **Table 1**), the excess energy available for bond breaking is modest, typically less than 300 kJ mol⁻¹. Consequently, for most thermal proton transfer reactions that occur between the hydronium ion and a typical organic analyte molecule, M, the dominant product ion is the protonated form of the analyte, *i.e.* MH⁺. Usually the MH⁺ parent ion forms the *base* (main) peak of the product mass spectrum and it is usually accompanied by few additional *daughter* (or *fragment*) products (Lindinger *et al.*, 1998).

However, as highlighted in the extensive SIFT-MS studies of Smith and Spanel (Smith and Spanel, 2005), direct PTR from hydronium does not always result simply in an MH^+ product ion. It has been shown that there are a number of species-specific exceptions for which a variety of other product ions can be formed and indeed dominate. For example, most alcohols and diols and some aldehydes and carboxylic acids have been observed to predominantly undergo dehydration following PTR with hydronium, to produce an ion of the form $MH^+(-H_2O)$ (Spanel and Smith, 1997b). For example, for the generic alcohol, MOH:

$$H_3O^+(g) + MOH(g) \rightarrow M^+(g) + 2H_2O(g)$$
 (R3.4)

It has been shown by Smith and Spanel that for alcohols, as the carbon chain increases in length and complexity, the contribution made by the MH^+ ion tends towards zero. Other reaction products observed following PTR include $M^+(-R)$ and $M^+(-OR)$ ions produced from ethers and esters (Spanel and Smith, 1998a), $M^+(-NH_2)$ ions from amines (Spanel and Smith, 1998b) and also MH^+ .(H₂O) association complexes from various organic molecules (depending on the *E/N* value of the system) (Spanel *et al.*, 1995). The formation of such product ions within the CIR-TOF-MS is discussed within the following sections.

With the CIR-MS and PTR-MS techniques, the application of an electric field along longitudinal axis of the drift cell forces all ion neutral reactions to occur at a greater KE_{cm} than would be found in similar instruments (such as SIFT-MS) which do not rely on the use of an external electric field (Lindinger and Hansel, 1997). Consequently the total energy of reaction (defined by equation (E3.1)) is generally higher with CIR-MS or PTR-MS, which

tends to result in a greater amount of product ion fragmentation than would be expected for unperturbed, thermal PTR. During the work presented within this chapter, the CIR-TOF-MS drift cell was operated with E/N ratios of ~ 120 and 150 Td. Consequently, the reactions between H₃O⁺ and the test analytes under inspection here occurred with (mass dependent) KE_{cm} within the range 0.17 – 0.36 eV.

Considering the kinetics involved with reaction (R3.3) and that the number density of hydronium within the drift cell reactor is at all times far in excess of that of the analyte, pseudo first order kinetics may be assumed and an expression may be derived for the measured signal of the protonated analyte, $i(MH^+)$:

$$i(MH^+) = i(H_3O^+)_0(1 - e^{-k[M]t})$$
 (E3.4)

where $i(H_3O^+)_0$ is the hydronium signal before reaction (R3.3) has proceeded to products and k, [M] and t are the proton transfer reaction rate constant, the analyte concentration and the reaction time respectively.

As, [M] << [H₃O⁺], equation (E3.4) may be simplified as follows (Steeghs, 2007):

$$i(MH^+) \approx i(H_3O^+)_0 [M] k t$$
 (E3.5)

Rearranging equation (E3.5) it becomes possible to see that the absolute concentration of the analyte, M, may be determined simply from knowledge of the measured $i(MH^+)/i(H_3O^+)_0$ signal ratio, the reaction rate constant, *k*, and the reaction time, *t*:

$$[M] = \frac{i(MH^{+})}{i(H_{3}O^{+})_{0}} \frac{1}{kt}$$
(E3.6)

However, as previously noted, PTR does not always yield a single MH^+ product ion, often at least some degree of fragmentation will occur. Consequently a fragmentation factor, *F*, must be included into equation (E3.6). With a value ranging from 0 - 1, *F* effectively acts to scale equation (E3.6) for non MH^+ product routes.

$$[M] = \frac{i(MH^{+})}{i(H_{3}O^{+})_{0}} \frac{1}{kt} F$$
(E3.7)

Substituting the previously determined expression for *t* (*i.e.* equation (E2.16) from Section 2.6 of Chapter 2) into equation (E3.7), the expression for [M] becomes:

$$[M] = \frac{i(MH^{+})}{i(H_{3}O^{+})_{0}} \frac{1}{k} \frac{\mu_{0}N_{0}}{L} \frac{E}{N}F$$
(E3.8)

Equation (E3.8) now demonstrates that the ultimate signal of $i(MH^+)$ achieved in the CIR-TOF-MS drift cell reactor (*i.e.* the amount of analyte converted to ionic form), is proportional to the reactor length and inversely proportional the reactor E/N value.

It has become convention to normalise the recorded PTR (and indeed the CIR) mass spectrum to 1 million primary reagent ion counts per second, such that $i(H_3O^+)_0$ always has the magnitude of 1 million counts. This normalisation procedure was adopted in order to account for the varying reagent ion signal over a period of time, which is of particular importance during long term monitoring periods. As a consequence, following normalisation the recorded ion signal, $i(MH^+)$, has units of *normalised counts per second*, *i.e.* ncps (Warneke *et al.*, 2003).

Work performed recently by Keck and colleagues (Keck et al., 2007) has highlighted that although equation (E3.7) may be successfully employed to techniques such as SIFT-MS in order to quantify an observed signal, it must be modified by a correction factor when applied to the analysis of data obtained from instruments employing a drift tube reactor with an applied electric field. In the CIR-TOF-MS (or standard PTR-MS) technique the drift cell electric field causes the ions to accelerate to a terminal drift velocity (v_d) . From the theoretical principles detailed in Sections 2.5 - 2.8 of Chapter 2, it is clear that under the influence of the same electric field an ion of lower molecular mass (and m/z) will achieve a larger v_d than an ion of much higher molecular mass (and m/z). As the primary reagent ion in the CIR-MS technique, hydronium for example, will usually be of much lower molecular mass than the analyte molecules; it will generally travel faster through the drift cell. Consequently, for any given volume element moving along the longitudinal axis of the drift cell reactor towards the exit/collision cell, reaction (R3.3) will not be the sole factor determining the number density of reagent ions, *i.e.* reagent ions will enter, move through and exit the element relative to the analyte molecules. Keck et al. refer to the movement of reagent ions relative to analyte molecules within a volume element and under the influence of an electric field, as drift cell 'advection'. The authors attempt to account for this by the introduction of an 'advective' factor into equation (E3.7), which they derive to be the ratio of reagent/analyte mobilities (measured within the specific buffer gas):

$$[M] = \frac{i(MH^{+})}{i(H_{3}O^{+})_{0}} \frac{1}{kt} \frac{\mu_{MH^{+}}}{\mu_{H,O^{+}}} F$$
(E3.9)

It has been estimated that exclusion of the advective correction factor (μ_{MH+}/μ_{H3O+}) from equation (E3.7) can result in errors greater than 20 % in the calculated value of [M] (Keck *et*

al., 2007). Clearly with the SIFT-MS technique, use of the advective correction factor is not required, as all ions comprising the sample matrix ensemble within the drift cell reactor travel at the same velocity. Keck *et al.* also suggest that a correction factor accounting for gas diffusivity within a CIR/PTR-MS drift cell reactor should be included in equation (E3.9), but this has yet to be determined.

If the transmission factor of ions into the mass spectrometer is well known (de Gouw *et al.*, 2003), if reaction (R3.3) results solely in the production of MH^+ (or if *F* is well characterised) and if only one species of reagent ion acts to ionise the sample gas, equation (E3.9) may be reliably employed to determine the concentration of a given compound, *i.e.* [M]. In cases where production of MH^+ is replaced by production of MH^+ (-H₂O) (or some other dominant ion), the parameters [M], *i*(MH⁺) and μ_{MH^+} in equation (E3.9) should be substituted appropriately.

In the presence of excess neutral water, hydronium is liable to undergo ion-neutral clustering to produce ions of the form $H_3O^+.(H_2O)_n$, where $n \ge 1$. As the various forms of the hydronium-water cluster ion possess different kinetics to those of the base hydronium ion, their presence is sometimes considered undesirable. Cluster ions, such as $H_3O^+.(H_2O)_n$ can be broken apart and hence removed from the reactor by increasing the magnitude of the electric field. Throughout this chapter the drift cell electric field was sufficiently large so as to minimise the abundance of hydrated hydronium, and consequently all reactions investigated principally involved only the base hydronium ion, H_3O^+ . A full discussion of the complexities of ionisation using hydrated hydronium is reserved for Chapter 5.

3.4.4 Alternative Chemical Ionisation Reagents: NO^+ and $O_2^{+\bullet}$

In a successful ion-neutral collision involving NO^+ or O_2^{+} as the charge carrying species, reaction can occur *via* one of several different pathways. These reaction pathways include (i) *charge transfer*, (ii) *hydride ion transfer* and (iii) *association complex formation*.

(i) The most simple reaction pathway available for organic molecules reacting with NO⁺ or O_2^{++} is direct charge transfer, *i.e.* extraction of an outer shell electron from the analyte by the reagent ion. This *electron transfer* process will therefore result in the production of an *odd electron radical cation* (carrying unit charge) and a neutral reagent molecule or radical. Taking the reaction of the neutral analyte M with NO⁺ as an example:

$$NO^{+}(g) + M(g) \rightarrow M^{+\bullet}(g) + NO^{\bullet}(g)$$
(R3.5)

In a charge transfer process such as that shown in reaction (R3.5), the electron extracted from the analyte, M, will be that which is most weakly bound, *i.e.* that corresponding to the lowest ionisation energy. This means that non-bonding electrons will be most preferentially removed, followed by π -bond and then σ -bond electrons (McLafferty and Turecek, 1993).

Reaction (R3.5) will only proceed however, if the reagent ion is *thermodynamically able* to extract an electron from the analyte. This can be determined by comparison of the first ionisation energy of the neutral analyte (IE(M)) with the recombination energy of the reagent ion (RE(NO⁺)), (*i.e.* the energy released when the charged constituents recombine to form the neutral equivalent of the ion). A charge transfer reaction will result only if the first ionisation energy of the neutral analyte is less than the recombination energy of the reagent ion, *i.e.* for reaction (R3.5) to proceed the condition IE(M) < RE(NO⁺), must be satisfied. It should be noted that in most cases the recombination energy for a given ion is equivalent to the first ionisation energy of its neutral counterpart (Lagg *et al.*, 1994), therefore RE(NO⁺) may be exchanged with IE(NO) in the above expression.

If the difference between the ionisation energies of the neutral forms of the reactants is small, the charge transfer process will be non-dissociative and the sole product of reaction will be the M^{+*} ion. However, if the ionisation energy of the analyte is substantially less than that of the neutral form of the reagent, the excess energy involved will elevate the M^{+*} ion to an excited state (M^{+*})* and bond cleavage may occur, resulting in the production of one or more daughter/fragment ions (Lagg *et al.*, 1994; de Hoffman and Stroobant, 2007). The dissociation process of the excited M^{+*} ion to form daughter products is believed to be rapid, generally << 10⁻⁷ s (Lagg *et al.*, 1994). If the charge transfer reaction is particularly energetic the M^{+*} ion population may be completely converted to fragmentation products, and typically the more energetic the reaction the more extensive the fragmentation.

The first ionisation energies of NO and O₂ are 9.2642 (\pm 0.00002) and 12.0697 (\pm 0.0002) eV, respectively (www.nistwebbook.com). As most atmospherically significant volatile organic compounds possess ionisation energies within the range 9 – 11 eV (see **Table 1**), charge transfer from both NO⁺ and O₂^{+•} is often feasible. Clearly, from inspection of the ionisation energies of the reactants involved, NO⁺ will act as a softer yet more selective ionisation reagent, whereas O₂^{+•} will ionise most compounds but may produce substantial fragmentation.

(ii) The second potential pathway for the analyte, M, reacting with either NO⁺ or O_2^{++} is a hydride ion transfer process (Smith and Spanel, 2005). Hydride ion transfer essentially constitutes the removal of a single hydride ion from the analyte by the reagent ion in order to produce the dehydrogenated, cationic form of the analyte and either HNO, following reaction with NO⁺ or HO₂⁺, following reaction with O_2^{++} . Again taking reaction of the neutral analyte, M, with NO⁺ as an example:

$$NO^{+}(g) + M(g) \rightarrow M(-H)^{+}(g) + HNO(g)$$
(R3.6)

Reaction (R3.6) essentially constitutes a form of dissociative charge transfer, such as described above (Spanel and Smith, 1997a), yet it is generally a species-specific process. The extensive SIFT-MS studies of Spanel and Smith have shown that hydride ion transfer dominates for most aldehydes, ethers and primary and secondary alcohols, where the $M(-H)^+$ ion is often the sole reaction product. Hydride ion transfer reaction between NO⁺ and ketones, acids and esters is not generally observed (Spanel and Smith, 1997b).

Hydride ion transfer between organic molecules and the O_2^{+} ion is a somewhat less common ionisation process than that involving NO⁺. Generally the high recombination energy of O_2^{+} (~12.1 eV) results in charge transfer followed by more extensive product fragmentation (Spanel and Smith, 1998a). However, there is some evidence to suggest that hydride ion transfer may occur between O_2^{+} and a number of small aldehydes (*e.g.* formaldehyde) and acids (*e.g.* formic acid) (Spanel and Smith, 1997b; Spanel and Smith, 1998a), producing the M(-H)⁺ ion and the hydroperoxy radical (HO₂⁺).

(iii) The third ionisation mechanism discussed here, available only to NO^+ , is ion-molecule association (Smith *et al.*, 2003; Smith and Spanel, 2005). In such association reactions the NO^+ ion will bond to the analyte, M, to produce the M.NO⁺ association complex. The NO^+ reagent ion will tend to add on to the analyte at an area of high electronegativity, such as the lone electron pairs of the oxygen heteroatom (Cullis, 2008). Generally when the M.NO⁺ complex is first formed, it lies in an excited state, and hence collision with a third body is required to remove any excess energy and confer stability to the ion (Smith *et al.*, 2003).

$$NO^+(g) + M(g) \rightarrow (M.NO^+)^*(g) \xrightarrow{B} M.NO^+(g) + B(g)$$
 (R3.7)

where, B denotes the reaction third body.

Reaction (R3.7) will only proceed however, if the analyte, M, has a first ionisation energy greater than that of NO (Blake *et al.*, 2006). Recent studies by Smith *et al.* (Smith *et al.*, 2003) have shown that as the ionisation energy of the analyte approaches that of NO, other ionisation reactions such as charge transfer begin to compete. The authors attribute this to assistance from residual vibrational energy in the NO⁺ ion.

The formation of a stable ion-molecule association complex is not the sole possible outcome for reaction (R3.7), it is also possible for the excited association complex $(M.NO^+)^*$ to immediately decay (Smith *et al.*, 2003). Decay of the excited complex will either result in regeneration of the reactants (*i.e.* reaction (R3.8)) or production of the M⁺⁺ ion following charge transfer within the complex (*i.e.* reaction (R3.9):

 $(M.NO^{+})^{*}(g) \rightarrow M(g) + NO^{+}(g)$ (R3.8)

$$(M.NO^{+})^{*}(g) \rightarrow M^{+}(g) + NO(g)$$
(R3.9)

The ionisation mechanism of association complex formation with the NO⁺ ion is most common for ketones (Spanel and Smith, 1997b) (Smith *et al.*, 2003), esters and carboxylic acids (Spanel and Smith, 1998a). A full review regarding reaction rates for the described processes can be found in the work of Smith, Spanel and co-workers (*e.g.* (Smith and Spanel, 2005) and references therein).

3.5 Results: Ion-Molecule Reactions within CIR-TOF-MS

Having reviewed the theoretical principles regarding ion-molecule chemistry, the following sections present the findings obtained from the current study using the CIR-TOF-MS technique. **Figure 1** gives the raw CIR-TOF-MS ion source mass spectra obtained from each of the reagent ions in absence of analyte. It is clear from **Figure 1** that the CIR-TOF-MS radioactive ion source constitutes an exceptionally clean CI reagent generator for each species of reagent ion, with strong signals achieved in all instances. The only contaminant ions of note were the NH₄⁺.(NH₃) cluster in the case of ammonia, and H₃O⁺ in the cases of NO⁺ and O₂⁺⁺. The NH₄⁺.(NH₃) cluster was most likely present as a consequence of employing a pure ammonia reagent gas, and could most probably be removed by either diluting the source gas or by increasing the magnitude of the drift cell electric field. The hydronium contamination in the case of NO⁺ and O₂⁺⁺ was seemingly due to the presence of residual water vapour within the ion source or reagent gases.



Figure 1: Raw ion source mass spectra of (a) H_3O^+ , (b) NH_4^+ , (c) NO^+ and (d) $O_2^{+\bullet}$ recorded by CIR-TOF-MS in absence of analyte. Peaks in the spectra of NO^+ and $O_2^{+\bullet}$ marked with * correspond to H_3O^+ contamination, the peak in the spectra of NH_4^+ marked with \bullet corresponds to the NH_4^+ .(NH₃) cluster.

The remainder of this section will now focus on the results obtained from the application of the various CI reagents for the ionisation and detection of the test organic compounds listed in **Table 1**. The findings obtained for each type of analyte with each specific reagent ion will be presented in turn.

3.5.1 Reactions of H_3O^+

As seen in **Table 1** all of the test compounds possess proton affinities greater than that of water, and hence rapid proton transfer is energetically feasible in each case. We assume from the structure and composition of those compounds whose proton affinities are not available, that they too are able to undergo rapid proton transfer ionisation from hydronium.

As a dry sample carrier gas was employed and as the drift cell reactor was operated at a high E/N value (*i.e.* 120 - 151 Td), virtually all of the reactions taking place would have involved only the base hydronium ion and the analyte, *i.e.* the H₃O⁺.(H₂O)_n cluster ion population was minimal. Consequently, in this simplified system we may focus solely on the kinetics of direct proton transfer reaction from H₃O⁺. The process of ionisation by hydrated hydronium clusters will be discussed in detail later in Chapter 5.

From first inspection of the CIR-TOF-MS findings, it appears that the test species may be loosely divided into three groups according to their product ion distributions, molecular structure and content and location of the functional group: the groups are (I) hydrocarbons, (II) species with a terminal functional group and (III) species with a central functional group. The results obtained for each the three groups will be discussed in turn.

3.5.1.1 Reaction of H₃O⁺ with a Selection of Hydrocarbons: Group (I) Compounds

The bar chart presented in **Figure 2** shows the distribution of ions produced following reactions of hydronium with the test hydrocarbons. Each bar is divided into sections, the size of which is proportional to the fractional contribution made by each product ion to the total mass spectrum, *i.e.* their relative abundance. Only the major product ions are labelled in **Figure 2**, for a full list of product ions the reader is referred to **Table A3.2** of the Section A3 of the Appendix.



Figure 2: Product ion distribution of a number of hydrocarbons (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor E/N of 151 Td.

As shown in **Figure 2** all of the test hydrocarbons underwent direct exothermic proton transfer from the hydronium ion to produce a protonated parent ion of the form MH^+ . Following ionisation each of the aliphatic hydrocarbons presented some degree of fragmentation, producing one or two major daughter products. Typical fragment ions produced from the ionisation of aliphatic hydrocarbons by the hydronium ion, include vinyl, ethyl, allyl and *n*-propyl cations (*m*/*z* 27, 29, 41 and 43, respectively). Unlike the aliphatic

compounds investigated, the aromatic hydrocarbons benzene and toluene did not fragment following proton transfer ionisation.

3.5.1.2 Reaction of H₃O⁺ with a Selection of Aldehydes, Alcohols and Acids: Group (II) Compounds

Figures 3, 4 and 5 display the product ion distributions obtained from reaction of the test aldehydes, alcohols and acids with hydronium under CIR-TOF-MS conditions. Only the major product ions are labelled, a full list of fragment ions can be found in Tables A3.3, A3.4 and A3.5 of Section A3 of the Appendix.



Figure 3: Product ion distribution of a selection of aldehydes (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor *E/N* of 151 Td.

The results presented in **Figures 3**, **4** and **5** show that with only three minor exceptions, all of the test aldehydes, alcohols and acids underwent reaction with hydronium to produce an ion of the form MH^+ , *i.e.* the protonated form of the analyte. However, the extent to which the MH^+ ion contributed to the overall mass spectrum varied markedly between compounds. For the smaller compounds of the group (II) species, the MH^+ ion was the most abundant product. For example propanal, methanol, formic acid and acetic acid reacted with hydronium to yield MH^+ ions with relative abundances of 80, 97, 100 and 79 %, respectively. In general for the saturated, straight chain aldehydes, alcohols and acids, the fractional contribution made by the MH^+ ion was observed to decrease with increasing carbon chain length. Also reacting primarily to produce the MH^+ ion were the saturated aldehyde methacrolein, the aromatic aldehyde benzaldehyde and the branched chain, multifunctional hydroxy acetone (relative

abundances of 87, 91 and 95 %, respectively). As well as producing a protonated parent ion, uniquely acetaldehyde appeared to undergo hydride ion loss following reaction with hydronium, to produce an ion of the form $M(-H)^+$.



Figure 4: Product ion distribution of a selection of alcohols (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor E/N of 151 Td.



Figure 5: Product ion distribution of a selection of acids (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor *E/N* of 120 Td.

Of the group (II) compounds only 1-propanol, 1-butanol and lactic acid did not react with hydronium to produce a stable MH⁺ ion. From comparison with findings made by SIFT-MS,

it appears that under thermal conditions these compounds do indeed react to form MH⁺, but the abundance of the MH⁺ ion formed is low (Smith and Spanel, 2005). Consequently within the CIR-TOF-MS reactor it is most likely that fragmentation dominates and the minor MH⁺ ions of 1-propanol, 1-butanol and lactic acid were removed from the system. The phenomenon of ion fragmentation within CIR-TOF-MS is discussed in further detail in Sections 3.6.1.3 and 3.6.3.4 below.

As can be seen from inspection of **Figures 3**, **4** and **5** the second most common type of product ion formed from reaction of hydronium with the group (II) compounds, was a hydrocarbon ion of the form $MH^+(-H_2O)$. From the CIR-TOF-MS data presented, it appears that the dehydration reaction channel is most important for the larger aliphatic aldehydes and alcohols; in general the relative abundance of the $MH^+(-H_2O)$ ion was observed to increase with increasing carbon chain length. Of the saturated, straight chain test compounds, butanal, hexanal, ethanol, 1-propanol, 1-butanol and acetic acid were all observed to undergo water elimination following PTR, as were the branched chain, unsaturated compounds MBO and methacrylic acid and the diol, cis-2-butene-1,4-diol.

Under the experimental conditions employed here, as well as producing ions of the form MH^+ and/or $MH^+(-H_2O)$, almost all of the test aldehydes, alcohols and acids were observed to undergo some degree of fragmentation following PTR from the hydronium ion. Generally, fragmentation was minor for the aldehydes and alcohols with the exception of hexanal, 1-propanol and cis-2-butene-1,4-diol. Following reaction with hydronium, both hexanal and 1-propanol underwent fragmentation to yield large hydrocarbon fragment ions of relative abundance 37 and 51 %, respectively. Cis-2-butene-1,4-diol was observed to undergo more extensive break up, ultimately producing a number of fragment ions with a combined relative abundance of 74 %. Of the test acids methacrylic, pyruvic and lactic acid were observed to fragment *via* loss of the functional group, producing ions of the form M(-COOH)⁺ of relative abundance 26, 96 and 9 %, respectively.

3.5.1.3 Reaction of H₃O⁺ with a Selection of Ketones, Esters and Nitriles: Group (III) Compounds

Figure 6 and **Figure 7** display the product ions formed from the reactions of the test ketones, esters and nitrile with hydronium. As can be seen from observation of **Figures 6** and **7** each of the test ketones and esters and the nitrile underwent direct exothermic proton transfer reaction with hydronium to produce a protonated parent ion of the form MH⁺. Unlike their

aldehydic counterparts, the selected ketones were generally not observed to produce other major product ions following PTR from hydronium, the minor exception being hexan-2-one, which exhibited a small water elimination channel to produce an alkyl ion of relative abundance 2 %.



Figure 6: Product ion distribution of a selection of ketones (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor E/N of 151 Td.



Figure 7: Product ion distribution of a selection of esters and acetonitrile (molecular weight given in parentheses) following reaction with H_3O^+ at a reactor E/N of 151 Td.

Hexan-2-one and hexan-3-one produced several minor fragment ions with a total relative abundance of only ~ 10 % and methyl vinyl ketone fragmented *via* loss of the C₂H₄ unit of the

carbon chain, to produce an acylium ion of relative abundance 5 %. The esters investigated exhibited varying degrees of fragmentation, but only ethyl acetate produced products of significant relative abundance, in this instance a fragmentation product formed following loss of the C_2H_3 segment of the hydrocarbon chain. A full list of product ions produced from reaction of the test ketones and esters with hydronium can be found in **Tables A3.6** and **A3.7** of the Appendix.

3.5.2 Reactions of NH_4^+

For simplification purposes, all experiments using the alternative CI reagents NH_4^+ , NO^+ and O_2^{++} were conducted with a less extensive set of test compounds, where one or two examples were assumed to be approximately representative of the compound (functionality) group as a whole. Consequently, the results obtained from all of the test compounds are reported together, *i.e.* unlike Section 3.5.1 there is no division according to reaction behaviour and compound structure.

Those compounds comprising the restricted test set were: acetaldehyde, hexanal, methacrolein, acetone, methyl vinyl ketone, ethanol, ethyl acetate, methyl benzoate, 1-butene, benzene, toluene and acetonitrile. Propanal, butanal, hexan-2-one and hexan-3-one were also included for NO⁺.

As can be seen from inspection of **Table 1**, none of the analytes within the restricted test set possess proton affinities greater than that of ammonia, and hence they are not expected to undergo direct exothermic proton transfer reaction with the ammonium ion. This hypothesis was verified by results obtained here using CIR-TOF-MS, from which no MH^+ ion was detected for any of the test compounds; indeed of the restricted test set only methacrolein, hexanal, acetone, MVK, ethyl acetate, methyl benzoate and acetonitrile were observed to react with NH_4^+ at all. The product ions formed from the reactions of ammonium with these compounds and their relative abundances are given in **Figure 8**.

Figure 8 shows that for those compounds that were able to react with ammonium, at most only two types of product ions were formed, both association complexes, of the type $M.NH_4^+$ or $M.NH_4^+.(NH_3)$. For all compounds the $M.NH_4^+$ ion exhibited the greatest relative abundance (90 – 100 %).



Figure 8: Product ion distribution of the test organic compounds (molecular weight given in parentheses) following their reaction with NH_4^+ and $NH_4.(NH_3)^+$ at a reactor E/N of 151 Td.

3.5.3 Reactions of NO^+

Figures 9, **10** and **11** presented below, show the distribution and type of product ions formed from the reactions of NO^+ with the organic molecules of the restricted test set. As with such previous plots, only the most significant and most abundant products are labelled: for a full list of all ions measured see **Table A3.9** of the Appendix. Contrary to findings obtained with ammonium, when the NO^+ ion was employed as the primary CIR reagent all of the test compounds were observed to undergo reaction.

As can be seen from inspection of **Table 1**, only hexan-3-one, benzene and toluene possess first ionisation energies less than that of NO, and hence only these three compounds would be expected to undergo charge transfer reactions under thermal conditions. **Figure 10** and **Figure 11** show that hexan-3-one, benzene and toluene do indeed reacted within the CIR-TOF-MS drift cell to produce an M⁺⁺ molecular ion, however unexpectedly, the CIR-TOF-MS mass spectra of propanal (**Figure 9**), butanone, hexan-2-one (**Figure 10**), 1-butene and acetonitrile (**Figure 11**) were also observed to contain mass peaks corresponding to their respective M⁺⁺ ions. As will be discussed in detail later in Section 3.6, this result is most likely a consequence of the relatively high ion and collision energies within the CIR-TOF-MS drift cell, which act to raise the ion-molecule kinetics above thermal conditions.



Figure 9: Product ion distribution of the test aldehydes (molecular weight given in parentheses) following their reaction with NO⁺ at a reactor E/N of 151 Td.



Figure 10: Product ion distribution of the test ketones (molecular weight given in parentheses) following their reaction with NO⁺ at a reactor E/N of 151 Td.

Several of the test compounds were observed to undergo hydride ion transfer with NO^+ , including all of the aldehydes, ethanol, hexan-2-one, MVK and 1-butene. Of these molecules acetaldehyde and ethanol reacted to produce $M(-H)^+$ spectral peaks of largest relative abundance (77 and 97 %, respectively), with all other compounds exhibiting a greater degree of fragmentation.



Figure 11: Product ion distribution of the test alcohol, ester and hydrocarbon compounds (molecular weight given in parentheses) following their reaction with NO⁺ at a reactor E/N of 151 Td.

Under the current CIR-MS conditions relatively little association complex formation was observed when NO⁺ was employed as the primary CI reagent. The mass spectra of acetone, butanone, hexan-2-one, hexan-3-one, MVK, ethyl acetate and 1-butene all contained spectral features that corresponded to the M.NO⁺ complex, however, in general the contributions made by such association complexes to the overall mass spectra were small. The acetone-NO⁺ adduct showed the greatest relative abundance of all of the complexing compounds, at 78 %. After this the 1-butene-NO⁺ adduct was the most prominent, with a relative abundance of only 12 %. The hydride ion transfer products of acetonitrile and MVK were also observed to undergo a small amount of association with NO⁺, producing an ion of the form M(-H).NO⁺.

With the exception of benzene, toluene and acetonitrile, all of the test compounds exhibited some degree of fragmentation following reaction with NO⁺. In general the degree of fragmentation was observed to increase with the size of the test molecule, highlighting the importance of the electric field and the resultant KE_{cm} . Common identifiable fragmentation products include, acylium and alkyl (m/z 29, 43, 57 and 71) and vinyl and allyl (m/z 27 and 41) cations. The mechanisms behind the production of such fragment ions are discussed in detail in Section 3.6.3.4.

Owing to a small amount of residual water vapour within the drift cell at the time of experiment, the mass spectra of propanal, butanal, butanone, hexan-2-one and hexan-3-one

contained some minor contribution from the MH^+ ion or the $MH^+(-H_2O)$ ion (derived from a small fraction of PTR with H_3O^+). As mass spectra obtained from reaction of these compounds with H_3O^+ are very simple and 'clean', any such 'contaminant' ions are easily identified and subtracted. It should be noted however, that if the residual MH^+ contaminant peak is removed form the butanone mass spectrum, the contribution made by the M.NO⁺ ion increases considerably in relative abundance to approximately 70 %.

3.5.4 Reactions of $O_2^{+\bullet}$

Figure 12 and Figure 13 display the product ions formed following reaction of the test compounds with O_2^{++} . A full list of product ions formed and their relative abundances can be found in **Table A3.10** of the Appendix. Compared to the other ionisation reagents used here, oxygen has a relatively high first ionisation energy of 12.0697 eV. This is higher than all of the test compounds employed, substantially so in some cases. As a consequence of this, direct charge transfer is energetically feasible in each case.



Figure 12: Product ion distribution of the test aldehydes, ketones and alcohol (molecular weight given in parentheses) following their reaction with O_2^{+} at a reactor E/N of 151 Td.

From **Figures 12** and **13** it is clear that not all of the test compounds produce stable M^{+} product ions. Indeed only the mass spectra of methacrolein, MVK, methyl benzoate, 1-butene, benzene, toluene and acetonitrile display evidence of the M^{+} ion under the present CIR-TOF-MS conditions. Also, the contributions made by these respective M^{+} ions to the overall spectra were minor in most cases. The exceptions to this were benzene, toluene and

acetonitrile, each of which underwent charge transfer to produce a molecular ion of 100 % relative abundance.



Figure 13: Product ion distribution of the test esters and hydrocarbons (molecular weight given in parentheses) following their reaction with O_2^{+} at a reactor *E/N* of 151 Td.

Surprisingly five out of the twelve organic compounds investigated appeared to undergo hydride ion transfer with O_2^{++} , producing parent ions of the form M(-H)⁺. Of these compounds acetaldehyde, ethanol, methacrolein and MVK exhibited similar behaviour upon reacting with NO⁺ (see Section 3.5.3).

As with NO⁺, all of the test compounds apart from benzene, toluene and acetonitrile underwent fragmentation following reaction with O_2^{++} . In fact from comparison of **Figures 9**, **10** and **11** with **Figures 12** and **13**, it can be seen that the fragmentation patterns produced following reaction of the test compounds with these two reagents are very similar. The major exception to this is hexanal, which showed more extensive break up following ion-molecule reaction with the O_2^{++} ion. As shown in **Figure 12** and **Table A3.10** of the Appendix, following reaction with O_2^{++} , hexanal proceeded to produce over seven different, low intensity fragment ions.

3.6 Discussion

3.6.1 The Mechanisms of CIR-MS Hydronium Ion-Molecule Chemistry

As previously stated all of the test analytes possess proton affinities greater than that of water, and hence each will readily undergo exothermic proton transfer reaction with the hydronium ion, as in reaction (R3.3). Reaction (R3.3) is rapid, *i.e.* it is assumed to proceed at the collision-limited rate. As the drift cell reactor energy was maintained at a high level throughout the present study (*i.e.* $E/N \sim 120 - 150$ Td) and as all sample/carrier gases were dry, the abundance of hydronium-water cluster ions was minimal and hence there was no appreciable contribution from such ions to the chemistry under investigation.

From the results presented in Section 3.5.1, it is appears that when the reagent ion population of the CIR-TOF-MS reactor is solely comprised of H_3O^+ ions, three major pathways exist for the formation of ion-molecule reaction products. These pathways are (i) direct proton transfer to produce an MH⁺ ion, (ii) water elimination to produce an ion of the form MH⁺(-H₂O) and (iii) post ionisation fragmentation. The mechanisms behind the three main ionisation methods described will be investigated in turn, with specific focus on the species susceptible to each type of reaction pathway.

3.6.1.1 Direct Exothermic Proton Transfer

By far the most common product ion formed during this study was the MH^+ ion. In fact only three out of the entire test set of thirty five volatile organic compounds showed no evidence for survival of the MH^+ ion in their mass spectra. The relative abundance of MH^+ varied from compound to compound and appears to be a species-specific and structure-dependent parameter.

The ionisation of a target neutral by proton transfer from a proton donor ion may essentially be described as an *electrophilic addition reaction*, where the proton is bound to the target following the formation of a dative covalent bond. In this instance the electrophile (*i.e.* the proton donor), is the hydronium ion and the nucelophile (*i.e.* the proton acceptor), is the neutral analyte. During reaction, the 'attack' of the electrophilic H_3O^+ ion will occur on the most electron rich site of the nucleophilic analyte.

For hydrocarbon compounds containing C=C double or triple covalent bonds, such as alkenes, alkynes and non-polar aromatics, electrophilic attack and proton addition will occur

at the bond of highest electron density. Several example mechanisms describing proton transfer reaction from H_3O^+ to a selection of the test hydrocarbons are given in **Figure 14**.



Figure 14: Proton transfer reaction mechanisms describing the production of the MH⁺ ion in the cases of 1-butene (Mechanism 1), isoprene (Mechanism 2) and benzene (Mechanism 3)

Taking 1-butene as an example; the hydronium-alkene proton transfer reaction proceeds by cleavage of the C1–C2 π bond, to allow the formation of a dative σ covalent bond between the C1 carbon and a proton of the hydronium ion. Here the π bond breaks in preference to the σ bond (within the C1–C2 double covalent bond), as its constituent electrons are located further from the nuclei and hence are more loosely bound (*i.e.* the π bond energy is lower than that of the σ bond). Once the donated hydrogen becomes associated with (*i.e.* bound to) the C1 carbon, the H–O bond within the hydronium ion will break to yield a molecule of neutral water and an MH⁺ carbocation, with positive charge localised on the C2 carbon.

It is important to note that for both 1-butene and isoprene proton addition will only occur at the C1 carbon in each case, as the resultant product is the most stable form of the various possible carbocations. From Markovnikov's rule, during the protonation of a double bond site, the donated proton will bind to the *least* highly substituted carbon, such that the positive charge of the ion formed is located at the *most* highly substituted carbon, thus conferring stability to the resultant cation (Markovnikov, 1870).

For the more polar oxygenated or nitrated volatile organic compounds such as the carbonyls, alcohols and acids, the electrophilic attack of hydronium and subsequent protonation will

occur at a lone electron pair located on the functional group. Several example mechanisms describing the proton transfer reaction process from the hydronium ion to a selection of the test OVOCs are given in **Figure 15**.



Figure 15: Proton transfer reaction mechanisms for acetaldehyde, acetone, ethanol, acetic acid and methyl acetate

Taking acetone as an example, OVOC protonation by the hydronium ion takes place *via* the electrophilic attack of the hydronium on one of the lone electron pairs of the oxygen. A dative covalent bond subsequently forms between the donated proton and the oxygen heteroatom, as the H–O bond within the hydronium ion severs to yield a molecule of neutral water and an MH⁺ carbonyl-cation, with positive charge localised on the oxygen of the functional group.

3.6.1.2 Direct Proton Transfer and Subsequent Water Elimination

The second most common process observed here following PTR to the oxygenated organic compounds, was the elimination of water from the nascent MH^+ (pseudo) molecular ion to yield a hydrocarbon cation of the form $MH^+(-H_2O)$. This dehydration process has been reported by several workers using SIFT and PTR-MS methods (Spanel and Smith, 1997a; Spanel and Smith, 1997b; Spanel and Smith, 1998a; Buhr *et al.*, 2002). As noted in Section 3.5.1 the water elimination channel appears to be primarily important for the aliphatic
aldehydes, alcohols and acids of carbon chain length ≥ 3 . Also from the CIR-TOF-MS results shown here, in general it appears that the water elimination channel increases in importance with the size of the carbon chain length.

Figure 16 below, displays the mechanism underlying the process of water elimination from a generic alcohol (the mechanism shown is applicable to all susceptible group (II) compounds). The water elimination process begins with the electrophilic attack of the hydronium ion on a lone electron pair located on the alcoholic oxygen. Once a dative covalent bond has formed between the oxygen and the donor proton, and once the H–O bond within the hydronium ion has been broken, the MH⁺ ion forms. In order to remove the excess energy associated with the reaction, the bonding pair of electrons comprising the C1–O bond will move to stabilise the protonated functional group, causing bond dissociation and the successive production of a molecule of neutral water and an alkyl/hydrocarbon cation. Subsequent rearrangement may occur to stabilise the resultant daughter ion and further fragmentation is possible, as in the case of hexanal.



Figure 16: Water elimination from the nascent MH⁺ ion of a generic alcohol

The relative prominence of the dehydration reaction channel for the saturated, straight chain aldehydes, alcohols and acids was observed to increase with analyte hydrocarbon chain length, which as can be seen from inspection of **Table 1**, correlates with proton affinity. For example the proton affinities of acetaldehyde, propanal, butanal and hexanal are 769, 786, 793 and 794 – 797 kJ mol⁻¹, respectively. Clearly then as shown in **Figure 17**, the more exothermic the reaction the larger the contribution made by the MH⁺(-H₂O) ion.

The relationship shown in **Figure 17** between the extent of dehydration of the group (II) compounds and reaction exothermicity, can be explained in terms of stability of the MH^+ product. The level of excitation of the nascent MH^+ ion will increase with the exothermicity of the reaction, and hence it is more difficult for those analytes that possess higher proton affinities to avoid subsequent fragmentation. Consequently, as water elimination is a significant channel *via* which excess energy can be removed, its importance increases with proton affinity and therefore hydrocarbon chain length.



Figure 17: Dependence of the water elimination channel on reaction exothermicity for the aliphatic test aldehydes, alcohols and acids. Symbol key: 1 =acetaldehyde, 2 =propanal, 3 =butanal, 4 =hexanal; 5 =methanol, 6 =ethanol, 7 =propanol, 8 =butanol; 9 =formic acid, 10 =acetic acid.

It should be noted however, that certain compounds within the group (II) sub-set, possess higher proton affinities than those compounds discussed above, and yet exhibit little or no water elimination. For example, the H_3O^+ + methacrolein and H_3O^+ + benzaldehyde proton transfer reactions are exothermic by ~ 118 and 143 kJ mol⁻¹, respectively, and yet no dehydration was observed. This response can be explained through examination of the structures of these compounds, *i.e.* methacrolein and benzaldehyde both contain features which allow resonance stabilisation of the nascent (MH⁺)* ion, the two double covalent bonds for the former and the benzene ring for the latter.

3.6.1.3 Dissociative Exothermic Proton Transfer and Molecular Ion Fragmentation

VOC fragmentation following PTR form the hydronium ion is generally thermodynamically unfeasible under thermal conditions. This result originates from the energy barriers to the various rearrangement pathways being slightly larger than the exothermicity associated with PTR ionisation. However, in CIR-MS type instruments which incorporate a drift tube reactor, the small amount of energy required to induce fragmentation (sometimes as low as 30 - 40 kJ mol⁻¹ (Mackay *et al.*, 1978; Milligan *et al.*, 2001)) can supplied by the reactor electric field, which acts to increase the *KE_{cm}* of the ion-molecule collision and hence the overall energy of the reaction. The excess energy released from the reaction will facilitate the production of the MH⁺ ion in an excited state, (MH⁺)* (Milligan *et al.*, 2001). The phenomenon of fragment ion generation in CIR-MS is discussed in detail in Section 3.6.3.4 for ionisation by NO⁺ and

 O_2^{+} , from which fragmentation is most significant, hence only a brief discussion is given here.

As noted in Section 3.5.1, a number of the test compounds were observed to undergo unimolecular dissociation following proton transfer from H_3O^+ to yield one or more types of fragment ion (F⁺), *viz*:

$$H_{3}O^{+} + M \rightarrow (MH^{+})^{*} + H_{2}O$$
 (R3.10)

$$(\mathrm{MH}^{+})^{*} \to \mathrm{F}^{+} + \mathrm{N} \tag{R3.11}$$

where N represents a neutral fragment.

For the hydrocarbons, saturated straight chain aldehydes, alcohols and acids the most common fragmentation products observed here were the allyl ion (m/z 41, CH₂=CHCH₂⁺), the alkyl type *n*-propyl ion (m/z 43, CH₃CH₂CH₂⁺) and the acylium type propionyl ion (m/z 43, CH₃CHO⁺). The allyl and alkyl ions were most likely formed following scission of the hydrocarbon chain and loss of methyl, alkyl, allyl and functional group units. As will be discussed in Section 3.6.3.4, in the case of the carbonyls, the m/z 43 feature may contain contribution from both the *n*-propyl and propionyl ions; however formation of the former is less kinetically feasible than its acyl equivalent (McLafferty and Turecek, 1993). This was confirmed by detailed inspection of the TOF-MS accurate mass data. Other minor fragment ions observed in the CIR-TOF-MS mass spectra following reaction with hydronium (and often in PTR-MS) include various alkyl and acylium type ions of m/z 29 (CH₃CH₂⁺ or CHO⁺), 57 (CH₃(CH₂)₃⁺ or (CH₂)₂CHO⁺) and 71 (CH₃(CH₂)₃⁺ or (CH₂)₃CHO⁺), the propargyl ion of m/z 29 (CH₂=C=CH⁺) and the vinyl ion of m/z 27 (CH₂=CH⁺).

3.6.2 The Mechanisms of Ammonium Ion-Molecule Chemistry

As reported in Section 3.5.2, because of the reaction thermodynamics involved, none of the test compounds underwent PTR with the ammonium ion. However, seven of the twelve compounds did undergo association reaction with ammonium, and to a lesser extent with the NH_4^+ .(NH₃) cluster, to form the M.NH₄⁺ and M.NH₄⁺.(NH₃) adducts, respectively:

$$NH_4^+ + M + B \rightarrow M.NH_4^+ + B$$
 (R3.12)

$$NH_{4}^{+}.(NH_{3}) + M + B \rightarrow M.NH_{4}^{+}.(NH_{3}) + B \qquad (R3.13)$$

It should be noted here that, as seen in **Figure 1**, the ammonium-ammonia adduct ion was a significant contributor to the reagent ion pool under the current CIR-TOF-MS conditions (\sim 19 % of the ammonium peak).

Of the test compounds, it was only those of highest PA (779 – 851 kJ mol⁻¹) and with the largest dipole moment (1.86 – 3.51 D) that were observed to undergo association with the ammonium ion. This finding is in line with the $M.NH_4^+$ cluster ion being generated following the formation of monopole-dipole and hydrogen bonds between the electronegative heteroatom of the analyte and the hydrogen atoms of the reagent (de Hoffman and Stroobant, 2007).

3.6.3 The Mechanisms of CIR-MS NO^+ and O_2^{+} Ion-Molecule Chemistry

From Sections 3.5.3 and 3.5.4 it is clear that the NO⁺ and O_2^{++} ions exhibit more complex ionmolecule chemistry in their reactions with VOCs than does H_3O^+ . As described earlier, the reactions of NO⁺ and O_2^{++} can be divided into three distinct categories according to ionisation method: (i) charge transfer to form the M⁺⁺ ion, (ii) hydride ion transfer to form a molecular ion of the form M(-H)⁺ (and HNO in the case of NO and the HO₂ radical in the case of O_2^{++}), and (iii) for NO⁺ only, the formation of an ion-molecule association complex, M.NO⁺. Each of these three mechanisms may be followed by subsequent (pseudo) molecular ion fragmentation. The relative prominence of these pathways depends to a large extent on the thermodynamics involved, which in turn are influenced by the relative magnitudes of the ionisation energies of NO and O₂ compared to the analyte molecules. NO⁺ and O₂⁺⁺ ionmolecule chemistry is rapid; with a small number of exceptions both reagents will react with organic compounds at or near the collision limited rate (Spanel and Smith, 1997a; Spanel and Smith, 1997b; Spanel and Smith, 1998a; Spanel and Smith, 1998c).

3.6.3.1 Direct Charge Transfer reaction Ionisation

3.6.3.1.1 Charge Transfer Reactions Involving NO⁺

Hexan-3-one, benzene and toluene are the exceptions amongst the molecules studied here, in that their first ionisation energies have been determined to lie slightly below that of NO (see **Table 1**), and therefore it is of no surprise to see relatively large M^{++} charge transfer product peaks in their mass spectra (see **Figure 10** and **Figure 11**). For such low ionisation energy compounds, charge exchange is expected to be a rapid bimolecular process, during which an outer shell electron is transfer from the neutral analyte to the NO⁺ ion producing the singly charged, radical analyte cation and the NO radical.

As the first ionisation energies of the remaining test compounds are larger than that of NO, we would initially expect no further role for charge transfer reactions. However, this

assumption would appear to be incorrect as $M^{+\bullet}$ ions were unexpectedly observed in several cases. Although many of the $M^{+\bullet}$ peaks produced were somewhat weak, reasonably strong signals were observed for 1-butene (24 %), and acetonitrile (100 %), as were many fragment ions that appear to result from the $M^{+\bullet}$ parent ion.

The presence of charge transfer products, derived from thermally endothermic reactions, is attributed to the effect of the electric field that is applied along the length of the drift cell assembly. As described earlier if an electric field is applied to the drift cell it will cause the ions present to accelerate, and hence will impart to them additional translational energy (according to equations (E2.12) – (E2.18) of Chapter 2). Increasing the kinetic energy of the ion pool will perturb the kinetics of all subsequent ion-molecule reactions, and will alter the propensity of certain compounds to undergo charge transfer ionisation in a number of ways.

First of all increasing the overall energy of the NO⁺ reagent ion may be sufficient to cause its excitation to a higher vibrational state. Using equation (E2.17) of Chapter 2, we see that KE_{ion} for NO⁺ under the current experimental conditions was ~ 0.49 eV, which is somewhat larger than the energy required to raise the NO⁺ ion to its first excited vibrational energy level, *i.e.* 0.28 eV (Smith *et al.*, 2003). As the ionisation energy of NO in its ground state lies very close to the first ionisation energy of most of the test compounds (by 0.06 – 2.94 eV), an increase in its vibrational energy would allow the charge transfer channel to become energetically feasible in several cases. Indeed it is for those compounds whose first ionisation energies exceed that of NO by the smallest margins that we observe unexpected M⁺⁺ spectral peaks, *i.e.* butan-2-one (+ 0.26 eV), hexan-2-one (+ 0.09 eV) and 1-butene (+ 0.29 eV).

Although in some cases, simple bimolecular electron exchange may be responsible for generating the M^{++} product ion, a second mechanism exists by which the NO⁺ ion may facilitate ionisation of a target compound by charge transfer. This channel requires the target compound to be able to form an ion-molecule association complex with the NO⁺ ion, hence it is only available to susceptible polar species such as ketones, esters and some carboxylic acids (ion-molecule association will be discussed in further detail below). Once bound within the ion-molecule association complex, near resonant charge exchange can occur internally between the reagent ion and the neutral analyte (Smith *et al.*, 2003). If the complex is sufficiently energetic such that it may dissociate, the M⁺⁺ ion and a neutral NO radical are produced. The excitation energy of the association complex, and therefore the ultimate abundance of the M⁺⁺ ion may be increased by raising the drift cell *E/N*, and in doing so the

centre of mass kinetic energy of the ion-neutral collision. This can be seen below in **Figure 18**, which displays the variation of the hexan-3-one $M^+/M.NO^+$ ratio with KE_{cm} as recorded by CIR-TOF-MS in the current study.



Figure 18: Variation of the $M^+/M.NO^+$ ratio with centre of mass collision kinetic energy (*KE_{cm}*) for hexan-3-one

Figure 18 clearly demonstrates that as the ion-neutral collision becomes more energetic and as dissociation of the $(M.NO^+)^*$ complex is encouraged, "*inter-complex charge transfer*" increases in importance as a pathway to M^{+*} formation. However as the collision energy was increased above ~ 0.35 eV, the M^{+*} ion was observed to decrease in abundance, presumably as dissociative pathways began to dominate.

Inter-complex charge exchange most likely increases in importance with the ionisation energy of the analyte. Consequently, as well as playing some role in the production of $M^{+\bullet}$ ions from the ketones, inter-complex charge exchange is most likely to be the dominant underlying ionisation method behind the formation of the $M^{+\bullet}$ ions observed in the mass spectrum of compounds such as acetonitrile.

The theory of inter-complex charge transfer was first proposed by Fairley *et al.* (Fairley *et al.*, 1999) in a study investigating the reactions of NO^+ with three test ketones (acetone, hexan-2-one and pentan-3-one). The authors presented direct evidence to show that charge exchange occurs within the association complex and that an increase in the kinetic energy of the reactants results in a decrease in the lifetime of the (M.NO⁺)* intermediate. The authors continued to demonstrate that the pentan-3-one–NO⁺ charge transfer rate constant increased by a factor of four, when the ionisation regime was moved from thermal conditions to one in which the centre of mass kinetic energy was equal to 0.50 eV. Beyond this energy threshold the authors comment that the magnitude of the dissociative charge transfer rate constant

increases sufficiently to dominate the fate of the reactants. These findings are entirely in line with those obtained here, except that the dissociative charge transfer threshold for the hexan-3-one–NO⁺ complex was somewhat lower than that reported by Fairely *et al.* for pentan-3one, by ~ 0.15 eV. This disparity however is most likely explained by the relative differences in binding energy of the two complexes.

3.6.3.1.2 Charge Transfer Reactions Involving $O_2^{+\bullet}$

As stated earlier, all of the test compounds except acetonitrile possess first ionisation energies considerably less than that of O₂; hence exothermic charge transfer reaction is feasible in each case. However, it was found in Section 3.5.4 that the reactions of the test compounds with O_2^{+} were generally characterised by strong fragmentation of the nascent $(M^{+})^*$ ion. The mass spectra of most compounds therefore typically contained only a minor peak corresponding to the M^{+} ion, and several peaks of lower m/z corresponding to its fragmentation products. This finding, which will be discussed in further detail below, can be partially explained through investigation of the exothermicity of the O_2^{+} charge transfer reactions, which in most cases was presumably large enough to generate a highly excited $(M^{+})^*$ product. Of all of the test compounds only benzene, toluene and acetonitrile underwent charge transfer reactions with the O_2^{+} ion without producing fragmentation products in significant abundance. This result is somewhat unusual as benzene and toluene have the lowest ionisation energies of all of the test compounds, and hence their reactions would be the most energetic. Clearly other factors must come into play, notably the energetics of bond dissociation, rearrangement processes in the parent and resonance stabilisation offered by the aromatic ring (McLafferty and Turecek, 1993).

3.6.3.2 Ionisation by Hydride Ion Transfer

Hydride ion transfer, *i.e.* removal of the H⁻ ion from a neutral analyte and the concomitant production of a stable radical cation, is amongst the least common of the ionisation pathways available, but it has been widely observed in reactions involving NO⁺ and many different organic analytes (Smith and Spanel, 2005). As seen in Section 3.5.3, all of the test aldehydes along with ethanol, hexan-2-one and MVK underwent hydride ion transfer reaction with the NO⁺ ion in the CIR-TOF-MS reactor. Also acetaldehyde, methacrolein, ethanol, MVK and methyl benzoate similarly reacted with O_2^{+*} *via* hydride ion transfer to produce an M(-H)⁺ (pseudo) molecular ion.

The relative abundance of the M(-H)⁺ parent ion varied considerably between the test compounds, with those molecules of highest ionisation energy producing the strongest peaks, *i.e.* the M(-H)⁺ products for acetaldehyde (IE = 10.2291 eV) and ethanol (IE = 10.48 eV) were of 77 and 97 % relative abundance, respectively, following reaction with NO⁺ and 100 and 66 %, respectively, following reaction with O_2^{++} . The remaining compounds produced hydride ion transfer products of relative abundance no greater than ~ 20 %. Such low branching ratios can be attributed again to the effect of the applied electric field, which has two main roles in this regard: (i) it opens up other competitive reaction channels, such as charge transfer, which are thermally endothermic as detailed above, and (ii) it causes a greater amount of molecular ion fragmentation by increasing the kinetic energy of all collisions.

The underlying mechanism behind the hydride ion transfer process is exemplified below in Mechanisms 9 and 10 of **Figure 19**, for the reactions of NO^+ with acetaldehyde and ethanol, respectively.



Figure 19: Hydride ion transfer mechanisms for the production of M(-H)⁺ from a typical saturated aldehyde and alcohol.

As seen in **Figure 19**, hydride ion transfer begins with the electrophilic attack of the NO⁺ cation on the electron pair comprising a C–H σ -bond of the analyte C1 carbon atom. In the tight intermediate ion-molecule reaction complex, the C–H bond within the analyte breaks as the N–H bond within the reagent forms, the result being the production of an oxonium ion (*e.g.* the acylium ion in the case of Mechanism 9) and a neutral molecule of HNO (Spanel and Smith, 1997a; Cullis, 2008). It should be noted that formation of HNO is the only possible fate for the reagent and the transferred hydride ion; the production of a split H⁻/NO⁺ ion pair is not energetically feasible (Smith and Spanel, 2005).

In general for all simple saturated aldehydes and alcohols, hydride ion transfer from the C1 carbon will always takes place in preference to hydride ion transfer from elsewhere on the

hydrocarbon portion of the molecule (Spanel and Smith, 1997a; Spanel and Smith, 1997b). This selective extraction mechanism occurs because of the binding energies of the bonds involved; typically extraction of the hydride ion from the functional-group-bearing C1 carbon is energetically possible, whereas extraction from the pendant carbon chain is often not. For example, for acetaldehyde reacting with NO⁺, hydride ion transfer from the functional group bearing carbon is exothermic by 0.7 eV, whereas transfer from the carbon chain is endothermic by 0.8 eV (Spanel and Smith, 1997b). Furthermore, if the charge site is located on the C1 carbon, resonance interaction with the oxygen heteroatom will facilitate stabilisation of the resultant ion (Cullis, 2008). Hydride ion transfer reactions with O_2^{++} are less common than with NO⁺, but the reaction mechanics presumably parallel those already discussed.

Similar to hydride ion transfer described above, alkoxide ion transfer was observed as a significant reaction channel for the two test esters, ethyl acetate and methyl benzoate. Alkoxide ion transfer involves the removal of the OR functionality at the ester linkage to form an oxonium type ion in the case of ethyl acetate, *i.e.* $M(-OCH_2CH_3)^+$, and an aromatic bearing oxonium type ion in the case of methyl benzoate, *i.e.* $M(-OCH_3)^+$ (Spanel and Smith, 1998a). The alkoxide ion transfer product was by far the most dominant ion in the mass spectra of both esters following reaction with NO⁺ and O₂⁺⁺, with relative abundances of 51 and 22 %, respectively for ethyl acetate, and 88 and 88 %, respectively for methyl benzoate. A minor hydroxide ion transfer channel in the reaction of ethanol with NO⁺ was also observed in the CIR-TOF-MS mass spectra.

3.6.3.3 Association Complex Formation

Association complex formation involving the NO⁺ ion was observed to proceed under CIR-MS conditions for certain analytes whose structures contain areas of high electron density. Of the test VOCs, adduct formation only occurred for those structurally susceptible compounds that also have first ionisation energies greater than or very close to that of NO. Of the limited test set, all of the ketones along with 1-butene and ethyl acetate were observed to undergo adduct formation to produce an ion of the form M.NO⁺.

It has previously been reported (Smith *et al.*, 2003) that as the first ionisation energy and proton affinity of the neutral analytes increases, so does their tendency to form association complexes with the NO^+ ion. This response has been attributed to the "charge transfer complexing" phenomenon described earlier (Fairley *et al.*, 1999; Smith *et al.*, 2003). Charge

transfer complexing is a mechanism by which the binding energy of the excited intermediate adduct $((M.NO^+)^*$ in this case) is increased by the binding electron (which is donated by the analyte M), moving freely between its parent and the reagent, such that states of M⁺ and NO⁺ exists within the complex. Increasing the binding energy of the intermediate will result in an increase in its lifetime, thus improving the probability that the excited complex will undergo a stabilising third body collision.

The findings reported here clearly support the theory of charge transfer complexing, in particular for the ketones and for 1-butene. For the ketones the relative abundances of the $M.NO^+$ product ion increased from 8 % for hexan-3-one (IE = 9.12 eV) to 78 % for acetone (IE = 9.703 eV).

As with the hydride ion transfer products, generally only relatively small $M.NO^+$ peaks were produced under the current CIR-TOF-MS conditions. This result can be attributed to both the competitiveness of other reaction channels and the relatively high drift cell energies involved. For example MVK and ethyl acetate both possess relatively high first ionisation energies, yet only exhibited minor NO⁺ adduct signals (6 and 4 % respectively). Indeed, as seen in **Figure 18** and as reported by Fairley *et al.*, (1999) and Smith *et al.*, (2003), the lifetime of the excited intermediate (M.NO⁺)* will decrease with *KE_{cm}*.

3.6.3.4 Dissociative Ionisation by NO^+ and O_2^{+}

The phenomenon of molecular ion fragmentation in mass spectrometry is a vast and complex topic, which can only be treated briefly here. As such focus is placed on the main underlying mechanisms behind the production of some of the most major fragment ions formed from reactions of the test organics with NO⁺ and O_2^{++} , the most aggressive reagents employed.

Following its production from an ion-neutral reaction, any given molecular ion may undergo fragmentation to produce two or more products, one of which will retain the original charge (McLafferty and Turecek, 1993). Post ionisation fragmentation is a unimolecular process, which will only occur if the molecular ion is sufficiently energetic, *i.e.* it must possess a minimum quantity of energy in order to decompose along a given pathway, *e.g.*:

$$O_2^{+\bullet} + M \to (M^{+\bullet})^* \to F^+ + N^{\bullet}$$
(R3.14)

Essentially, this means that the parent ion must possess enough energy to overcome the activation energy barrier for rearrangement to products, *i.e.* energy is required for movement of electrons, bond cleavage, bond formation, *etc.* The required amount of energy for the 104

production of a particular fragment ion is known as the *Appearance Energy*, and it must be supplied in the form of vibrational energy (de Hoffman and Stroobant, 2007). After the application of some perturbation to the total energy of an ion, that new overall energy will be redistributed in a statistical manner over the various degrees of freedom; consequently an increase in the ion vibrational energy will result (de Hoffman and Stroobant, 2007). This redistribution is rapid, occurring within 10⁻¹⁰ s. The internal energy of a given molecule will be increased first during the ionisation event, and again subsequently when the newly formed ion comes under the influence of collisions driven by the drift cell electric field.

Often the greatest perturbation to the total energy of the molecular ion comes from the energy released during the ion-molecule reaction (*e.g.* reactions (R3.3) and (R3.5)). The exothermicity of an ion-molecule reaction under thermal conditions, can be determined simply from knowledge of the ionisation energies of the reactants (or for PTR, the proton affinities), *i.e.* a reaction is exothermic by an amount of energy equivalent to the ionisation energy difference between the target molecule and the neutral reagent ($\Delta E = IE(M) - IE(R)$).

As molecular oxygen has a relatively high first ionisation energy with respect to most organic molecules (12.06 eV), the reactions of O_2^{++} were expected be the most energetic of all of those studied here. Indeed from inspection of **Table 1** we find that the reactions of the test molecules with O_2^{++} were exothermic by between 1.58 and 3.23 eV. As most hydrocarbons possess dissociation limits of only ~ 2 eV (Lagg *et al.*, 1994), the degree of fragmentation observed under the current CIR-MS conditions is easily explained. However, from comparison of **Figures 9**, **10** and **11** with **Figures 12** and **13**, it becomes clear that the fragmentation products obtained from reactions with O_2^{++} were similar to those obtained following reaction with NO⁺, even though for some of the analytes charge transfer from the latter is endothermic. As discussed above, this result is attributed to the significant role played by the reactor electric field, enhancing the *KE* of all ions and in doing so the *KE* associated with each collision event (*KE_{cm}*). From the application of equations (E2.12) – (E2.18) (of Chapter 2) we find that the centre of mass kinetic energies of the NO⁺ and O₂⁺⁺ ion molecule collisions investigated range from ~ 0.30 – 0.42 eV.

In the event that a newly formed ion is sufficiently energetic to overcome the activation energy barrier to decomposition, it may fragment *via* a number of different mechanisms, the most common of which are discussed below.

1) Direct Dissociation

Also known as *sigma-bond dissociation* or σ -*bond cleavage*, this fragmentation mechanism is only available to odd electron radical ions formed by charge/electron exchange ionisation (McLafferty and Turecek, 1993). Such direct dissociation occurs when charge transfer takes place at the site of a saturated sigma bond. During the ionisation process one of the electrons comprising the bonding pair is removed causing the subsequent fragmentation of the analyte ion. The result is the production of a cationic fragment ion and a free radical. As the removal of an electron from a sigma bond site is less favourable than the removal of an electron from a double bond (specifically the π bond) or a non-bonding electron pair, direct dissociation is almost exclusively reserved for fully saturated species such as alkanes. Mechanism 11 of **Figure 20** gives an example of the σ -bond fragmentation mechanism for a generic alkane.



Figure 20: σ -bond dissociation following ionisation of a generic alkane

Stevenson's rule states that in the decay of an odd electron ion, such as that shown in **Figure 20**, the daughter fragment that has the lowest ionisation energy will retain the original charge (McLafferty and Turecek, 1993). Stevenson's rule is a direct result of the higher ionisation energy fragment having the greater affinity to retain the odd electron. Consequently in **Figure 20**, $IE(R_2CH_2) > IE(RCH_2)$.

2) Cleavage Mechanisms

As was noted in Section 3.5, there are several key features in the fragmentation patterns of test analytes that are common across all species and across the various ionisation methods. Initial inspection of the CIR-TOF-MS data reveals that fragment ions of m/z 27 and 41 were present in the mass spectra of most of the test carbonyls and 1-butene (see **Tables A3.9** and **A3.10** of the Appendix). These peaks correspond to the vinyl (CH₂=CH⁺) and allyl (CH₂=CHCH₂⁺) cations, respectively. As the most abundant product ions for most of the aldehydes, these ions could be used as species fingerprint identifiers when NO⁺ or O₂⁺⁺ chemical ionisation is employed.

Also present in the mass spectra of most of the test compounds (to varying degrees) were fragment ions of m/z 29, 43, 57 and 71. For simple saturated and unsaturated hydrocarbons,

these peaks correspond to alkyl ions, *i.e.* fragments of the hydrocarbon chain of the form $CH_3(R)_n^+$, where $R = CH_2$ and $n \ge 1$, *e.g.* $m/z \ 43 = CH_3(R)_2^+ = CH_3CH_2CH_2^+$, the *n*-propyl cation. Similarly for the alcohols these common daughter peaks also correspond to alkyl fragments of the hydrocarbon chain, formed following removal of the functional group *via* a water elimination mechanism (see later discussion) (McLafferty and Turecek, 1993; Buhr *et al.*, 2002). However, for the carbonyl species the product ions of $m/z \ 29 - 71$ could have one of two different identities: (1) they may be ions composed entirely of segments of the hydrocarbon chain or (2) they may be ions containing the functional group. For example, from the nominal value alone, the peak at $m/z \ 29$ in the mass spectrum of propanal could correspond to either the $CH_3CH_2^+$ alkyl ion or the CHO^+ acylium ion, and so on for increasing chain length.

Some insight into the identity of these common fragments may be gained from the mass spectra of those compounds that are only able to produce one of the two types of daughter product. For example in the case of acetone, the m/z 43 fragment can only be the functional group bearing acylium ion, CH₃C=O⁺. Similarly, for hexan-3-one the pendant hydrocarbon chain is not large enough to produce an alkyl ion of m/z 57, hence without structural rearrangement the fragment must be an acylium ion, this time ⁺O=CCH₂CH₃.

The accurate mass data obtained in the current study from the time-of-flight mass spectrometer assists further in the identification of such fragmentation products. As exemplified in **Figure 21**, measurements made here suggest that the m/z 43, 57 and 71 peaks derived from odd electron (parent) carbonyl ions, are primarily composed of functional group bearing acylium ions. Production of the acylium ion in favour of the alkyl ion is also in line with Stevenson's rule, as the hydrocarbon section of any given aldehyde or ketone will always posses a higher ionisation energy than its functional group bearing counterpart (see **Table 2**).

Furthermore, as well as possessing a lower IE, retention of charge by the acyl fragment is also favoured by resonance interaction within the C=O functionality, which will provide stability to the resultant ion. In general in mass spectrometry the most abundant fragment ion will always be that which is best able to stabilise the charge (McLafferty and Turecek, 1993).



Figure 21: Peak shapes produced by fragment ions of m/z (a) 41, (b) 43, (c) 57 and (d) 71. In each plot the solid vertical line marks the theoretical spectral position of the acylium ion and the broken vertical line marks that of the alkyl ion. In (a) the broken vertical line marks the theoretical position of the allyl ion

Table 2: Ionisation energies of the various alkyl and acyl fragments that are produced following dissociation of odd electron parent ions. Note: n/a = not applicable and u/a = data unavailable. Ionisation energy data taken from NIST (www.nistwebbook.com).

m/z	Alkyl Fragment (IE / eV)	Aldehyde Acyl Fragment (IE / eV)	Ketone Acyl Fragment (IE / eV)
29	CH ₃ CH ₂ (8.26)	СНО (8.12)	n/a
43	CH ₃ CH ₂ CH ₂ (8.09)	CH ₂ CHO (u / a)	COCH ₃ (7.0)
57	CH ₃ CH ₂ CH ₂ CH ₂ (8.01)	CH ₂ CH ₂ CHO (6.6)	$COCH_2CH_3$ (u / a)
71	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ (7.94)	CH ₂ CH ₂ CH ₂ CHO (u / a)	$CH_2COCH_2CH_3$ (\mathbf{u}/\mathbf{a})

The accurate mass data obtained from the TOF-MS does, however, suggest that some exceptions to Stevenson's rule may exist. For example, the measured accurate mass of the butanal m/z 43 peak was more indicative of (alkyl) *n*-propyl ion, rather than (acylium) propionyl ion formation (see Figure 21(b)). The TOF-MS accurate mass data also supplies confidence to the assignment of m/z 41 as the allyl ion, as exemplified for butanal in Figure 21(a).

The common alkyl and acylium daughter ions observed here in CIR-TOF-MS, are produced following two of the most common fragmentation mechanisms encountered in mass spectrometry, *i.e.* (i) *radical site initiated unimolecular reaction*, followed by α -cleavage, or (ii) charge site initiated unimolecular reaction, followed by inductive cleavage.

(i) Radical site initiated fragmentation and α -cleavage

Radical site initiated reactions are likely to be responsible for the production of the more common allyl and acylium fragment ions, which typically form from odd electron unsaturated hydrocarbon and carbonyl parent ions, respectively.

Radical site initiated reactions involve rearrangement of the unpaired electron produced in the ionisation process, and a second electron from an established bond, in order to form a new covalent bond. Clearly, movement of this second electron will cause dissociation of the original bond. The radical site initiated/ α -cleavage mechanism behind the production of the allyl ion from alkenes in CIR-TOF-MS is shown in **Figure 22** and is described below.



Figure 22: Allyic/α-cleavage of a typical alkene following charge transfer ionisation in CIR-TOF-MS (adapted from (McLafferty and Turecek, 1993))

In the case of simple alkenes, following charge transfer ionisation at a double bond site the remaining lone π electron may undergo migration from its original location towards the α -carbon. The concomitant migration of a bonding electron from the weakest remaining σ -bond of the α -carbon towards the lone π electron will result in the formation of a new double bond. Movement of the σ electron will cause bond dissociation at the original α -carbon, hence the term α -cleavage. In the case of alkene radical site initiated fragmentation, this dissociation is also known as allyic cleavage and the products of reaction are an allyl cation and an alkyl radical. The presence of the double bond in the allyl ion confers a measure of stability to the product through resonance stabilisation and the existence of a corresponding resonance canonical (McLafferty and Turecek, 1993; Cullis, 2008).

In the case of the carbonyls, the new bond is formed between the heteroatom and the function group carbon, and the bond dissociated will often be the weakest of the remaining α -bonds, hence again the term α -cleavage. The resultant products of reaction are an acylium type cation and an alkyl radical. A generalized example of the radical site initiated cleavage mechanism behind the production of the common acylium ions observed with the CIR-TOF-MS technique, is given below in **Figure 23**.



Figure 23: Radical site initiated fragmentation of carbonyl species following charge transfer ionisation. For the aldehydes, R = H and R_2 represent the pendant hydrocarbon chain, *e.g.* in Mechanism 13 for propanal $R_2 = CH_2CH_3$. For the ketones, R and R_2 represent the hydrocarbon chain, *e.g.* in Mechanism 13 for butanone R = CH₃ and $R_2 = CH_2CH_3$. The fragmentation shown in Mechanism 13 is classified as α -cleavage, whereas that shown in Mechanism 14 is technically classified as β -cleavage (Cullis, 2008).

Bond dissociation by movement of a single electron, such as that described here is also referred to as *homolytic* cleavage. During homolytic cleavage, the charge site remains fixed, such that it is located at the same point on the fragment ion as it was the parent (de Hoffman and Stroobant, 2007).

(ii) Charge site initiated fragmentation and i-cleavage

Charge site initiated reactions are analogous to the radical site initiated reactions described above, and they are responsible for the production of the alkyl fragment ions sometimes formed, for example, from odd electron carbonyl parent ions.

Charge site initiated fragmentation takes place when a bonding electron pair are drawn towards a site of positive charge, which following charge transfer ionisation of a carbonyl, will be the oxygen heteroatom. Once the electron pair come under the inductive influence of the charge site bearing heteroatom, the ion must be stabilised by establishing equilibrium with its corresponding resonance canonical. Subsequent migration of the electron pair to the functional group carbon atom will cause dissociation of an α -carbon σ -bond. As the process involves movement of an electron pair due to the attractive influence of the charge site, it is also known as *inductive cleavage*, or simply *i-cleavage*. The products of reaction are the alkyl ion and the acyl radical. An example of *i*-cleavage is given in Mechanism 15 of **Figure 24**:



Figure 24: *i*-cleavage of carbonyl species following charge transfer ionisation. For the aldehydes, R = H and R_2 represents the pendant hydrocarbon chain (McLafferty and Turecek, 1993).

Bond dissociation by movement of an electron pair, such as that described here, is also referred to as *heterolytic* cleavage. During heterolytic cleavage, the charge site migrates, such that it is located at a different point on the fragment ion to where it was located on the parent. Charge site displacement is energetically less feasible than radical site displacement; hence further the favourable production of acylium rather than alkyl ions (where possible) in odd electron CIR-MS (McLafferty and Turecek, 1993).

From close inspection of the CIR-TOF-MS mass spectrum of hexan-3-one (ionised by NO⁺) shown in **Figure 25**, which was recorded with a drift cell potential of 2700 V (*i.e.* E/N = 151 Td), we note that the m/z 43 feature is composed of two separate peaks.



Figure 25: m/z 43 peak obtained following charge transfer ionisation of hexan-3-one by the NO⁺ ion at various drift cell voltages

The lower mass peak seen in **Figure 25** matches the accurate mass value of the acylium ion and the higher mass peak matches that of the alkyl ion. Consequently, it appears that in some cases both fragment ions may be produced. It is interesting to note that because of the positioning of the functional group on the C3 carbon, the m/z 43 acylium ion cannot be formed through simple heterolytic or homolytic cleavage of hexan-3-one, hence internal rearrangement must occur. From further inspection of **Figure 25** we note that the ratio of the acylium peak to the alkyl peak increases with increasing E/N and therefore reactor energy. This is most likely due to the reactor electric field supplying the energy required to overcome the activation energy barrier to internal rearrangement, which will ultimately result in the formation of the acylium ion. This example proves yet further the versatility of the CIR-TOF-MS technique and opens up new opportunities to explore the kinetics of ion-molecule chemistry.

3) Internal Rearrangement Mechanisms

Many other different fragmentation mechanism are commonly observed in mass spectrometry, which often require the formation of an intermediate transition state and involve the internal movement and rearrangement of electrons, charge sites and even hydrogen atoms. These internal rearrangements are many and diverse and are often observed following the more energetic electron impact ionisation technique, where energies are as high as 70 eV (McLafferty and Turecek, 1993). At lower CI energies, such as typically found with the CIR-TOF-MS technique, fragmentation following internal rearrangement is less common and only the two most common examples were observed here.

Observation of the mass spectra obtained from the ion molecule reactions of NO⁺ and hexan-2one reveals the presence of a product ion of m/z 58. This even mass channel corresponds to the radical cation CH₂=C(O⁺H)CH₃, formed following perhaps the most well known form of internal rearrangement, known as *McLafferty rearrangment* (McLafferty and Turecek, 1993). As shown in Mechanism 16 of **Figure 26**, McLafferty rearrangement involves the transfer of a γ -hydrogen atom to the oxygen heteroatom of the carbonyl group in a five member ring transition state. Following hydrogen rearrangement the ion undergoes β -cleavage.



Figure 26: McLafferty rearrangement of the hexan-2-one M^{+} ion following charge transfer ionisation by the NO⁺ ion.

A ring transition state or '*tight complex*', such as that shown in the McLafferty rearrangement of **Figure 26**, is often formed by an ion as it lowers the activation entropy barrier to reaction (de Hoffman and Stroobant, 2007). Generally because of steric effects, formation of a ring transition state is only possible for compounds with longer hydrocarbon chains (\geq C4).

The second most common rearrangement mechanism (already encountered with PTR), results in the elimination of a molecule of neutral water. Often observed following electron impact ionisation of long chain alcohols, water elimination also most likely involves the formation of an intermediate ring transition state (de Hoffman and Stroobant, 2007). During the experiments conducted here, hexan-3-one was observed to undergo water elimination following charge transfer from the NO⁺ ion, yielding a base peak fragment ion of m/z 72 (relative abundance 19 %).

3.6.4 Comparison of CIR-TOF-MS with SIFT-MS

Despite some similarities between the CIR-TOF-MS results presented here and those obtained using SIFT-MS, there remain some significant differences. Comparisons between CIR-TOF-MS and SIFT-MS have been made previously (Blake, 2005; Wyche *et al.*, 2005; Blake *et al.*, 2006), hence only a brief note is made here.

The most significant difference between the spectra obtained by SIFT-MS and those obtained by CIR-TOF-MS is the complexity of products. The published SIFT-MS spectra of those compounds investigated here are simpler than was found with CIR-TOF-MS, generally containing only one or two product ions. For example, the SIFT-MS ion-molecule reactions between hydronium and almost all organics generally produce only one or two strong product peaks, which usually take the form MH⁺, MH⁺(-H₂O) or M⁺(-OR) (Smith and Spanel, 2005). Although CIR-MS typically produces more fragmentation products than SIFT-MS, the dominant product ions do tend to coincide. Similarly in the reactions of NO⁺, the SIFT technique again generates simple spectra, usually with a dominant M⁺⁺, M(-H)⁺ or M.NO⁺ ion, whereas once more CIR-MS produces considerably more fragmentation, particularly of the M.NO⁺ adduct ion. As with CIR-MS, SIFT O₂⁺⁺ chemistry generates a reasonable amount of fragmentation, but, again the extent of fragmentation appears greater with the CIR-TOF-MS technique (Smith and Spanel, 2005). Considerably less work has been conducted with NH₄⁺ in SIFT-MS; hence no comparison with CIR-TOF-MS is made here. As has been discussed previously within this chapter, the somewhat more extensive fragmentation observed with the CIR-MS technique can be directly attributed to the magnitude of the electric field employed. In this instance the E/N value of the system was reasonably large (~ 150 Td), which results in an increase in the collision energy of reaction by ~ 0.3 - 0.4 eV over the thermal conditions employed by SIFT-MS. In many cases the greater resultant collision and therefore reaction energy was sufficient to cause molecular ion fragmentation. Also, it is important to note that further fragmentation is facilitated when the ion beam traversed the exit/collision cell region of the CIR-TOF-MS reactor, which increases the ion kinetic energy to ~ 0.4 - 0.7 eV over the final 0.83 cm of the drift cell.

In the case of H_3O^+ , comparable reaction products to those obtained here have been reported with the conventional PTR-MS technique (Hansel *et al.*, 1995; Warneke *et al.*, 2003).

3.6.5 Use of CIR-TOF-MS to Distinguish Between Nominally Isobaric Compounds

To provide an initial demonstration of the ability of CIR-TOF-MS to speciate isobaric molecules, the final section of this chapter will focus on a comparison between the ionisation products obtained from the ion-molecule reactions of a number of isobaric aldehyde/ketone pairs with two different reagents, H_3O^+ and NO^+ . The test analytes employed for comparison were: propanal and acetone, butanal and butanone, hexanal, hexan-2-one and hexan-3-one, and methacrolein and MVK.

The mass spectra presented in **Figure 27** compare the fragmentation patterns of the test isobaric species following ionisation by H_3O^+ and NO^+ . In the reactions of propanal/acetone, methacrolein/MVK, and 2-hexanone/3-hexanone, the PTR mass spectra are dominated by a single MH⁺ peak at identical *m/z* for each pair of isobaric molecules. Consequently, in a mixture of these species it would not be possible to distinguishing the contributions made from aldehyde or ketone. Butanal and butanone give different PTR spectra because of the tendency of the former to undergo water elimination on protonation. However, the single dominant peak for butanal occupies the same spectral position as the H_3O^+ .(H_2O)₂ complex (*m/z* 55) which can form in substantial yields in a PTR reactor under humid conditions. Consequently, it may be difficult to quantify butanal reliably even in a relatively simple mixture if the CI reagent is restricted to H_3O^+ . Similar problems exist for hexanal, which also produces a significant fragment ion of *m/z* 55.

Implementation of NO⁺ as the CI reagent clearly yields different mass spectra from H_3O^+ for the aldehydes and ketones studied here. As has already been discussed, the ion-molecule chemistry of NO⁺ is more complex than that of H_3O^+ and it tends to produce a greater degree of molecular ion fragmentation and a more diverse array of products.

From Section 3.5 and from inspection of **Figure 27** it is clear that the spectral patterns of the isobaric aldehydes and ketones differ markedly when NO⁺ is employed as the primary CI reagent. For instance ion-molecule association complexes (*i.e.* M.NO⁺ species) are only found in the spectra of ketones, whereas the aldehydes tend to show more extensive fragmentation, with characteristic fragment ions at m/z = 43 (acylium and alkyl), 41 (allyl), 39 (propargyl) and 27 (vinyl). Although some of the ketones also show a number of these fragmentation products, they generally appear in lower abundance than for the aldehydes. Additionally, the ketones exhibit evidence of McLafferty rearrangements and water elimination, which for odd electron radical cations, produce unique even mass fragments in the mass spectra. Such fragmentation pattern differences between the aldehydes and ketones following CI from NO⁺, provide compound and species specific 'fingerprints' that are, at least for those compounds studied here, sufficient to discriminate between isobaric molecules. This observation even applies to the structural isomers, hexan-2-one and hexan-3-one, which show very different product branching ratios with NO⁺.

For sample matrices such as ambient air, which contain complex mixtures of VOCs, the extensive fragmentation obtained with NO⁺ would prevent its routine use as the primary CI reagent species. Unless the reactor energy is lowered below those values employed here, the spectral congestion produced would severely hamper analysis. Instead such alternative CI reagents could be employed alongside more conventional species such as hydronium in a two-stage process. For instance, during on-line VOC monitoring using the PTR technique, if there is cause to suspect that two or more molecules with the same mass contribute to a given peak, then the user could record separate spectra with NO⁺ and look for the distinct features expected for a particular molecule. Combined with the high-resolution capabilities of the TOF-MS, CIR-MS has the capability to provide a more detailed image of a given sample matrix than has been possible previously.



Figure 27: Processed mass spectra of the isobaric aldehyde/ketone pairs, generated by ion molecule reaction with either H_3O^+ or NO^+ . All mass spectra have been normalised to the most abundant ion, which has been set nominally to 100 % abundance. Note: minor contaminant ion contributions resulting from the presence of residual water vapour have been removed here to better allow comparison. For mass spectra containing all peaks, see Wyche *et al.*, 2005. *MVK dimer peak.

3.7 Conclusions

Within this Chapter the first successful generation and application of four different chemical ionisation reagents has been demonstrated in a novel drift tube type mass spectrometry system. The four reagent ions, H_3O^+ , NH_4^+ , NO^+ and O_2^{++} were generated in a clean radioactive ion source without the need for pre-selective filtering, and their reactions with a wide range of analytes have been characterised. As well as forming the base for future endeavour within this field, the work presented within this chapter introduces new analytical opportunities to the technique of fast, *real-time* monitoring of volatile organic compounds. The radioactive ion source employed here allows the reagent gas to be switched rapidly between the different species, with no need for settling time. Consequently, it is entirely possible for the reagent ion to be switched from one species to another during on-line monitoring, which would easily allow the CI chemistry to be tailored to best suit the target.

Of the reagent ions employed, the hydronium ion proved by far to be the most universally successful across the whole range of test compounds. However, the other reagent species do offer some important benefits. For example, the NO⁺ ion proved to be useful in the ionisation of ketones, the adduct formation pathway producing a distinct ion of higher mass, which lifts the target out of the generally congested lower m/z end of the mass spectrum. Owing to the large amount of fragmentation it produces, O_2^{++} would not generally be of use in the monitoring of atmospheric hydrocarbons; however it could be employed for the ionisation of compounds such as ammonia (Norman *et al.*, 2007). Although not tested here, NO⁺ and O_2^{++} could be used in future to provide measurements of NO, NO₂ and CFCs, as well as VOCs (Spanel and Smith, 1997a). It has also been shown that as an extension of the CIR-TOF-MS technique, the use of such multiple reagent species allows a system to be probed in greater depth than has been possible previously with PTR type mass spectrometry. It has been demonstrated that with the application of multiple CI reagents we are now able to distinguish in some cases between nominally isobaric species without the need for CID.

The CIR-TOF-MS technique will be expanded in Chapters 4 and 5 to follow, where it will be demonstrated that the various CI reagent ions investigated here can also be employed to provide quantitative measurements of a range of atmospherically significant VOCs and OVOCs.

Work published in Wyche et al., 2005, *Rapid Commun. Mass Spectrom.*, 19(22), 3356 – 3362 and Blake, *Wyche et al.*, 2006, *Int. J. Mass Spectrom.*, 254(1 – 2), 85 – 93.

Chapter 4

Validation of the Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry Technique: Measurement of Atmospherically Significant Oxygenated Volatile Organic Compounds

4.1 Summary

In this chapter the performance of Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS) for the measurement of atmospheric oxygenated volatile organic compound (OVOC) is described. Utilising the environment chamber SAPHIR (Simulation of Atmospheric Photochemistry In a large Reaction Chamber-Forschungzentrum Jülich, Germany) the present work took place as part of the ACCENT (Atmospheric Composition and Change the European NeTwork for excellence) OVOC measurement intercomparison during January 2005. The experiment entailed the measurement of fourteen different atmospherically significant OVOCs at various mixing ratios in the approximate range 10.0 – 0.6 ppbV. The CIR-TOF-MS operated throughout the exercise with the hydronium ion (H_3O^{\dagger}) as the primary chemical ionisation (CI) reagent in order to facilitate proton transfer to the analyte OVOCs. The results presented show that the CIR-TOF-MS is capable of detecting a wide range of atmospheric OVOCs at mixing ratios of around 10 ppbV in *real-time* (*i.e.* detection on the one-minute time scale), with sub-ppbV measurement also achieved following an increase in averaging time to tens of minutes. It is shown that in general the CIR-TOF-MS is able to make accurate and precise OVOC measurements, with integration time, mixing ratio and compound dependent accuracy and precision statistics as good as 4 - 13 % and 3 - 15 %, respectively. It is demonstrated that CIR-TOF-MS has rapid multi-channel response at the required sensitivity, accuracy and precision for atmospheric OVOC measurement.

4.2 Introduction

Oxygenated volatile organic compounds (OVOCs) are ubiquitous within the troposphere (Singh *et al.*, 1995). They have both primary and secondary sources, being emitted by anthropogenic and biogenic processes, as well as being formed from the gas-phase oxidation of parent hydrocarbons. OVOCs exist in the atmosphere at trace levels in the parts per trillion to parts per billion (by volume) range and are key players in many atmospheric processes.

OVOCs constitute a subdivision of the Volatile Organic Compound (VOC) family and include species with a variety of functional groups, including aldehydes, ketones, alcohols, acids, esters, ethers, furans and epoxides (Finlayson-Pitts and Pitts, 2000). Typical primary sources of anthropogenic VOCs and OVOCs include petroleum based fuels, industrial use of solvents and the escape of gas from natural sources and commercial pipelines (Penkett *et al.*, 1993). Urban air generally carries the characteristic signature of VOCs and OVOCs originating from human activities and will usually contain aromatic compounds and species such as formaldehyde, acetaldehyde and acetone (Blake *et al.*, 1993; Wayne, 2002). With approximately 40 % of the Earth's land surfaces covered by plant life (Wayne, 2002), the global biogenic emissions of VOCs and OVOCs can reach significant proportions. For example, it is estimated that the Earth's biosphere is responsible for the emission of ~ 1150 Tg C of non-methane VOCs every year (Guenther *et al.*, 1995). Example gaseous OVOC that characterise a biogenic atmosphere include oxygenated terpenes (*e.g.* camphor and linalool), oxidation products of isoprene (*e.g.* methacrolein and methyl vinyl ketone) and methanol.

OVOCs are able to react with the primary atmospheric oxidants, *i.e.* the hydroxyl (OH) and nitrate (NO₃) radicals, as well as ozone (O₃) if the compound in question contains unsaturated bonds. In certain environments OVOCs may also undergo reaction with the chlorine radical (Cl) (Finlayson-Pitts and Pitts, 2000). OVOCs possess a range of reactivities with the various atmospheric oxidants and will oxidise by numerous mechanisms, as was discussed within Chapter 1. In general, however, reaction with the OH radical *via* hydrogen abstraction tends to be fastest. Rate constants for OVOC reactions with OH vary from ~ 10^{-13} cm³ molecule⁻¹ s⁻¹ for less reactive compounds such as methanol, formic acid and acetone, to ~ 10^{-11} cm³ molecule⁻¹ s⁻¹ for simple aldehydes and compounds such as glyoxal (Finlayson-Pitts and Pitts, 2000). OVOCs are also liable to undergo photolysis at wavelengths less than 380 nm (Apel *et al.*, 2008).

Following their oxidation in the atmosphere OVOCs are able to contribute towards many different atmospheric processes, including the cycling of HO_x and RO_x species (Monks, 2005)

and the formation of tropospheric O_3 *via* conversion of NO to NO_2 (Finlayson-Pitts and Pitts, 2000). Recent research has also identified a potential role for certain OVOCs in the formation and growth of secondary organic aerosol (SOA) (Jang and Kamens, 2001; Kanakidou *et al.*, 2005; Kroll and Seinfeld, 2008).

Current methods for measuring OVOCs and VOCs include liquid and gas chromatography based techniques (LC and GC, respectively), often coupled with mass spectrometry (MS) or flame ionisation detection (FID) (*e.g.* (Lewis *et al.*, 2005)). Differential optical absorption spectroscopy (DOAS) (*e.g.* (Sinreich *et al.*, 2005)) and more recently proton transfer reaction mass spectrometry (PTR-MS) (*e.g.* (Lindinger *et al.*, 1993; Warneke *et al.*, 2001)) have also been used. As was discussed earlier the *modus operandi* of PTR-MS is the chemical ionisation, by proton transfer, of a gas sample inside a drift tube. The fixed length of the drift tube provides a fixed reaction time for the ions as they pass along the tube: the reaction time can be measured or it can be calculated from ion transport properties. If the proton donor is present in large excess over the acceptor molecules, then a measurement of the ratio of donor/protonated acceptor ion signals, allows the concentration of the acceptor molecules to be calculated. The PTR-MS method allows fast *real-time* measurements of a range of VOCs in air, including OVOCs. On-line methods offer a new dimension to VOC analysis as they can begin to assess the rapid fluctuations in concentration with time.

In conventional PTR-MS the mass spectrometer has usually been a quadrupole (*e.g.* (Hansel *et al.*, 1997)) or more recently an ion-trap (Warneke *et al.*, 2005). In contrast the CIR-TOF-MS technique employs time-of-flight mass spectrometry. More recently Ennis *et al.* (Ennis *et al.*, 2005) and Inomota *et al.* (Inomata *et al.*, 2006) have developed similar systems. TOF-MS comes into its own when dealing with complex mixtures since an entire spectrum is, in effect, captured in an instant. Furthermore, there is no formal upper mass limit and the standard resolution in TOF-MS is usually far higher than in quadrupole mass spectrometers. These characteristics confer a number of potentially important advantages for the analysis of complex mixtures, particularly when coupled to chemical ionisation.

A number of extensive intercomparison exercises have been carried out for the measurement of non-methane hydrocarbons (NMHCs) (*e.g.* (Apel *et al.*, 2003) and (Plass-Dulmer *et al.*, 2006) and references therein). The aim of these intercomparison campaigns has been to assess the accuracy and comparability of NMHC measurements from groups around the globe. Many of these exercises have concentrated on the measurement of NMHCs from various multi-component mixtures and canisters of ambient air. These comparisons have been useful in highlighting a wide range of sampling and analytical problems. However, to date there have been no similar exercises for OVOCs, which present a particular analytical challenge owing to their polar nature and the potential for interference from various sampling artefacts (*e.g.* (Northway *et al.*, 2004)).

Several smaller scale instrument comparisons have been conducted over the last five years in an attempt to validate the emerging PTR-MS technique (Warneke *et al.*, 2003; de Gouw *et al.*, 2003a; de Gouw *et al.*, 2003b). Despite obtaining favourable results, these studies focused on the measurement of ambient air samples and involved only the comparison of PTR-MS data with that obtained by GC-MS. Also, these PTR-MS/GC-MS intercomparison experiments were not 'officially' regulated and were not conducted under controlled and well defined conditions.

In an attempt to provide better understanding of the measurement capability of modern atmospheric monitoring instrumentation and to help validate a number of techniques, an OVOC comparison exercise was organised in January 2005 (Apel *et al.*, 2008) as part of the ACCENT QA/QC project (see www.accent-network.org). Fourteen atmospherically significant OVOC species were selected for intercomparison including aldehydes, ketones and alcohols, of both biogenic and anthropogenic origin (see Section 4.3.1). Two NMHC compounds (*n*-butane and toluene) were also included in the study to act as tracers in order to monitor the dilution of the chamber air, with toluene specifically chosen for the benefit of PTR-MS instruments, which are unable to detect short chain alkanes.

The intercomparison exercise employed a large atmospheric simulation chamber as the sample reservoir. Atmospheric simulation chambers provide an ideal platform from which to conduct such experiments, constituting a simplified and highly characterised simulation of the atmosphere in which it is possible to control and alter a host of variables within the sample matrix, including pressure, humidity, ozone levels and other matrix constituents.

This chapter details the results, performance and validation of the chemical ionisation reaction time-of-flight mass spectrometry system (operating in the proton transfer mode), for the determination of OVOC concentrations. As will be described, this study demonstrates that CIR-TOF-MS is a highly effective tool for quantifying a multitude of OVOCs with good time resolution (*ca.* 1 - 10 min depending on sensitivity to and concentration of the compound under inspection). This is an important finding which provides a firm foundation for the *real-time* analysis of OVOCs in complex trace gas mixtures such as atmospheric air.

4.3 Experimental

4.3.1 The Target Compounds

Fourteen different OVOCs of both biogenic and anthropogenic origin were selected for intercomparison on account of their specific importance in the contemporary troposphere. The list of target compounds was also devised to cover a range of functional groups and structural types. The chosen compounds included aldehyde, ketone, alcohol, ester, aromatic, saturated and unsaturated, branched and straight chain species. The target compounds are listed in **Table 1**, along with details regarding their major sources and significance within the atmosphere, and their structures are given in **Figure 1**.

Compound	Mass / amu	Source ¹	Relevance ²
formaldehyde	30	AS,BS	R
methanol	32	BP, BB	U, B
acetaldehyde	44	AS, BS, BB	R, U, O
ethanol	46	AP/S, BP/S, BB	U, B
acetone	58	AP/S, BP/S	R, U, B, O
1-propanol	60	AP	U
methacrolein	70	BS	O, B
methyl vinyl ketone (MVK)	70	BS	O, B
butanal	72	AS	R, O
acetic acid methyl ester (AAME)	74	AP	В
1-butanol	74	AP	U
2-methyl-3-buten-2-ol (MBO)	86	AP	В
toluene	92	AP	U, A
hexanal	100	AP, AS	О
benzaldehyde	107	AS	Ο

Table 1: Target compounds, mass, source and relevance (Apel et al., 2008)

¹Sources: AP = Anthropogenic Primary, BP = Biogenic Primary, AS = Anthropogenic Secondary, BS = Biogenic Secondary, BB = Biomass Burning.

²**Relevance:** $\mathbf{U} = \text{Urban Tracer}, \mathbf{B} = \text{Biogenic Tracer}, \mathbf{O} = \text{Oxygenation process}, \mathbf{R} = \text{Radical recycling}, \mathbf{A} = \text{Secondary organic aerosol formation}.$

n-butane was also included for the benefit of GC-MS users.

The short chain aldehydes and ketones (*e.g.* formaldehyde, acetaldehyde and butanal) constitute common tertiary products derived from the oxidation of many different anthropogenic and biogenic primary VOCs. Such carbonyl species appear late in the oxidation chain, with formaldehyde often constituting the final stage (O)VOC product (GAW,

2006). Carbonyl species are able to contribute to ozone formation *via* the conversion of NO to NO₂ and they also play a crucial role in radical recycling; in particular the photolysis of formaldehyde constitutes a significant source of HO₂ during sunlit hours (Finlayson-Pitts and Pitts, 2000). Recent research has also identified the presence of certain carbonyl species within the aerosol phase, highlighting their potential importance in secondary organic aerosol (SOA) formation and growth (Jang and Kamens, 2001; Kanakidou *et al.*, 2005; Kroll and Seinfeld, 2008).



Figure 1: Target compounds chosen for intercomparison grouped by functionality

Acetone is of particular interest, being emitted by both anthropogenic and biogenic sources on the global scale, as well as being formed by atmospheric oxidation processes (GAW, 2006). Having a relatively long lifetime, acetone may undergo transport and perturb the chemistry of regions far from source. Photolysis of acetone also constitutes a source of HO_x within the upper troposphere and lower stratosphere (Finlayson-Pitts and Pitts, 2000).

The alcohols methanol, ethanol and 2-methyl-3-buten-2-ol, are emitted in relatively significant quantities by the Earth's biosphere and along with acetaldehyde and formaldehyde are significant constituents of biomass burning plumes (Holzinger *et al.*, 1999; Wayne, 2002). Primary emissions of alcohols (including 1-propanol and 1-butanol) are increasing in the modern urban environment, as fuel usage has begun to include bio- and other alcohol-based fuels (Finlayson-Pitts and Pitts, 2000). Being emitted globally from a host of plant life and constituting a major oxidation product of methane, methanol is the most abundant OVOC

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found in the Earth's troposphere (Apel *et al.*, 2008). It has a long lifetime compared to other OVOCs, and hence is able to undergo regional transport.

The isobaric compounds methyl vinyl ketone (MVK) and methacrolein are major primary oxidation products of the biogenic diene, isoprene (Michel *et al.*, 2005), emissions of which make up ~ 44 % (Warneke *et al.*, 2001) of all non-methane VOCs released from the Earth's biosphere annually, *i.e.* 503 Tg yr⁻¹ (Guenther *et al.*, 1995). Methyl vinyl ketone and methacrolein therefore act as tracers for isoprene oxidation, which has been shown to constitute a significant O₃ source in polluted environments (Apel *et al.*, 2002). Also, recent studies have shown that methacrolein constitutes a key mass conduit through which the oxidation of isoprene can lead to SOA formation (see Chapter 7 and for example (Surratt *et al.*, 2006)).

Primary aromatic compounds such as toluene and their oxidation products (*e.g.* benzaldehyde) have extensive atmospheric oxidation mechanisms and as such possess high photochemical ozone creation potentials (44 % for toluene, (Derwent *et al.*, 2007)). Toluene is a key atmospheric marker, measurements of which can be employed with corresponding measurements for benzene to provide information regarding OH concentrations and the photochemical age of transported air masses (Warneke *et al.*, 2001). Aromatic species such as toluene have been determined to act as significant precursors to SOA formation in the urban environment (Hamilton *et al.*, 2003; Baltensperger *et al.*, 2005).

4.3.2 Simulation of Atmospheric PHotochemistry In a Large Reaction Chamber (SAPHIR)

The intercomparison experiments described here were conducted at the Forschungzentrum Jülich (De) SAPHIR facility (Simulation of Atmospheric PHotochemistry In a large Reaction chamber). An illustration of SAPHIR is given in **Figure 2** and photograph is given in **Figure 3**. SAPHIR is an outdoor facility consisting of a double-lined cylindrical bag constructed from chemically inert fluorinated ethylene propylene (FEP) Teflon. The Teflon material used has a wall thickness of 150 μ m and allows the transmission of roughly 80 % of solar radiation (in the wavelength range 290 – 420 nm) (Karl *et al.*, 2004). A continuous nitrogen flow is passed through the cavity between the inner and outer walls of the bag to ensure that ambient air does not diffuse into the chamber sample matrix. The SAPHIR chamber has a volume of 270 m³ (20 m in length with a diameter of 5 m) and a surface area to volume ratio of 0.88 m⁻¹, which is relatively small when compared to other environment chambers, allowing wall

effects to be minimised. The chamber bag is held by a large metal frame incorporating a staged series of louvers that shield the bag and sample gas matrix from solar radiation when required (see Figure 3).



Figure 2: Illustration of the SAPHIR environment chamber facility (www.fz-juelich.de/icg/icg-2)

Experiments at SAPHIR are conducted in a matrix of synthetic air, with an N₂:O₂ ratio of ~ 80:20 (gas supplied from liquid source, purity grade: 7.0). The bulk matrix resides at 60 Pa above ambient atmospheric pressure to further ensure no ambient air diffuses into the chamber interior. As sampling by instrumentation reduces the amount of gas within the chamber, the internal pressure is monitored and kept constant by a continuous compensation synthetic air flow of ~ $3 - 10 \text{ m}^3 \text{ h}^{-1}$ (Apel *et al.*, 2008). The chamber temperature resides at ambient atmospheric temperature; no internal heating system is employed.



Figure 3: Photograph of the SAPHIR environment chamber. This shows SAPHIR with louvers closed in order to shield the chamber bag from solar radiation ('dark experiment' conditions).

For the intercomparison experiments the target compounds were introduced into the chamber bag in either gaseous or liquid form. Gas phase VOC injection took place directly from cylinder, whereas liquid delivery was performed *via* syringe injection of the liquid compounds into a heated injection system, which facilitated their volatilisation before entry into the bag. For the experiments described here, the target compounds were introduced individually into the chamber over a period of roughly 1 hour. The uncertainty of OVOC injection quantity *via* syringe was determined to be 5 % at most (Apel *et al.*, 2008).

Ozone used in chamber experiments was supplied from a silent discharge ozonator, held under pure oxygen in order to reduce possible impurities and contamination. Chamber humidification was facilitated by vaporising (Dampf-OMat) ultra pure deionised water (Milli-Q, Millipore), through which a continuous stream of high purity nitrogen (purity grade 7.0) was passed to remove dissolved trace impurities (Wegener and Holzke, 2005). The SAPHIR gas injection system is shown in **Figure 4**. Once inside the chamber the gases were comprehensively mixed by a series of mechanical fans, with chamber characterisation experiments suggesting that a minimum mixing time of 30 minutes was required in order for the sample matrix to become homogeneous (Karl *et al.*, 2004; Wegener *et al.*, 2004).



Figure 4: Diagram of the SAPHIR supporting gas delivery network (Wegener et al., 2004)

For further details regarding the SAPHIR environment chamber and its accompanying suit of instruments see www.fz-juelich.de/icg/icg-2.

4.3.3 Experiment Design

The OVOC measurement intercomparison exercise was designed such that five main experiments would be conducted, each approximately a single day in duration. The conditions of the synthetic air sample matrix were varied between experiments in order to explore the effects of humidity and ozone on the ability of the instruments to reliably monitor the target compounds. The details of conditions employed during each experiment were as follows:

- Experiment 1 ('Chamber blank'): Dry synthetic air (N₂:O₂ ratio of 80:20, purity grade 7.0) followed by humidification (approximately 80 90 %) and ozone addition (approximately 50 ppbV). No OVOC injection. Experiment 1 was designed to constitute a 'chamber blank', providing an instrument + chamber baseline and hence information regarding background impurities.
- Experiment 2: Target OVOCs sampled from a dry synthetic air matrix. No humidification or ozone addition.
- Experiment 3: Target OVOCs (at different initial concentrations to experiment 2), sampled from a moist synthetic air matrix (relative humidity ~ 60 100 %, see Figure A4.1 in Section A4 of the Appendix). No ozone addition.
- Experiment 4: Target OVOCs (at different initial concentrations to experiments 2 and 3), sampled from a moist synthetic air matrix (relative humidity 50 80 %) containing approximately 40 50 ppbV ozone. (see Figure A4.1 in Section A4 of the Appendix)
- Experiment 5: Sampling of 'real' atmospheric air from SAPHIR, followed by introduction of the target OVOCs (again at different initial concentrations).
 Measurement conducted at ambient relative humidity and ozone concentration.

To eliminate any potential photochemistry and hence reaction of the target compounds, all experiments were conducted under dark conditions with chamber louvers closed.

The initial compound concentrations were varied from day to day, and knowledge of exact concentrations was withheld from participants until after the exercise. In order to allow the instruments to measure the OVOCs at various mixing ratios, the synthetic air sample matrix was diluted twice during each day. Consequently, each experiment was composed of three individual *sub-experiments* termed A, B and C, during which the OVOCs were sampled at mixing ratios of roughly 6 - 10, 2 - 3 and then 0.6 - 1 ppbV, respectively. These concentration ranges were chosen in order to cover approximate values at which the target compounds exist in the atmosphere, with the lowest values being sufficient to test 'bottom

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end' instrument detection capability. A period of 1 hour was allocated for the dilution process and subsequent equilibration of the chamber matrix. Because of constraints imposed by SAPHIR and the minimum sampling time required by some instruments present, the minimum length of each sub-experiment was set to 3 hours. The total length of each daily experimental period was of the order of 10 - 12 hours. The sampling and dilution procedure of a single experiment is shown diagrammatically in **Figure 5**.



Figure 5: Planned OVOC, water and ozone concentration with time for campaign experiments 2, 3 and 4 (adapted from (Wegener *et al.*, 2004))

The concentration slope depicted in **Figure 5** during each sub experiment 'plateau', represents the dilution of the target compounds as the bulk gas matrix was replenished in order to keep the chamber at a constant pressure. The compound dilution rate was determined to be ~ 3 % hr^{-1} (Apel *et al.*, 2008).

During each experiment chamber relative humidity was monitored using a frost point hygrometer (General Eastern model Hygro M4) and ozone concentrations were measured online (measurement interval *ca.* 90 s) through UV absorption (Ansyco O341M). In order to maintain a given relative humidity and ozone mixing ratio throughout the entire day and hence to account for the effects of dilution, compensation injections were made during the flushing phases between sub-experiments (see **Figure 5**). Ozone and OVOC concentrations and experiment duration were all designed to be sufficiently low to ensure that ozonolysis reactions, and hence loss of susceptible OVOCs, would be insignificant. The chamber was flushed thoroughly with dry synthetic air for several hours after each experiment in order to ensure that the sample matrix was free from 'carry-over' contamination from a previous experiment. Measurement of the chamber gas prior to each experiment revealed that there was no contamination from prior use of the target OVOCs (see Section 4.3.5).

4.3.4 Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry: Experimental Details

The Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer employed during the intercomparison exercise was as described in Chapter 2, and hence only experiment-specific details are presented here.

For the entire exercise proton transfer was used as the means of ionisation, with the hydronium ion (H_3O^+) constituting the proton donor. In order to generate the primary reagent ions, water vapour was delivered to the ion source at a rate of 52 sccm by bubbling a nitrogen carrier gas (purity: 99.99999 %) through a glass vessel containing high purity deionised water (15 M Ω). Hydronium ions were generated within the ion source by allowing the water vapour to flow through the ion source chamber as detailed in Section 2.2.1 of Chapter 2.

The sample gas containing the OVOCs was delivered to the drift cell at a flow rate of 275 sccm *via* a common insulated glass manifold and a 2 m long Teflon line. The Teflon sample line was heated to 40 °C (\pm 1 °C) to limit wall loss of the target compound on route to detection. The combined reagent and sample gas flows provided a drift cell operating pressure of 7.4 mbar. A positive potential difference of 2700 V was distributed across the entire electrode array of the ion-source drift cell assembly, generating a reactor *E/N* value of 151 Td. For all experiments the ion-source/drift cell assembly was held at a constant temperature of 40 °C (\pm 0.5 °C). Under such conditions, the residence time of ions in the drift cell was of the order 0.06 ms. For the entire exercise the radioactive ion source-drift assembly was operated with the Mk.1 variant of the exit/collision cell (see Section 2.2.3 of Chapter 2 for further details).

For the OVOC intercomparison exercise all mass spectra were recorded for an averaging period of 60 s and over the mass range 0 - 143 Da. Over this specific mass interval the instrument operates at a frequency of approximately 10^4 scans s⁻¹, with a duty cycle of approximately 2 %.

4.3.5 Background Measurement

In order to provide an instrument and chamber background and hence to facilitate the removal of any possible contaminants or artefacts from the final data, the chamber air was measured for 3 - 4 hours at the start of each experiment before the injection of the test compounds. The data acquired were subsequently employed to subtract away any undesired background signal from the final OVOC measurements. A typical background mass spectrum recorded during the exercise is given in **Figure 6**. The spectrum shown in **Figure 6** focuses on the baseline signal (hydronium excluded at ~ 110,000 cps) and reveals very few background impurities. The only VOC contaminants detected were methanol at m/z 33, acetone at m/z 59 and an unknown contaminant at m/z 121, all of which were minor. Other signals measured included singly charged nitric oxide, singly charged oxygen and monohydrated hydronium (H₃O⁺.(H₂O)) at m/z 30, 32 and 37, respectively.



Figure 6: Mass spectrum showing the typical instrument + chamber background during the intercomparison exercise (acquired over a 10 minute period). Note, m/z 121 peak originates from the use of 'Viton' material within the reactor (see Chapter 2).

The combined CIR-TOF-MS and chamber baseline signal level was stable for the majority of mass channels throughout the intercomparison campaign. When background mass scans were integrated over successive one minute periods, the standard deviation of the total ion count taken over one hour was typically less than 0.4 %. If the primary reagent ion (H₃O⁺) count is excluded from the background scan when investigating such statistical variation in the instrument baseline, the typical total ion count variation rises to ~ 3 %.

When conducting observations of ambient air, an instrument baseline is typically obtained at regular intervals during measurement by passing the sample gas first through a hydrocarbon trap in order to filter out the trace species of interest. Again the background is subtracted from the measured signal to remove contaminants or artefacts from the final data.
4.3.6 CIR-TOF-MS Calibration

In order to facilitate absolute quantification of the OVOCs detected during the intercomparison experiments, the CIR-TOF-MS was calibrated using three separate multi-component gas mixtures containing compounds of known concentration (Air Environmental, Inc., courtesy of University of Bristol, UK and Paul Scherrer Institut, Ch., compound mixing ratio accuracy \pm 5 %). Full details regarding the multi-component gas standards employed for calibration purposes during the current study can be found along with their mass spectra in **Tables A4.1 - A4.3** and **Figure A4.2** of Section A4 of the Appendix.

Two separate phases of calibration were conducted, first of all during and then subsequently after the intercomparison, from which an instrument sensitivity value was determined for each of the target OVOCs, with two exceptions. In the cases of formaldehyde and acetic acid methyl ester no calibration standards were available, and hence calculated sensitivities were employed.

CIR-TOF-MS calibration is generally conducted using a stepwise dilution technique, in which the instrument is applied to the measurement of a gas mixture containing compounds of known concentration. The calibrant gas is diluted a number of times in order to provide measurements over a range of applicable concentrations. The ion signal acquired at each calibrant concentration can be subsequently employed to determine the instrument *sensitivity* to the calibrant compound.

Following Warneke *et al.* (Warneke *et al.*, 2001), the instrument *sensitivity* to a given compound (for a specific set of operating conditions) is defined as the number of ion counts acquired by the instrument per ppbV of that compound, after normalisation of the entire mass scan to 10^6 primary CI reagent ion counts s⁻¹ (given in units of *normalised counts per second per ppbV*, *i.e.* ncps ppbV⁻¹), *viz*:

$$Sensitivity = \frac{\text{Normalised MH}^{+} \text{ counts per second}}{\text{Concentration of M in ppbV}}$$
(E4.1)

Consequently, instrument sensitivity to a certain compound may be determined through the construction of a *calibration curve*, which constitutes a plot of compound concentration *versus* normalised ion signal acquired. It follows therefore that the gradient of the calibration curve is the instrument sensitivity. As an example, **Figure 7** shows a methanol calibration curve acquired by the CIR-TOF-MS. Following the standard calibration procedure, the data presented therein have been normalised to 10⁶ primary reagent ion counts and the instrument

background signal has been subtracted. One-minute precision during calibration was of the order 5 - 30 % over the mixing ratio range 80 - 5 ppbV. These values are typical for OVOC calibration of the CIR-TOF-MS.



Figure 7: Methanol calibration curve, derived from 10-minute data acquisition per calibrant concentration at an E/N of 151 Td. Error limits determined from the relative standard deviation within the data. Correlation coefficient (r^2) = 0.998.

As was discussed in Chapter 3, with knowledge of the ion-molecule reaction kinetics inside the drift cell, *e.g.* reaction rate constant, time and fragmentation behaviour, it is possible to determine an instrument sensitivity value for a given compound without an experimentally derived calibration curve. With no experimentally derived sensitivity value available for the quantification of formaldehyde and acetic acid methyl ester, theoretical sensitivities were calculated using the steady state approximation in equation (E4.2). As was described in detail within Chapter 3, this equation can be derived from reaction (R4.1) assuming that the proton transfer reaction obeys pseudo first-order conditions:

$$i(MH^{+}) \approx i(H_{3}O^{+})_{0}[M] k t$$
 (E4.2)

$$H_3O^+ + M \xrightarrow{k} MH^+ + H_2O$$
 (R4.1)

In equation (E4.2), $i(MH^+) =$ normalised, protonated analyte ion signal (ncps), $i(H_3O^+)_0 =$ normalised hydronium ion signal (by definition 10⁶ counts per second), [M] = analyte concentration (molecule cm⁻³), k = proton transfer reaction rate constant (cm³ molecule⁻¹ s⁻¹) and t = reaction time (s) (for further details see Chapter 3 and references therein). If the MH⁺ ion is known to fragment following ionisation, a fragmentation factor (*F*) must also be included in equation (E4.1) (see Chapter 3 for further details).

As detailed in Chapter 3, the proton transfer reaction technique is a relatively soft ionisation process compared to other methods, and invariably results in the production of a protonated parent ion with little accompanying fragmentation. For the intercomparison exercise

calibration of a given compound was conducted using data for either the protonated parent ion or its most abundant daughter fragment (using information obtained from the studies conducted in Chapter 3). Choosing the most abundant ion for calibration and quantification reduces statistical errors resulting from inherent signal variability and instrument noise, and thus a degree of reliability is conferred to the final concentration value. Details of CIR-TOF-MS calibration for the intercomparison exercise are given in **Table 2** along with key physical data for the target compounds.

Compound	Vapour pressure	Proton affinity /	Data ion ^c / m/z	Data ion identity	Data ion	CIR-TOF-MS
8	/ mmHg ^{a,b}	kJ mol ⁻¹			contribution ^d	Sensitivity / ncps ppbV ⁻¹
formaldehyde		713	31	MH^+	٩	
methanol	98	754.3	33	MH^{+}	100%	28
acetaldehyde	755	769	45	MH^+	47%	49.8
ethanol	45	776.4	ı	I	- f	ı
acetone	184	812.1	59	MH^{+}	100%	50.8
n-butane		n/a	r	t.	f.	
l-propanol	786.5	786.5	41	$M.H^{+}(-H_{2}O.H_{2})$	51%	45.7
methacrolein ^g	121	808.8	71	MH^{+}	87%	40.9
MVK ^g	71	834.7	71	MH^{+}	95%	40.9
outanal	06	792.7	55	$MH^{+}(-H_{2}O)$	84%	42.6
AAME	165	821.6	75	MH^+	a I	40.1
1-butanol	4	789.2	57	$MH^{+}(-H_{2}O)$	79%	48.3
MBO	$51^{\rm h}$		87	$^{+}\mathrm{HM}$	16%	6.6
toluene	22	78.1	93	MH^+	94%	26
hexanal	10	794 - 797	83	$MH^+(-H_2O)$	52%	9.7
benzaldehyde	4 ^j	834	107	MH^{+}	0%66	57.4

Table 2: Physical and CIR-TOF-MS	calibration data f	or the target	compounds
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Vapour pressures measured at 20 °C unless otherwise noted

http://www.sigmaaldrich.com

^c Ion employed for quantification of the named compound

^d Percentage contribution of the data ion to the total mass spectrum of the named compound

^e Calculated sensitivity employed (see text for details)

Compound not detected

^e Isobaric compounds, measured in the same mass channel using the PTR-MS technique

^h Vapour pressure measured at 25 °C

ⁱ Not known

^j Vapour pressure measured at 45

4.3.7 CIR-TOF-MS Measurement Uncertainty Analysis

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The quantitative measurements made by any analytical instrument such as the CIR-TOF-MS have a degree of uncertainty associated with them, *i.e.* potentially there is some amount of error in every result. In order to confer a degree of confidence to any quantitative results and thus to allow full interpretation of any findings, this instrument uncertainty (or *potential error*) must be defined. The uncertainty in any given CIR-TOF-MS measurement is composed of several systematic and random factors which may be combined to generate an overall instrument uncertainty factor. **Table 3** provides a list of all possible sources of uncertainty associated with CIR-TOF-MS measurements. The estimated magnitude of each uncertainty is expressed in terms of percentage.

 Table 3: Source and estimated magnitude of uncertainty associated with CIR-TOF-MS quantitative measurements

Uncertainty Source	Uncertainty magnitude / ± %
Reagent gas mass flow controller (σ_{RMFC})	1
Sample gas mass flow controller (σ_{SMFC})	1
Drift cell pressure measurement (σ_{DC})	1
Gas standard composition (σ_{GSC})	5
Calibration experiment (σ_{Cal})	Various ^a
PTR rate constant (σ_{RC})	20 ^b
Hydronium count variability (X_H)	$100\sqrt{(1/N_y)}$
Analyte count variability (X_x)	$100\sqrt{(1/N_y)}$
Hydronium count variability during calibration (X_{SH})	$100\sqrt{(1/N_y)}$
Analyte count variability during calibration (X_{Sx})	$100\sqrt{(1/N_y)}$

^a Estimated from statistical variation in ion counting or from the uncertainty in the calibration curve slope value ^b Uncertainty in the PTR rate constant is typically $\sim \pm 20$ %

The overall uncertainty associated with CIR-TOF-MS measurements can be distinctly divided into two separate parts, that associated with the instrument itself and that associated with instrument calibration.

The main systematic uncertainty factors associated with the CIR-TOF-MS involve delivery of the sample and reagent gases into the ion source/drift cell assembly, and therefore the drift cell pressure and overall E/N. As detailed in Section 2.3 of Chapter 2, the flows of reagent and sample gases into the instrument are governed by two Tylan FC260 mass flow controllers (the reagent mass flow controller, dubbed RMFC and the sample mass flow controller,

dubbed SMFC). The manufacturer quoted uncertainty for the gas flow rate controlled by each device is ± 1 %. These uncertainties, combined with the manufacturer quoted uncertainty of pressure measurement made by the Baratron pressure transducer (± 1 %), are used to account for uncertainty in the drift cell pressure and hence E/N. It should be noted that the voltage on each plate is well characterised and hence associated errors are negligible.

Along with the systematic uncertainties noted above, there exists a certain amount of statistical uncertainty in the ion counting of both the hydronium and the analyte ions. This statistical counting variability arises from random electrical noise superimposed on the mass spectrum and from occasional inhomogeneity in the sample gas. The statistical variability of ion counting is expressed as a percentage coefficient of variation X, (Chapman, 1998):

$$X = 100 \sqrt{\frac{1}{N_y}} \tag{E4.3}$$

where N_v = the number of ions registered in a spectral peak at m/z = y.

Generally, one of the largest contributors towards overall measurement uncertainty originates from instrument calibration. For instance the components of the gas standards employed during this study are quoted to a given value ± 5 %. To give an overall calibration uncertainty this value must also be combined with the potential error associated with the calibration experiment itself. The uncertainty associated with a typical calibration experiment can be estimated from the statistical variability of the ion counting (as in equation (E4.3)), or it can be obtained by quantifying the uncertainty associated with the calibration curve slope value (which inherently also accounts for statistical counting variability).

When employing a calculated sensitivity in order to facilitate measurement quantification (*i.e.* using equation (E4.1)), the potential error in the value of the rate constant must be taken into account in place of the uncertainty of the calibration. Generally, the uncertainty in the absolute value of the proton transfer rate constant is of the order $\pm 15 - 20$ % (see for example work by Zhao and Zhang, and references therein (Zhao and Zhang, 2004)).

The overall uncertainty associated with any given CIR-TOF-MS measurement ($\sigma_{\rm U}$) is quoted as a combination of the individual uncertainties stated in Table 3:

$$\sigma_{\rm U} = \sqrt{\left[\left(\sigma_{\rm RMFC} \right)^2 + \left(\sigma_{\rm SMFC} \right)^2 + \left(\sigma_{\rm DC} \right)^2 + \left(X_{\rm H} \right)^2 + \left(X_{\rm x} \right)^2 + \left(\sigma_{\rm GSC} \right)^2 + \left(\sigma_{\rm Cal} \right)^2 \right]}$$
(E4.4)
where $\sigma_{\rm Cal} = \sqrt{\left[\left(X_{\rm SH} \right)^2 + \left(X_{\rm Sx} \right)^2 \right]}$ (E4.5)
or $\sigma_{\rm Cal} =$ Uncertainty in calibration curve slope ($\sigma_{\rm slope}$)(E4.6)

or

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For overall measurement uncertainties associated with calculated concentrations, the variables σ_{GSC} and σ_{Cal} , which determine the potential error derived from experimental calibration, must be replaced with σ_{RC} , the uncertainty in the value of the proton transfer reaction rate constant.

Ultimately, σ_U is quoted as a percentage of the final CIR-TOF-MS measured concentration. It must be noted however, that such uncertainty estimations derived for all instrument made measurements constitute a lower limit, as they account only for known and well characterised potential sources of uncertainty.

A note on the use of pseudo first order kinetic theory to calculate compound concentration

It is important to note that the steady state approximation of equation (E4.2) assumes that reaction (R4.1) constitutes the sole route to MH⁺ formation; however, this is not necessarily true. As will be discussed in detail within Chapter 5, depending on the reactor *E/N* value and the humidity of the sample matrix, hydronium ions may react with neutral water to form hydrated hydronium cluster species (*i.e.* H₃O⁺.(H₂O)_n, where $n \ge 1$). Hydrated hydronium cluster ions may also react with certain species of analyte, M, to produce the protonated analyte ion, MH⁺. As the rate and efficiency of MH⁺ formation *via* reaction of the analyte, M, with hydrated hydronium may be different to that of MH⁺ formation *via* reaction (R4.1), equation (E4.2) must be modified to take into accounted the various forms of hydronium-water cluster ions that may be present within the reactor, *e.g.*:

$$iMH^{+} = \sum_{n=0}^{\infty} i(H_{3}O^{+}.(H_{2}O)_{n})_{0}[M]k_{n}t$$
 (E4.7)

As all PTR-MS type instruments employ an 'energy ramp' over the exit/collision cell region at the base of the reactor, ions of the type $H_3O^+.(H_2O)_n$ are typically fragmented prior to detection. Consequently, as will be demonstrated in Section 4.4.2.2 and in detail within Chapter 5, the true distribution of hydronium amongst its various cluster species may be masked. Without knowing the true distribution of reagent ions within the reactor, it is sometimes difficult to obtain a reliable analyte concentration when using equation (E4.2).

4.4 **Results and Discussion**

4.4.1 Preliminary Observations

All mass scans recorded during the intercomparison exercise were normalised to 10^6 primary reagent ion counts (*i.e.* $\Sigma(H_3O^+ + H_3O^+.(H_2O)))$), and were processed by subtracting an appropriate normalised background scan. Generally, the background data employed was that recorded over a two hour period prior to the OVOC injection phase of each experiment. The residual spectra therefore contain only those peaks produced by reaction of H_3O^+ (and to a minor extent its corresponding hydrates) with the target OVOCs.

Before giving a detailed discussion of instrument performance during the intercomparison exercise, it is pertinent at this stage to consider a general overview of the basic overall findings common to each experiment. Figure 8 displays the summary mass spectra recorded over each experiment, in which the data have been grouped by sub-experiment, *i.e.* the mass spectra shown in Figure 8 were generated by summing the processed data over each sub-experiment.

Initial inspection of the data presented in Figure 8 reveals the clear presence of fourteen out of the (total) sixteen intercompared compounds, ten of which are unambiguously observed as protonated parent ion peaks. In addition to those peaks corresponding to various MH⁺ ions, seven other major features are observed in each of the mass spectra presented in Figure 8. Following the application of the characterisation work described in Chapter 3, these features have been identified as various daughter/fragment ions of the sample OVOCs. As would be expected considering the number of different alcohol and aldehyde compounds present, the most common type of ion observed besides MH^+ was the $MH^+(-H_2O)$ fragment ion. Indeed, 1-propanol, 1-butanol, MBO, butanal and hexanal all produced MH⁺(-H₂O) ions of significant abundance. Strong signals were also observed in the m/z 39, 41 and 43 mass channels, which again through application of compound characterisation experiments, have been identified as carbonyl and alcohol fragmentation products (see Chapter 3). All compounds were observed to react with hydronium according to the functionality specific pathways discussed within Chapter 3 (e.g. dehydration of certain alcohols and aldehydes etc). Owing to the relatively high reactor E/N employed and the presence of an energy 'ramp' over the ECC, no ligand association products (*i.e.* MH^+ .(H₂O)) were observed.



Figure 8: Mass spectra for the OVOCs recorded during all experiments $(\mathbf{a} - \mathbf{d} = \exp 8.2 - 5)$. Identifiers 'F' and 'MF' indicate fragment and multiple fragment ions, respectively. Green peaks give data recorded from sub-experiment A, red from B and blue from C (see text for details).

The relatively large number of fragmentation products observed (and the subsequent spectral congestion), is attributed to the heightened translational kinetic energies applied to the ions by the drift cell electric field. Under the operating conditions employed during the intercomparison, the centre-of-mass kinetic energies (KE_{cm}) of the various OVOCs undergoing reaction (R4.1) were of the order 0.32 – 0.36 eV. The specific analyte ion used for compound quantification (generally the most abundant product), its relative abundance and corresponding sensitivity is listed in **Table 2**. In the case of butanal (fragment m/z = 55) and propanal (fragment m/z = 41), contributions to the spectral peak from fragment ions of other compounds had first to be removed.

As can be seen from **Figure 8**, ethanol does not appear in the mass spectra of any experiment, either as the protonated parent (m/z = 47) or as a clear fragment ion. Subsequent experiments have proven the CIR-TOF-MS technique capable of detecting protonated ethanol but only with 'softer' drift cell conditions (< 120 Td) or at higher ethanol mixing ratios (of the order 1 ppmV). As reported in work by Warneke *et al.* (Warneke *et al.*, 2003), it is currently believed that following proton transfer reaction the protonated ethanol ion will undergo some degree of fragmentation, resulting in the production of daughter ions of m/z = 29 and 19. Clearly, with a mass fragment occupying the same channel as the primary reagent ion (*i.e.* m/z = 19), monitoring ethanol using the PTR-MS technique can be somewhat problematic. As Warneke *et al.* made their measurements at a lower E/N than was used during this study (*i.e.* 106 rather than 151 Td), it is reasonable to assume that the majority of the ethanol ionised in the reactor of the CIR-TOF-MS suffered fragmentation to mass channel 19, and hence its detection was masked by the reagent ion signal. *n*-butane is also not observed in the mass spectra, which is expected given the unfavourable proton affinity relative to water.

A comparison of **Figure 8(a)** with **Figures 8(b)** – (d) reveals that spectral composition was generally unaffected by the addition of water and/or O_3 , to the sample matrix *i.e.* no spectral features were conspicuously absent or altered when moving from experiment 2 to 5. This result presents a first indication that CIR-TOF-MS sensitivity to the target OVOCs is not dramatically affected by the presence of water vapour or O_3 in the sample matrix. The sole exception to this, however, is formaldehyde, a special case that is treated separately below.

Chapter 4

CIR-TOF-MS Validation

4.4.2 Comparison of Measurements with Chamber Values: Measurement Accuracy, Precision and Linearity

4.4.2.1 Sampling from Dry Synthetic Air

In order to ascertain the ability of the CIR-TOF-MS to quantitatively measure the detected OVOCs both reliably and reproducibly, a comparison has been made between measured concentrations and *estimated chamber values*^{*a*}. The *estimated* (or *calculated*) *chamber values* were determined from knowledge of the amount of liquid OVOC initially injected into SAPHIR, the chamber volume, the ambient temperature and pressure and the air dilution rates over time. It should be noted however, that such estimated chamber concentrations are not definitive and the 'true' chamber concentration for any given OVOC may have varied from this theoretical value by as much as \pm 7 %. This calculated chamber concentration uncertainty is composed of all quantifiable uncertainties involved *i.e.* the uncertainty in chamber (\pm 2 %) and the uncertainty in the absolute quantity of liquid OVOC initially injected into the chamber (\pm 5 %). The precision of injection and therefore, the calculated chamber concentration was determined to be \pm 2 %. For further information regarding determination of chamber concentrations the reader is referred to the work of Apel *et al.* (Apel *et al.*, 2008).

For the comparison between measured and calculated OVOC concentrations, the CIR-TOF-MS data for each sub-experiment were first integrated over intervals of ~ 50 minutes, producing three repeat measurements at each concentration. On account of the longer measuring time allotted, the data for all part C sub-experiments were integrated over intervals of ~ 90 minutes. In the following discussion the first measurement of a given sub-experiment will be designated the identifier '1', the second measurement '2' and the third measurement '3'. For example repeat measurement number 2A1 refers to the first of the three repeat measurements made during part A of experiment 2, whereas 3B2 refers to the second of the three repeat measurements made during part B of experiment 3, and so on.

Figures 9 - 12 present all CIR-TOF-MS measured OVOC concentrations alongside all calculated concentrations over the entire intercomparison exercise. In Figures 9 - 12, measured concentrations are displayed as red points with error bars, whereas calculated chamber values are shown as a blue line. Also shown are the corresponding correlation plots for each of the measured compounds during experiments 2, 3 and 4.

^a 'Official' *estimated* (*calculated*) *chamber* OVOC concentrations for SAPHIR determined by and presented with permission of Eric Apel, Theo Brauers, Ralph Koppmann and the ACCENT OVOC intercomparison team.



Figure 9: Comparison of CIR-TOF-MS measured concentrations (red circles) with chamber values (blue line) throughout all experiments for **(a)** methanol, **(b)** 1-propanol and **(c)** 1-butanol and their corresponding regression plots (in regression plots blue circles = experiment 2, red squares = experiment 3 and white triangles = experiment 4).



Figure 10: Comparison of CIR-TOF-MS measured concentrations (red circles) with chamber values (blue line) throughout all experiments for **(a)** MBO, **(b)** acetaldehyde and **(c)** butanal and their corresponding regression plots (in regression plots blue circles = experiment 2, red squares = experiment 3 and white triangles = experiment 4).



Figure 11: Comparison of CIR-TOF-MS measured concentrations (red circles) with chamber values (blue line) throughout all experiments for (a) hexanal, (b) acetone and (c) methacrolein + MVK and their corresponding regression plots (in regression plots blue circles = experiment 2, red squares = experiment 3 and white triangles = experiment 4).



Figure 12: Comparison of CIR-TOF-MS measured concentrations (red circles) with chamber values (blue line) throughout all experiments for (a) acetic acid methyl ester (AAME), (b) toluene and (c) benzaldehyde and their corresponding regression plots (in regression plots blue circles = experiment 2, red squares = experiment 3 and white triangles = experiment 4).

The small slope in OVOC concentration which can be seen over each measuring period of the various temporal profiles presented in **Figures 9** – **12**, results from compound dilution as the sample matrix air was replenished in order to maintain a constant chamber pressure.

The ability of the CIR-TOF-MS to measure the target oxygenated volatile organic compounds can be described using a series of instrument *accuracy* and *precision* values, which have been derived from the comparison of measured versus calculated OVOC concentrations. In this instance the compound specific instrument accuracy is defined as the modulus of the percentage excursion of the CIR-TOF-MS measured concentration from the calculated chamber value, simply determined from the ratio of the former to the latter. Thus the accuracy value determines how close any given CIR-TOF-MS measurement is to the 'true' value. The precision values quoted here have been calculated from the ratio of the standard error of the mean in a given data set of repeats to the specific mean value of that data set. Thus the precision value determines how reliably the CIR-TOF-MS can repeat any given measurement. Resultant accuracy and precision values have been expressed in terms of All values of accuracy and precision have been averaged over the nine percentage. measurements taken during the three sub-experiments of a single day and the results are given for each compound in Table 4.

Also given in **Table 4** are compound specific slope, intercept and correlation coefficient (r^2) values obtained from the regression plots of CIR-TOF-MS measured concentrations *versus* calculated values, as shown in **Figures 9** – **12**. The slope, intercept and correlation coefficients for each individual experiment (*i.e.* experiment 2, 3 and 4) are quoted in **Table 4** for each of the measured OVOCs (excluding formaldehyde, which is discussed later). In order to provide a general overview of compound specific instrument performance the slope, intercept and r^2 values obtained from the combined data set of experiments 2, 3 and 4 (*i.e.* all experiments) are also provided. None of the data presented have been forced through the origin.

As shown in **Table 4**, in general throughout the exercise most species were measured by the CIR-TOF-MS with an average accuracy of around 25 % or better, with the compounds acetaldehyde, butanal and toluene consistently measured with the greatest accuracy throughout. Particularly high measurement accuracies were achieved for these three compounds during all part A sub-experiments, where values were on average 5.5 % for mixing ratios of the order 10 ppbV.

Compound	Accuracy ^{a,b} / %	Precision ^{a,b} / %	Slope	Intercept	Correlation coefficient (r^2)
	(Exp. 2/3/4)	(Exp. 2/3/4)	(Exp. 2 / 3 / 4 / All ^c)	(Exp. 2/3/4/All ^c)	(Exp. 2/3/4/Average)
methanol	25.7/25.5/37.6	20.2 / 25.5 / 20.4	0.77 / 0.83 / 0.64/ 0.77	0.65 / -0.01 / 1.34 / 0.58	0.975 / 0.964 / 0.806 / 0.915
1-propanol	25.2/21.3/16.2	12.0 / 11.4 / 5.2	0.60 / 0.60 / 0.60 / 0.59	0.50 / 0.61 / 0.63/ 0.60	0.991 / 0.971 / 0.987 / 0.983
1-butanol	64.2 / 72.2 / 55.8	14.4/28.1/8.4	0.26 / 0.31 / 0.29 / 0.29	0.14 / -0.04 / 0.36 / 0.15	0.992 / 0.950 / 0.956 / 0.966
MBO	27.0/25.5/24.4	31.2 / 27.4 / 17.2	0.67 / 0.71 / 0.94 / 0.87	0.67 / 0.71 / -0.47 / -0.02	0.990 / 0.945 / 0.944 / 0.960
acetaldehyde	13.5/21.9/3.8	4.0 / 7.0 / 3.2	0.99 / 1.05 / 0.97 / 1.02	0.26/-0.41/0.16/-0.06	0.993 / 0.996 / 0.997 / 0.995
butanal	14.6 / 14.7 / 3.9	6.5 / 5.5 / 4.5	1.02 / 0.89 / 0.97 / 1.00	0.17 / -0.04 / 0.02 / -0.05	0.995 / 0.995 / 0.996 / 0.995
hexanal	18.7/28.2/31.4	6.9 / 11.2 / 11.2	0.88 / 1.07 / 0.97 0.89	0.44 / 0.23 / 0.71 / 0.64	0.998 / 0.957 / 0.956 / 0.970
acetone	26.4 / 14.7 / 10.0	23.4 / 15.4 / 11.9	1.10 / 1.05 / 1.06 / 1.12	0.13 / -0.15 / -0.26 / -0.28	0.983 / 0.962 / 0.982 / 0.976
Methac. + MVK	17.9 / 15.8 / 14.5	2.8/3.2/3.2	0.83 / 0.77 / 0.86 / 0.83	-0.05 / 0.19 / -0.04 / 0.03	866.0 / 266.0 / 666.0 / 266.0
AAME	24.6/15.9/12.4	7.3 / 7.0 / 4.4	0.69 / 0.72 / 0.76 / 0.71	0.36 / 0.32 / 0.44 / 0.41	0.995 / 0.993 / 0.995 / 0.994
toluene	6.8 / 10.0 / 6.2	7.0 / 10.1 / 6.3	0.94 / 0.94 / 0.91 / 0.95	0.16/0.01/0.19/0.06	166.0 / 866 / 0.988 / 0.998 / 0.991
benzaldehyde	31.9/36.9/35.4	5.1/8.1/6.5	0.61 / 0.63 / 0.61 / 0.62	0.11 / 0.00 / 0.08 / 0.06	0.997 / 0.992 / 0.986 / 0.992

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^a See text for details regarding methods for calculating accuracy and precision
 ^b Stated accuracies and precision obtained by averaging over all repeat measurements for each experiment
 ^c Coefficients obtained using data over all experiments

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In order to demonstrate the performance level of the CIR-TOF-MS during the intercomparison and to provide an overview of measurement accuracy, a series of scatter plots showing the ratios of measured to calculated concentration for each compound are presented below in the following discussion. The plot for experiment 2 is given in **Figure 13**.



Figure 13: Scatter plot showing compound specific ratios of measured/calculated concentration during experiment 2 (dry synthetic air)

As shown in **Figure 13**, when compounds were sampled from the simplest matrix, (*i.e.* dry synthetic air) most measurements were made within accuracy bounds of $\sim \pm 20$ %. During experiment 2, along with toluene, the aldehydes (*i.e.* acetaldehyde, butanal and hexanal) were consistently measured with the greatest accuracy. As well as being measured with high accuracy, the line fits describing the relationship between measured versus calculated values for toluene and the aldehydes all gave slopes of ~ 1 and near 0 intercepts (with the exception of hexanal, discussed below). Average accuracies for toluene and the aldehydes were ~ 6.8 and 15.6 %, respectively.

Measurement of hexanal proved more difficult at lower concentration, with accuracies in excess of 20 % for all three repeat measurements. The data in Figure 13 suggests that the poor accuracies achieved for hexanal could be attributed to an inadequate estimation of the instrument base line. Figure 13 shows an increase in the ratio of measured to estimated chamber concentrations as the chamber air was diluted, which tends to imply that data extracted from the hexanal peak at m/z = 83 contained a residual, unknown quantity of

contamination not fully removed during background subtraction. Inspection of **Table 4** reveals that hexanal has the largest (positive) intercept value of all of the compounds (+ 0.638), further supporting this premise.

Of the fourteen compounds detected benzaldehyde and the alcohols proved the most difficult to monitor with respect to accuracy, in particular 1-butanol. Average accuracies for benzaldehyde and the alcohols (excluding 1-butanol) during experiment 2 were \sim 31.9 and 26.0 %, respectively. Throughout the exercise the slopes for benzaldehyde and the alcohols were generally < 1.

In the case of 1-butanol and benzaldehyde, the CIR-TOF-MS consistently underestimated the calculated chamber concentrations. **Figure 13** demonstrates this and verifies a roughly constant percentage difference between calculated values and those measured. Such findings are consistent with the presence of an unknown sink for these compounds on route to detection. **Table 2** shows that benzaldehyde and 1-butanol have the lowest vapour pressures of the target compounds (4 mmHg at 45 and 20 °C, respectively), making these the most likely candidates to undergo condensation out of the vapour phase. The possibility of sink/loss *via* this route is reinforced by consideration of the average ambient temperatures throughout the intercomparison exercise, which were consistently low, in the range – 1 to + 4 °C. With such compound loss not accounted for in the calculated chamber concentrations, deposition in this manner could explain the poor measurement accuracy obtained for benzaldehyde and 1-butanol.

Measurement reproducibility throughout each experiment was generally high, with compound specific instrument precision of the order 10 % or better for most species. As expected those compounds with smaller sensitivities or weaker spectral signals showed the poorest precision, being adversely affected by experimental noise. For example, for MBO (which has the lowest (PTR) sensitivity of the target compounds) the average measurement precision was ~ 31 % during experiment 2. Results for acetone and methanol are further exceptions to overall high instrument precision. Here the greater scatter can be attributed to minor internal instrument contamination of both methanol and acetone originating from transport and instillation. Such problems could easily be removed by a better estimate of the instrument baseline at the time of measurement.

The CIR-TOF-MS response was found to be strongly linear over the concentration range investigated, with correlation coefficients (r^2) ranging between 0.975 and 0.999 for the chosen

set of compounds under dry sample conditions. Overall for most of the test compounds the slope in the data was close to 1, with 1-butanol being the major outlier (slope = 0.287). In general, the offset of each data set was around 0.5 ppbV or less.

4.4.2.2 Effect of Humidity and Ozone

Generally, when the humidity of the sample matrix is increased, there is a corresponding rise in the abundance of hydrated hydronium ions (*i.e.* $H_3O^+.(H_2O)_n$, where $n \ge 1$) within the (PTR) drift cell, at the expense of H_3O^+ abundance. This can be somewhat problematic, as not all VOCs/OVOCs are able to react with $H_3O^+.(H_2O)_n$ ions, as is the case for some of the target OVOCs studied here. For a compound to undergo reaction with hydrated hydronium (*via* direct PTR or ligand switching), it must possess a proton affinity greater than that of the neutral form of the reagent cluster ion, and have a sufficiently large dipole moment (Spanel and Smith, 1995; Spanel and Smith, 2000) (Warneke *et al.*, 2001), however, even if a compound does react, the efficiency of reaction is sometimes less than with bare H_3O^+ .

Consequently, it is expected that sample humidity can affect the ability of CIR-TOF-MS to measure certain species when operating with hydronium as the primary reagent ion. For example, sensitivity to non-polar compounds such as toluene will decrease in the presence of water vapour, as 'useful' hydronium becomes locked away in the form of hydrated hydronium, with which toluene cannot react. However during the intercomparison experiments, CIR-TOF-MS measurement capability for the majority of the test compounds was unaffected by the introduction of humidity into the sample matrix (with the exception of hexanal). As can be seen in both **Table 4** and **Figure 8**, neither instrument accuracy nor precision was adversely affected by the increase in water vapour concentration. Also, following the introduction of water vapour, very little difference was observed in the slope and intercept parameters for the correlations in **Figures 9** – **12**, which describe the relationship between measured and calculated values.

The reason that CIR-TOF-MS measurement performance was unaffected by moisture was the relatively high reactor energy employed in this instance. By operating the central reactor of the drift cell at an E/N value of 151 Td, a shift was facilitated in the hydronium partitioning balance back towards non-hydrated hydronium, *i.e.* the electric field brought about the conversion of H_3O^+ . $(H_2O)_n$ to H_3O^+ via fragmentation mechanisms. Consequently, relatively little hydronium became 'locked' into the reservoir of cluster species and the requirement for reaction to occur via exclusive ionisation pathways was removed.

It should be noted, however, that although the conditions employed here were sufficient to 'dampen' the negative sensitivity effect for certain compounds to humidity, operating at high E/N values is not necessarily ideal for all compounds. In general, heightened reactor energies will cause fragmentation *via* collision induced dissociation and hence may result in a decline in sensitivity (CIR-TOF-MS drift cell performance is discussed in detail within Chapter 5).

During experiment 3 both toluene and butanal were measured closest to calculated values, with other aldehydes and ketones also measured well, with accuracies generally ~ 20 % or better. In particular, acetone measurements were markedly improved in terms of both accuracy and precision when compared to experiment 2, owing to impurities from transport and installation being finally purged from the system. More specifically, during experiment 3 acetone measurement accuracy and precision improved to ~ 15 %. Data from experiment 3 therefore constitutes a better representation of the ability of CIR-TOF-MS to measure acetone.



Figure 14: Scatter plot showing compound specific ratios of measured/calculated concentration during experiment 3 (moist synthetic air)

Once more the most difficult compounds to measure with high accuracy were the alcohols and benzaldehyde, for reasons explained above. The decrease in hexanal measurement accuracy, observed during experiment 3, most likely originates from interference effects. During proton transfer ionisation, hexanal is liable to fragment yielding a significant daughter ion of m/z = 55, particularly under the high drift cell energies employed here. As the hexanal fragment is isobaric with the hydronium-water cluster ion H₃O⁺.(H₂O)₂, which is likely to be found in greater abundance in a moist drift cell, it becomes somewhat more difficult to extract an exact concentration. Despite the high drift cell E/N removing most cluster species from the reactor, the remaining trace levels were sufficient in this instance to cause spectral interference and affect measurement performance at the lowest hexanal mixing ratios.

When employing proton transfer reaction from hydronium as the ionisation method, the presence of H_3O^+ . $(H_2O)_n$ ions in the drift cell reactor can often lead to a more complex and convoluted mass spectrum over many mass channels, with the production of not only the MH⁺ ion following direct proton transfer, but also MH⁺. $(H_2O)_n$ cluster ions and fragments thereof. Such unwanted signals can be removed from the mass spectrum by minimising the water cluster ion abundance with respect to that of the primary reagent ion, as detailed above, with the application of a relatively large electric field along the drift cell reactor. To facilitate further the removal of MH⁺. $(H_2O)_n$ ions (particularly if the central reactor is operated at low energies) and to assist focusing of the ion beam, the electrical potential gradient over the exit/collision cell is also increased relative to that of the central reactor.

During the intercomparison campaign the ECC 'ramp' was set to have voltage distributions of ~ 953 and 253 V cm⁻¹, respectively over the two stages (of 0.04 and 1.7 mm) of ion transit through the Mk.1 ECC before entry into the mass spectrometer. Using the Mk.1 variant of the ECC and under the drift cell conditions employed during the intercomparison exercise (*i.e.* 151 Td with exit potential ramp), the measured monohydrate signal obtained when sampling from a dry synthetic air matrix (*i.e.* experiment 2), was typically ~ 0.4 % of the hydronium ion signal. The measured signal of monohydrate with respect to that of the hydronium ion increased to only ~ 0.8 % when sample humidity was raised to approximately 60 % during experiment 3 and ~ 0.7 % during experiment 4. Correspondingly, little variation was observed in the hydronium abundance between dry and moist conditions, with the mean count rate at 60 % relative humidity within one standard deviation of that seen during dry sampling.

As was discussed in Section 4.3.7, the removal of water cluster ions by the potential ramp at the base of the drift cell will mask the true distribution of reagent ions present within the main reactor (above the collision region). For example, if the electric field is kept constant within the main body of the drift cell reactor and the ramping field applied to the ECC is reduced, first by 15 % and then by 29 % (*i.e.* to give voltage distributions of ~ 810 and then 677 V cm⁻¹ over the first ECC stage and ~ 215 and then 180 V cm⁻¹ over second stage), the abundance of the monohydrate ion with respect to that of the hydronium ion increases to ~ 6.5 and 23.1 %,

respectively. Therefore, an estimate of the absolute number concentration of hydrated hydronium ions in a CIR or PTR reactor cannot simply be obtained through observation of measured signals; the condition of the ECC must also be accounted for (see Chapter 5 for detailed discussion).

An estimate of the distribution of hydronium amongst its various cluster species within the reactor may be calculated using a simple model; this will be discussed within Chapter 5. However, in brief as an example here, at an E/N of 100 Td the theoretical H₃O⁺.(H₂O)/H₃O⁺ ratio has been calculated to be ~ 1.5, whereas (dry sample) measurements (with an ECC E/N of 170 Td) give a ratio of ~ 0.04. Above a reactor E/N of ~ 120 Td, both measured and calculated H₃O⁺.(H₂O)/H₃O⁺ ratios are minimal.

Inspection of **Table 4** and **Figure 15** verifies that there was no significant effect on measurement accuracy and precision for the majority of the test compounds, following addition of ozone to the sample matrix. The only two exceptions to this were methanol and hexanal, whose poor accuracy and precision values for experiment 4 can be explained through previously discussed background interference in their respective mass channels.



Figure 15: Scatter plot showing compound specific ratios of measured / calculated concentration during experiment 4 (moist synthetic air + ozone)

With a total inlet residence time of only 11 seconds for the sample gas on route to the drift cell; and with relatively low ozone concentrations in the sample matrix (of the order 40 - 50

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ppbV), any possible ozone/surface effects during measurement using the CIR-TOF-MS technique are expected to be minimal.

4.4.2.3 Measurement of Formaldehyde

As can been seen from observation of **Figure 8**, the CIR-TOF-MS operating in PTR mode, was able to detect only a minor formaldehyde signal during each experiment. It has been shown that formaldehyde is somewhat difficult to measure using the PTR-MS technique on account of the reaction kinetics involved (Hansel *et al.*, 1997), *i.e.* the exothermicity of the forward proton transfer reaction (R4.2) is relatively low, at ~ 5.2 kcal mol⁻¹. Because of the relatively small exothermicity involved, very little additional energy is required to overcome the activation energy barrier to the thermally endothermic backwards reaction (R4.3) between the HCHO.H⁺ ion and neutral water:

$$HCHO + H_3O^+ \rightarrow HCHO.H^+ + H_2O$$
 (R4.2)

$$\text{HCHO.H}^+ + \text{H}_2\text{O} \rightarrow \text{HCHO} + \text{H}_3\text{O}^+ \tag{R4.3}$$

As noted by Hansel and co-workers (Hansel *et al.*, 1997), the energy supplied to the reactant ions by the drift cell electric field is usually sufficient to force reaction (R4.3) to proceed. Consequently, protonated formaldehyde ions will undergo conversion back to their neutral form, and hence they will be lost from detection. As yet the CIR-TOF-MS has not been fully characterised for the detection of formaldehyde, therefore the formaldehyde measurements made during the intercomparison exercise are reported separately in **Figure 16**.



Figure 16: Comparison of CIR-TOF-MS measured concentrations (red circles) with chamber values (blue line) throughout all experiments for formaldehyde and corresponding regression plots (in regression plots blue circles = experiment 2, red squares = experiment 3 and white triangles = experiment 4).

As can be seen from **Figure 16** the CIR-TOF-MS was unable to measure formaldehyde with any reasonable degree of accuracy or precision, with the exception of experiments 2A and 3A. This result is not surprising considering the large reactor electric field employed and consequently, the relatively large ion kinetic energies involved.

Recently the CIR-TOF-MS has been applied to the monitoring of atmospheric VOC oxidation mechanisms at the EUropean PHotO REactor (EUPHORE), a large (200 m³) simulation chamber similar in design to SAPHIR (http://EUPHORE.es). These experiments are not reported within this thesis; however, an example is given in **Figure 17** of CIR-TOF-MS made formaldehyde measurements.



Figure 17: (a) concentration-time profile of and **(b)** correlation between CIR-TOF-MS (red line and red error bars) and Aerolaser AL4021 made formaldehyde measurements (black line and grey error bars) during the ozonolysis of isobutene

Figure 17 shows a comparison between CIR-TOF-MS (red line) made formaldehyde measurements and those made by a commercial formaldehyde monitor (Aerolaser AL4021, black line, grey error bars) during the ozonolysis of isobutene under dry conditions (100 ppbV isobutene, 200 ppbV ozone, 500 ppmV CO and relative humidity < 0.3 %). For the acquisition of these data the CIR-TOF-MS reactor energy was reduced to 90 Td ($KE_{cm} \sim 0.1$ eV). In this instance CIR-TOF-MS and Aerolaser formaldehyde measurements are in very good agreement ($r^2 = 0.97$), suggesting that when instrument conditions have been appropriately tuned, the CIR-TOF-MS technique may be used to provide reliable formaldehyde measurements. Reducing the reactor energy aids formaldehyde measurement

by (i) minimising the energy of the ion pool and hence minimising the rate of deprotonation *via* reaction (R4.3) and (ii) increasing the reactor transit time and hence increasing the fractional conversion of M to MH^+ . From the correlation plot made in **Figure 17(b)** the CIR-TOF-MS sensitivity to formaldehyde was determined to be 7.89 (± 0.30) ncps ppbV⁻¹. In comparison with other OVOCs, sensitivity to formaldehyde is somewhat low, being more similar to that of the hydrocarbons (see Chapter 5). However, due to the relatively low instrumental noise of the CIR-TOF-MS, atmospheric measurements of formaldehyde at this sensitivity level are entirely possible.

4.4.3 Signal-to-Noise Statistics

Ion signals for the target OVOCs, integrated over the specific time periods as detailed above, possessed good signal-to-noise ratio (S/N), generally far in excess of 2:1 (a criterion often employed in order to determine whether a signal is discernable). All S/N values were calculated according to equation (E4.8):

$$\frac{S}{N} = \frac{S_{av}}{\sqrt{\overline{S}_n^2}}$$
(E4.8)

In equation (E4.8) S_{av} = the average ion signal in a given mass channel taken over the entire measuring period and S_n = the ion signal (in the stated mass channel) obtained during the n^{th} measurement, hence \overline{S}_n = the root-mean-square noise (Wayne, 1995). The compound specific *S/N* ratios presented by the OVOC signals shown in **Figure 8** for sub-experiments A, B and C lay within the bounds 17 - 270, 19 - 178 and 3 - 50, respectively.

4.4.4 Real-Time Monitoring and Time-of-Flight Mass Spectrometry

One major advantage of the CIR-TOF-MS technique is its ability to monitor a multitude of trace compounds in *real-time*, which is defined here as time scales of around one minute. This is exemplified, in respect of *real-time*, in **Figure 18**, which displays the data recorded for acetaldehyde during experiment 2 alongside the calculated chamber concentrations. As expected the typical signal-to-noise ratio for all one-minute data, across all values of mixing ratios was substantially lower than the equivalent value achieved following fifty-minute integration. For example, over the entire experiment sub-section, the one-minute acetaldehyde data recorded during experiment 2 possessed average *S/N* ratios of approximately 8:1, 5:1 and 4:1 at concentrations of around 10, 3 and 1 ppbV respectively. With the exception of hexanal and MBO, for which sensitivities were considerably low, the average *S/N* ratios in the one-minute data for most compounds were in the range 2:1 - 3:1 or greater for both sub-experiments A and B.



Figure 18: Example comparison of *real-time* CIR-TOF-MS measured concentration of acetaldehyde (circle points) versus time with calculated chamber concentrations (blue line) during experiment 2

The detection limit of the CIR-TOF-MS for a given compound can be determined through knowledge of the signal-to-noise ratios achieved during measurement of that target compound at a number of concentrations over a wide mixing ratio range. In general the CIR-TOF-MS one-minute limits of detection for OVOCs are of the order 4 - 26 ppbV min⁻¹ at S/N = 2:1. A full account detailing how CIR-TOF-MS detection limits are determined is presented in Chapter 5, with examples for a range of VOCs.

During sub-experiment 2A, where mixing ratios were of the order of 10 ppbV, the average one-minute accuracy for acetaldehyde over the entire three-hour period was exceptionally good at 12.5 %, comparing remarkably well with the fifty-minute data. One-minute precision was also comparable, at 15.4 %. However, as the chamber air was diluted and mixing ratios decreased, accuracy and precision both fell. In the case of acetaldehyde, average accuracy and precision values were 32.4 % and 66.7 %, respectively, for sub-experiment 2B and 37.7 % and 76.3 % for sub-experiment 2C.

Combining the benefits of fast and reliable data acquisition with time-of-flight mass spectrometry allows the construction of a highly detailed picture of the sample matrix, in which all mass channels are observed simultaneously, unlike conventional quadrupole instruments where only a single mass channel is monitored at any instant in time. As a result the CIR-TOF-MS technique allows even the most complex and transient events to be monitored in high detail. This is exemplified in **Figure 19**, which shows the normalised ion count (colour scale on the *z*-axis) acquired in each mass channel of the CIR-TOF-MS throughout experiment 2 of the intercomparison. Close inspection of **Figure 19** reveals features typical to each of the intercomparison experiments (as shown in **Figure 18** for example), including the three distinct measurement periods and the two dilution events.



Figure 19: Evolution of CIR-TOF-MS ion count (signal) in all mass channels with time (data taken from experiment 2).

4.4.5 Sensitivity Intercomparison

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In order to present a measure of relative instrument performance, a brief comparison is made between sensitivities acquired by the CIR-TOF-MS for a number of common atmospheric VOCs, with published experimental sensitivities obtained by several other PTR-MS instruments. Included in this comparison are findings by Ennis *et al.* (Ennis *et al.*, 2005), Hanson *et al.* (Hanson *et al.*, 2003) and de Gouw *et al.* (de Gouw *et al.*, 2003b) for the detection of methanol, acetaldehyde, acetone and toluene (see **Table 5**). The relative normalised sensitivity values given in **Table 5** were obtained by the various authors under a range of drift cell conditions (*E/N* from ~ 110 – 147 Td), with each instrument individually optimised for the detection of such trace species.

	This work	Ennis <i>et al</i> .,	Hanson <i>et al.</i> ,	de Gouw <i>et al.,</i>
		2005	2003	2003b
<i>E/N</i> / Td	151	~ 120	~ 114	*
methanol	28	-	60 - 30	24
acetaldehyde	50	-	115 – 90	27
acetone	51	28	240	64
toluene	26	4	-	45

Table 5: Sensitivity comparison made between four different PTR-MS instruments (all sensitivities are given in ncps/ppbV)

* Drift cell reportedly operated at 2 mbar pressure and with an applied electric field of 710 V

The CIR-TOF-MS sensitivities for acetone and toluene obtained during this work are significantly larger than those obtained by Ennis and co-workers (Ennis *et al.*, 2005), who operate a similar time-of-flight instrument (Kore Technology Ltd., UK) coupled to a custom hollow cathode ion source. CIR-TOF-MS instrument sensitivities compare favourably with results by de Gouw and colleagues (de Gouw *et al.*, 2003b) obtained during the New England Air Quality Study in 2002, using a commercial hollow cathode discharge ion source/quadrupole device (Ionicon Analytik, Au.). The CIR-TOF-MS sensitivity is slightly greater in the cases of methanol and acetaldehyde than was achieved by de Gouw, but slightly lower in the case of acetone and toluene.

Sensitivities obtained by the CIR-TOF-MS also compare reasonably with results from the PTR-MS system of Hanson *et al.* (Hanson *et al.*, 2003), which comprises a similar radioactive ion source alternatively coupled to a quadrupole mass spectrometer. Results taken from Hanson *et al.* (shown in **Table 5**) are given as a range in order to cover the different sensitivities achieved under various sample humidities, with the larger sensitivities achieved under less humid conditions. The (dry) compound sensitivities quoted in this work were around 2 - 5 times lower than Hanson's with the major differences being attributed to the higher working pressure of that drift tube.

4.5 Conclusions

The data presented within this chapter demonstrates that Chemical Ionisation Reaction Timeof-Flight Mass Spectrometry is capable of providing accurate, reproducible and quantitative measurements of a wide range of atmospherically important OVOCs. The instrument performance with respect to the measurement of a range of OVOCs has been quantified. It has been demonstrated that a time-of-flight device is capable of providing on-line measurements of atmospheric trace species, with relative sensitivities entirely comparable to instruments employed by other workers, including commercially available devices. The potential benefits of using a TOF based device for atmospheric monitoring are considerable, with the sample matrix being probed in more depth and detail than has been possible previously.

Work published in Wyche et al., 2007, Atmos. Chem. Phys., 7(3), 609 – 620 and Apel, Wyche et al., 2008, J. Geophys. Res., 113(D20), (doi: 10.1029/2008JD009865)

Chapter 5

Detailed Characterisation of the Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry Technique

5.1 Summary and Introduction

In the development of any new instrument a substantial degree of characterisation is required in order to understand how the system works and how to optimise it to achieve the best possible results. So far within this thesis the CIR-TOF-MS has been introduced and described, the chemical ionisation reaction technique has been thoroughly tested and applied to the ionisation of a wide range of compounds, and the instrument has been validated for quantitative measurement under controlled conditions. Having performed these first crucial tasks with a high level of success, focus is now directed to understanding the more detailed aspects that can affect instrument performance.

As the hydronium ion was undoubtedly the most successful reagent species during initial testing, PTR ionisation was primarily employed throughout the remainder of work described within this thesis. As such, the main body of characterisation work performed and described here, focuses on understanding the PTR system within the context of the CIR-TOF-MS technique.

One major factor that can affect instrument performance when operating with hydronium is the presence of water vapour within the sample matrix. It has been shown that the sensitivity of PTR-MS to certain compounds is dependent on the water vapour concentration of the sample gas (Warneke *et al.*, 2001; Tani *et al.*, 2004), as hydronium is able to react with neutral water to form clusters, which have less favourable kinetics for reaction with certain VOCs (de Gouw and Warneke, 2007). Also the presence of ion-water clusters can cause spectral interference and severely hamper data interpretation. As was stated earlier within this thesis, the energy supplied by the drift cell electric field can be employed to dissociate these cluster species, but at what cost to sensitivity as fragmentation is induced and as ion residence time is lowered? As atmospheric samples will always contain some level of water vapour and a host of different species of VOCs, it is crucial that the interaction between drift cell energies, water vapour loading and the reagent cluster ion distribution be examined and understood. Moreover, perhaps most critical of all, is to obtain an understanding of how and why these parameters affect the sensitivity of the instrument to the various target species. As well as examining reagent ion distributions and compound sensitivities, various other characterisation studies are described within this chapter. The findings obtained from these experiments are brought together in the final section, where the performance of the CIR-TOF-MS is described during a field test, monitoring VOCs in the 'real' atmosphere.

5.2 Hydronium-Water Cluster Formation in CIR-MS

Not all of the neutral source gas within a CI ion source will be converted to ionic reagent, *i.e.* ion generation is not 100 % efficient. Consequently, as a saturated nitrogen carrier gas is employed for hydronium generation, there will always be an excess of neutral water vapour within the CIR-TOF-MS ion source. Because of this, nascent hydronium ions are liable to take part in ternary reactions with neutral water molecules to produce ion-neutral cluster complexes bound by hydrogen bonds:

$$H_3O^+.(H_2O)_{n-1} + H_2O + B \xleftarrow{K_{CL}} H_3O^+.(H_2O)_n + B$$
 (R5.1)

Here B represents a reaction third body (usually N2 within the CIR reactor)

The rate of reaction (R5.1) is, however, quite slow. For example when *n* is 1 and 2, K_{CL} is around 1×10^{-28} and 1×10^{-27} , respectively. The value of K_{CL} has been shown to increase with *n* and is known to exhibit strong negative temperature and energy dependencies (de Gouw and Warneke, 2007; Blake *et al.*, 2008).

As some quantity of the neutral source gas 'leaks' from the ion source, in 'hydronium mode' the CIR reactor matrix will always be seeded with neutral water molecules, even when a dry sample gas is investigated. Thus, as neutral water molecules are present within the reactor, it is likely that hydrated hydronium ions of the type H_3O^+ .(H_2O)_n, will also form outside of the ion source chamber. For the standard (commercial) PTR ion source (Ionic Analytik, Au.), the flow of neutral water vapour into the reactor has been estimated to be approximately 5 % of

the total water injected into the ion source, *i.e.* around 0.4 cm³ min⁻¹ (the remainder being pumped away or converted to hydronium) (Warneke *et al.*, 2001). It was estimated that this ion source 'leakage' resulted in a reactor relative humidity of approximately 45 % at 23 $^{\circ}$ C.

It is important to note that water leakage from the ion source does not constitute the sole pathway to *in situ* hydronium-water cluster formation within the reactor. The water vapour loading of the drift cell is also known to vary with the humidity of the sample being measured (Warneke *et al.*, 2001). It follows therefore, that the greater the number density of neutral water molecules within the reactor, the greater the number density and extent of hydronium-water (and indeed analyte-water) clustering. Certainly, hydronium-water cluster ions with n as high as 3 are common with very high sample humidities. However, at 300 K, n has an upper limit of 4 (Spanel *et al.*, 1995). As shown in reaction (R5.1), the association process is reversible, with hydronium-water cluster complexes being formed and broken apart continuously as the gas matrix travels the length of the drift cell (de Gouw and Warneke, 2007).

The degree of hydronium-water clustering within the CIR-TOF-MS drift cell can be controlled through modulation of the reactor electric field. As was described in Chapters 2 and 3, applying an overall increase to the system E/N will result in an increase in the energy of all ion-molecule collisions, and hence ion fragmentation will be facilitated (*i.e.* collision induced dissociation (CID) is introduced). Also, as the focusing electric field of the exit/collision cell (ECC) is generally operated at a larger value than that of the central reactor, additional removal of hydronium-water and analyte water-adduct ions is facilitated before the nascent ion beam enters the mass spectrometer. Although the potential 'ramp' of the ECC aids interpretation of the mass spectrum by removing such potentially unwanted ions, it does disadvantage the user by masking the true distribution of hydronium within the reactor amongst it various water cluster species.

Figure 1 shows the observed variation in the relative abundance of monohydrated hydronium (with respect to the bare hydronium, *i.e.* $[H_3O^+.(H_2O)/H_3O^+] \times 100$), within the CIR-TOF-MS reactor as a function of sample humidity and reactor *E/N*. For the data presented in **Figure 1** the ECC *E/N* value was fixed at 170 Td.



Figure 1: Variation of measured H_3O^+ .(H_2O) cluster relative abundance (with respect to H_3O^+) with sample humidity and reactor *E/N*. ECC *E/N* set to 170 Td.

From first inspection of Figure 1 it can be seen that the observed relative abundance of the H_3O^+ .(H_2O) ion at a reactor *E/N* of 80 Td, increased from ~ 4 to 26 % as the sample humidity was increased from 0 to 100 %. Further to this and as expected, the abundance of monohydrated hydronium was observed to decrease with increasing reactor energy, *i.e.* the relative abundance of the H_3O^+ .(H_2O) ion at 100 % relative humidity, fell from 26 to 23 % as the reactor E/N was increased from 80 to 140 Td. However, with an ECC E/N of 170 Td (required to facilitate focusing of the ion beam into the mass spectrometer), the resultant collision energy (KE_{cm}) was sufficiently large to bring about dissociation of a large proportion of all water cluster ions as they exited the reactor. Consequently, the mass spectra recorded are not necessarily directly representative of drift cell composition. With this in mind the true distribution of hydronium must be biased toward the first and higher cluster hydrates, as was found in a recent study for a commercially available PTR-MS instrument (Warneke et al., 2001). Even though the absolute value of monohydrated hydronium abundance within the reactor is not thought to be a true representation, the trends extorted from the data presented in Figure 1 are believed to be accurate. Figure 2 given below, clearly demonstrates the profound effect that variation of the ECC E/N has on the observed relative abundance of hydrated hydronium.



Figure 2: Variation of measured hydronium-water cluster ion abundance with ECC E/N. Drift cell reactor E/N 100 Td.

For the data presented in **Figure 2**, the drift cell reactor was operated at a relatively low *E/N* of 100 Td and the sample gas simply comprised dry nitrogen. Consequently, all hydronium-water cluster formation would have been due to standard water vapour leakage from the ion source. At an ECC *E/N* of 110 Td, the recorded levels of mono-, di- and tri- hydrated hydronium (n = 1, 2 and 3, respectively), were ~ 2.5, 0.4 and 0.01 times that of base hydronium. As the ECC energy was increased and as the CID introduced brought about cleavage of their relatively weak H₃O⁺–H₂O bonds (134 kJ mol⁻¹ (Tani *et al.*, 2004)), the abundance of all forms of the hydronium-water cluster ion were observed to decrease. As the ECC *E/N* was increased to 190 Td, the observed relative abundance of H₃O⁺.(H₂O) with respect to H₃O⁺ fell to ~ 1.5 %, and all other forms to negligible levels.

The theoretical distribution of hydronium amongst its various cluster ions within the CIR-TOF-MS reactor can be calculated by application of a simple model based on the Gibbs free energy change of the association reactions (*i.e.* (E5.1)) (Warneke *et al.*, 2001). By using measured values of ΔH^{Θ} and ΔS^{Θ} for each association reaction (Kebarle *et al.*, 1967; Lau *et al.*, 1982), and by assuming that the ion temperature (T_{ion}) is equivalent to the effective temperature of the reaction (T_{eff}) (Warneke *et al.*, 2001), equation (E5.1) can be solved for the equilibrium constant (K_{CL}):

$$\Delta G^{\Theta} = \Delta H^{\Theta} - T_{ion} \Delta S^{\Theta} = -RT_{ion} \ln K_{CL}$$
(E5.1)

where

$$T_{ion} \equiv T_{eff} \equiv \frac{3}{2k_B} \left(\frac{3}{2} k_B T + \frac{1}{2} m v_d^2 \right)$$
 (E5.2)

and k_B is Boltzmann's constant.

The value of K_{CL} derived from equation (E5.1) can be employed along with the water vapour concentration of the reactor to determine a given cluster ratio (*i.e.* [H⁺.(H₂O_n)]/[H⁺.(H₂O)_{n-1}]):

$$K_{CL} = \frac{[\mathrm{H}^{+}.(\mathrm{H}_{2}\mathrm{O})_{n}]}{[\mathrm{H}^{+}.(\mathrm{H}_{2}\mathrm{O})_{n-1}].[\mathrm{H}_{2}\mathrm{O}]}$$
(E5.3)

The relative abundance of the first hydronium hydrate with respect to hydronium as calculated using equations (E5.1) – (E5.3) is shown in **Figure 3** for various reactor E/N values. For this simple model the relative abundance of H₃O⁺.(H₂O) was determined assuming a reactor relative humidity of 100 %.



Figure 3: Calculated variation of $H_3O^+(H_2O)$ abundance with respect to H_3O^+ using equations (E5.1) – (E5.3)

As can be seen from observation of **Figure 3**, the theoretical $H_3O^+.(H_2O)/H_3O^+$ ratio unsurprisingly decreases dramatically with increasing reactor *E/N*. At an *E/N* of 100 Td the model predicts a $H_3O^+.(H_2O)/H_3O^+$ ratio of approximately 1.5 (*i.e.* monohydrated hydronium relative abundance ~ 150 %), which compares somewhat favourably with the experimentally derived value of ~ 2.5, obtained by reducing the ECC *E/N* to 110 Td (see **Figure 2**). Model results suggest that the abundance of monohydrated hydronium becomes minimal at a reactor *E/N* of ~ 120 Td (monohydrated hydronium relative abundance ~ 1.5 %). The close correlation obtained between the modelled and measured $H_3O^+.(H_2O)$ abundance, permits the use of model results with some level of confidence, as a guide when attempting to optimise hydronium/cluster distributions.

As noted by de Gouw and Warneke (de Gouw and Warneke, 2007), there are a number of inherent uncertainties associated with this calculation, which may explain the differences observed between modelled hydrated hydronium abundance and measured values. These uncertainties originate from: (i) the exclusion of kinetic and internal energies of the neutral constituents of the system from equation (E5.2), (ii) the fact that the velocity distribution may

not be Maxwellian and (iii) inaccuracies in the estimation of reactor water vapour concentration.

5.3 The Role of Hydronium-Water Clusters in Chemical Ionisation

5.3.1 Chemical Ionisation by Hydronium-Water Cluster Ions

When employing proton transfer reaction ionisation from hydronium, it is often undesirable to have hydrated hydronium ions present within the drift cell reactor. One major reason for this is that when bound in the ion-neutral cluster, the hydronium ion is able to share its positive charge with those water molecules associated with it. As a result the cluster ion will be more stable than the base hydronium ion and it will possess a higher proton affinity (PA) (Blake *et al.*, 2008). For example, the water-water dimer has a proton affinity 117 kJ mol⁻¹ greater than that of the water molecule (*i.e.* PA((H₂O)₂) = 808 (± 6) kJ mol⁻¹) (Goebbert and Wenthold, 2004). The stability of the hydronium-water ion complex, and therefore its proton affinity, is known to increase with *n* (Blake *et al.*, 2008).

For a molecule to react with hydrated hydronium, it must not only possess a sufficiently high proton affinity, but it must also be suitably polar (Spanel *et al.*, 1995; de Gouw and Warneke, 2007). It has been shown that the ability of an analyte molecule to react with hydrated hydronium is strongly related to its permanent dipole moment (μ_D), with highly polar molecules such as acetone ($\mu_D = 2.88$ D) able to react with hydronium-water clusters with *n* as high as 3 (Spanel *et al.*, 1995). This effect is a result of the moderately strong ion-dipole bonding which is established between the hydrated hydronium ion and the polar analyte. The ion-dipole bonding will add stability to the intermediate reaction complex, thus increasing the probability of the reactants proceeding to products. The ion-induced dipole interaction between hydrated hydronium and a non-polar compound is unlikely to be sufficient to aid the reaction intermediate. Should therefore, the hydronium population become locked into the cluster ion pool, the ionisation potential of the system will clearly move to a more selective regime, which excludes most alkanes, certain aromatics and other low polarity hydrocarbons that would otherwise have been able to react with the base hydronium ion.

A further significant problem associated with the presence of hydronium-water clusters within the CIR-MS drift cell, is the complexity of their reactions, *i.e.* when a molecule reacts with hydrated hydronium, the result will not necessarily be simple direct proton transfer and the production of the MH⁺ molecular ion. There are three possible reaction pathways available to
the analyte, M, when it reacts with hydrated hydronium, the availability of each being governed by the proton affinities and polarities of the reactants. Taking monohydrated hydronium as an example, these are:

$$H_3O^+.(H_2O) + M \xrightarrow{k_1} MH^+ + 2H_2O$$
 (R5.2)

$$H_{3}O^{+}.(H_{2}O) + M \xrightarrow{k_{2}} (MH^{+}.H_{2}O) * + H_{2}O \xrightarrow{k_{dec}} MH^{+} + 2H_{2}O \qquad (R5.3)$$

$$H_3O^+.(H_2O)^+ + M \xrightarrow{k_3} MH^+.H_2O + H_2O$$
 (R5.4)

The simplest possible outcome from reaction of the molecule, M, with hydrated hydronium is the production of MH^+ , the protonated form of the analyte. Analogous to reaction with the base hydronium ion, this result is achieved *via* pathway (R5.2) or (R5.3). Reaction (R5.2) represents direct proton transfer from the cluster ion H_3O^+ .(H_2O) to the analyte M at rate k_1 , which is equal to the collision-limited rate (de Gouw and Warneke, 2007). This mechanism is only possible if the analyte molecule has a proton affinity greater than that of the water dimer.

An alternative route to the production of MH^+ from hydrated hydronium is reaction (R5.3). In reaction (R5.3), the analyte molecule first undergoes ligand switching with the H_3O^+ .(H_2O) ion to form the short-lived intermediate complex, (MH^+ . H_2O)*. If the energy released from the ligand switching reaction is greater than the bond energy involved in binding the water molecule to the complex, the ligand will thermally decompose to yield a second neutral water molecule and the MH^+ ion (Spanel *et al.*, 1995). As shown by Tani *et al.* (Tani *et al.*, 2004) the energy dissociation limit of the ligand can be determined from the proton affinity of the base reagent molecule/complex and the binding energies (BE) of the bonds involved. For example, for reaction (R5.3) to proceed M would require a proton affinity of:

 Σ PA(base reagent) + BE(reagent-neutral bond) - BE(ligand)

i.e. 691 (PA(H₂O)) + 134 (BE(H₃O⁺-H₂O)) - 15 (BE(H₂O-H₂O)) = 810 kJ mol⁻¹ (Tani *et al.*, 2004)

Reaction (R5.3) therefore essentially constitutes a dissociative ligand switching process. In combination the rates of the ligand switching reaction and the subsequent thermal decomposition are considered to be fast, either at or close to the collision-limited rate. The rate of reaction of all organics with hydrated hydronium decreases with increasing n (Spanel *et al.*, 1995).

As shown in reaction (R5.4), the third potential pathway available for reaction of the analyte, M, with hydrated hydronium is a simple ligand switching process, which results in the production of an ion of the form $MH^+(H_2O)_n$. In the $MH^+(H_2O)_n$ cluster, the proton is

coupled to the molecule of highest proton affinity, *i.e.* the analyte M, to which the water molecule(s) are loosely bound by hydrogen bonds. Reaction (R5.4) will generally be the dominant fate for a given analyte, if that analyte is sufficiently polar but does not have a proton affinity large enough to cause decomposition of the intermediate ligand. For many susceptible VOCs the ligand switching reaction rate is fast (at or near the collisional rate (Blake *et al.*, 2008)), in which case instrument sensitivity is not detrimentally effected by the presence of H_3O^+ . (H_2O) rather than H_3O^+ . Although polar compounds are able to react with hydrated hydronium despite not having a large enough proton affinity, the presence of analyte association complexes within the drift cell can ultimately lead to spectral congestion and interference which can severely complicate data interpretation. As will be discussed below, the exit/collision cell can be employed to cause dissociation of the MH⁺–H₂O bond in order to prevent such issues.

As was noted in Chapter 4, neglecting the reactions of hydrated hydronium within the reactor will result in inaccuracies in the calculated value of analyte concentration if PTR kinetics (*i.e.* equation (E3.7) of Chapter 3) alone are used without calibration. Section A5 of the Appendix provides a brief overview of modifications required to equation (E3.7) in order to account for the presence of hydronium cluster ions.

5.3.2 CIR-TOF-MS Sensitivity: Effect of Reactor Energy and Sample Humidity In order to explore the complex effect that hydronium water cluster ions have on the detection capability of CIR-TOF-MS, the instrument sensitivity has been determined for a number of atmospherically significant compounds over a range of sample humidities and reactor energies. For this investigation the CIR-TOF-MS was calibrated for ammonia, acetaldehyde, acetone, pent-1-ene and hexan-2-one at drift cell reactor E/N values of 80, 100, 120 and 140 Td, with a fixed ECC E/N of 170 Td. The reactor E/N was varied by modulating the electric field, the drift cell pressure was held constant at 6 mbar. The compounds were delivered at set concentrations in a nitrogen carrier gas (purity 99.9999 %) from permeation tubes (Eco-Scientific) held in a gas dilution system (Kintec, model: 491-M). The dilution system was used to vary the relative humidity of the carrier gas from 0 – 100 % (at 21 °C) in intervals of 20 %. Calibration and sensitivity determination was otherwise conducted as described in Chapter 4. The results obtained are presented in **Figures 4**, **5** and **6** below as 'sensitivity maps', which display the instrument sensitivity to each compound as a function of both reactor E/N and sample relative humidity. Inspection of Figure 4 reveals that ammonia and the two ketones, acetone and hexan-2-one, exhibit similar behaviour within the CIR-TOF-MS reactor, *i.e.* the instrument sensitivity for each of the compounds appears to be generally unaffected by variation of sample humidity, but in each case sensitivity shows strong negative energy dependence. The effect of humidity variation on the CIR-TOF-MS sensitivity for these molecules can be explained through consideration of their proton affinities and polarities. As ammonia, acetone and hexan-2-one have proton affinities greater than that of the water dimer, *i.e.* 853.6, 812 and 843.2 kJ mol⁻¹, respectively, they are able to react with hydrated hydronium via reactions (R5.2) and (R5.3) (de Gouw and Warneke, 2007). For these molecules, reactions (R5.2) and (R5.3) are rapid, occurring close to the collisional rate, with rate constants similar to those for their corresponding direct proton transfer reactions with H_3O^+ (*i.e.* R3.3). For example for acetone, $k_{(R3.3)} = 4.1 \times 10^{-9}$ and $k_{(R5.2)} = 3.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Spanel *et al.*, 1995). Consequently the ionisation efficiency of, and therefore sensitivity to these (and all high PA) compounds is unaffected as the dominant form of reagent ion changes from H_3O^+ to H_3O^+ .(H₂O) with increasing humidity and decreasing energy. Because of the large value of their dipole moments (2.88 and > 2.6 D, respectively), both acetone and hexan-2-one are also able to react with hydrated hydronium via reaction (R5.4).



The decrease in sensitivity observed with increasing E/N is most likely due to two main factors: (i) the resultant decrease in ion transit (reaction) time and (ii) the resultant increase in fragmentation. As ammonia, acetone and hexan-2-one are able to react rapidly with the various forms of hydrated hydronium, no significant sensitivity benefit is gained from an increase in E/N converting hydronium-water cluster ions back to their base hydronium form. On the contrary, any minor benefit gained from the presence of hydronium rather than hydrated hydronium within the reactor, is offset by the reduced ion residence time and fragmentation of the molecular ion as collisions become more energetic. For ammonia, acetone and hexan-2-one, sensitivities were observed to fall by ~ 40 - 50 % over the 60 Td range in going from 80 to 140 Td.

Acetaldehyde has a proton affinity of 769 kJ mol⁻¹, and therefore it will readily undergo reaction with hydronium, but not with its water cluster counterparts, *e.g.* reaction of acetaldehyde with monohydrated hydronium is endothermic by 39 kJ mol⁻¹ at 300 K. However, acetaldehyde does possess a relatively large dipole moment, *i.e.* 2.97 D, and hence it will react with H_3O^+ .(H_2O)_n via reaction (R5.4) to produce the protonated acetaldehyde-water complex, *i.e.* MH⁺.(H_2O)_n (Spanel *et al.*, 1995). The ligand switching reactions of acetaldehyde are rapid, occurring close to the collisional rate, *i.e.* $k_{(R5.4)}$ for n = 1, 2 and 3 has been measured to be 3.2, 3.1 and 2.8 ×10⁻⁹ cm³ s⁻¹, respectively (Spanel *et al.*, 1995). These values compare favourably with the PTR rate of acetaldehyde with hydronium, *i.e.* 3.5 ×10⁻⁹ cm³ s⁻¹. Consequently, the detection efficiency for acetaldehyde (as measured via the MH⁺.(H₂O) ion) is not expected to be compromised by humidity. The sensitivity maps obtained during this study for protonated acetaldehyde and the protonated acetaldehyde-water complex (MH⁺.(H₂O)) are shown in **Figure 5**.



Figure 5: CIR-TOF-MS sensitivity maps for acetaldehyde and the acetaldehyde-water adduct. Colour scale legend gives sensitivity in ncps ppbV⁻¹.

At low reactor energy (*i.e.* 80 Td) and low relative humidity (*i.e.* 0 %), CIR-TOF-MS sensitivity to acetaldehyde *via* the MH⁺ ion was relatively large, being ~ 140 ncps ppbV⁻¹. The corresponding sensitivity to acetaldehyde *via* the MH⁺.(H₂O) ion was minimal under these conditions. The findings presented within Section 5.2 suggest that at such low reactor energies a substantial fraction of total hydronium exists in hydrated form; hence one would expect sensitivity to the acetaldehyde MH⁺.(H₂O) ion to be much larger. In this instance the low sensitivity observed for MH⁺.(H₂O) and the high sensitivity for MH⁺, are most likely an effect of CID in the ECC facilitating the dissociation of the MH⁺.(H₂O) ion prior to detection. Further results will be presented in Section 5.5 to verify this finding.

As the sample matrix relative humidity was increased up to ~ 60 %, a small decline in sensitivity to the acetaldehyde MH^+ ion was observed, along with a small concomitant rise in sensitivity to the MH^+ .(H₂O) ion, presumably as the distribution of H₃O⁺ within the reagent ion pool was forced further towards cluster species. Ultimately, as the sample matrix relative humidity was increased to 100 %, it is expected that the degree of hydronium-water clustering would have been extensive, with a large fraction of total H₃O⁺ existing in di- and tri-hydrated forms. Consequently, little or no direct PTR would have occurred and ligand switching reactions would have resulted in acetaldehyde MH^+ .(H₂O)_n cluster ions with *n* of 2 and 3. Subsequent, CID induced within the ECC would have facilitated the conversion of MH^+ .(H₂O)_n to MH^+ .(H₂O)_{n-1}, hence the rise in sensitivity for the monohydrated acetaldehyde cluster shown in **Figure 5** at high relative humidities. As was the case with ammonia, acetone and hexan-2-one, the decrease in CIR-TOF-MS sensitivity to acetaldehyde with increasing energy, can be explained by the effects of fragmentation and reduced reactor residence time overtaking any sensitivity benefits gained from regeneration of H₃O⁺.

As pent-1-ene has low polarity (0.36 D) and a proton affinity less than that of the water dimer, it is unable to undergo reaction with hydrated hydronium *via* reactions (R5.2) – (R5.4). Consequently, as shown in **Figure 6**, sensitivity to pent-1-ene was found to be low at high humidities and low reactor energies, where hydrated hydronium dominates. As the reactor energy was increased, H_3O^+ .(H_2O)_n was converted back to H_3O^+ and sensitivity was observed to improve as pent-1-ene became able to accept a proton. However, above 100 Td molecular ion fragmentation became significant, causing sensitivity to decrease. This is clearly demonstrated in **Figure 6**, which shows measured sensitivity to the CH₃CH₂CH₂⁺ alkyl fragment ion increasing with *E/N* as the pent-1-ene molecular ion underwent dissociation. As

the reactor E/N was increased up to 140 Td, collisions became sufficiently violent to bring about extensive fragmentation of both the molecular MH⁺ ion and the alkyl product, and consequently sensitivity to both ions was observed to fall.



Figure 6: CIR-TOF-MS sensitivity maps for pent-1-ene and its allyl fragment ion. Colour scale legend gives sensitivity in ncps ppbV⁻¹.

5.4 Reactor Energy and Ion Fragmentation

The concepts of molecular ion fragmentation and collision-induced dissociation were first introduced in a qualitative sense in Chapter 2, since which they have been discussed in brief at various points. It was stated in Chapter 3 that fragmentation would result if a reaction or collision was sufficiently violent such that bond rearrangement and/or dissociation could be facilitated by the excess energy available. It was also discussed that a collision might be made suitably energetic, such that fragmentation results, by increasing the kinetic energy of the ion pool, and in doing so the energy of all ion-neutral collisions. This can be done by increasing the drift cell reactor *E/N* ratio. In Section 5.3.2 it was shown that instrument sensitivity for certain compounds can be improved by increasing the reactor *E/N* ratio and in doing so enhancing the abundance of H_3O^+ at the cost of H_3O^+ .(H_2O)_{*n*}. However, for such molecules a limit is reached when collisions become so energetic that fragmentation dominates and sensitivity to the molecular ion falls. The role of the CIR-TOF-MS reactor *E/N* ratio in ion fragmentation is further demonstrated in **Figure 7**, which shows the variation in measured ion signal of the fragment ions produced from hexanal, with increasing electric field strength at constant pressure.



Figure 7: Fragmentation of hexanal facilitated by increasing the reactor E/N ratio. F/MH^+ denotes fragment/molecular ion ratio.

Figure 7 shows that above an E/N of ~ 120 Td, fragmentation dominates the fate of the MH⁺ (m/z 101) and MH⁺(-H₂O) (m/z 83) hexanal product ions. Also, as was seen with pent-1-ene, as the reactor energy is increased further, fragmentation becomes excessive and the mass spectrum becomes populated with various low mass fragment ions (*e.g.* m/z 41 and 43, see Chapter 3). Production of such fragment ions at the cost of the molecular ion is undesirable, as they are often produced by various organic molecules, and hence sample speciation is lost.

It follows therefore that a balance must be struck when determining the magnitude of the drift cell reactor E/N ratio, to maximise hydronium abundance, minimise fragmentation and cluster formation, whilst offering a reasonable reactor residence time and therefore optimising instrument sensitivity. Clearly however, from the discussion presented above and from the findings of Chapters 3 and 4, the high PA and high polarity oxygenated and nitrated compounds will require a different regime for sensitivity optimisation than that required by the low PA and low polarity hydrocarbons. Therefore, ideally, a CIR-MS instrument operating with H_3O^+ reagent ions should be tuned to suit the target analyte.

Finally, it should be noted that the applied electric field and the fragmentation that it can induce, may also be employed to aid compound identification. For example, if two isobaric species exist in the same sample, the E/N of the system can be modulated to induce fragmentation. As the dissociation products are likely to be parent specific, compound identification becomes possible. Similarly, modulation of the electric field can be employed

to identify potential MH^+ .(H₂O) cluster ions, which may be significant contributors in particularly humid samples. Compound identification *via* fragmentation can also be facilitated with the modulation of the ECC *E/N*, as is discussed further in Section 5.5.

5.5 Role of the Exit Collision Cell

As was discussed above and in Chapter 2, the primary role of the ECC is to facilitate focusing of the ion beam into the transfer optics of the mass spectrometer. In order to do this, the electric field established between the electrodes of the ECC must be greater than the electric field elsewhere within the drift cell. As a consequence of this the *E/N* ratio within the ECC is usually higher than that of the central reactor. A major benefit of this is that the ECC energy can be sufficiently modulated to cause dissociation of the MH⁺–H₂O bond in all analyte-water adduct ions, thus eliminating them from detection and increasing the signal observed in the often more favourable MH^+ channel. This was seen for acetaldehyde in Section 5.3.2. However, the presence of an energy ramp at the base of the reactor does have a number of disadvantages. First of all, if the energy ramp is large enough to facilitate dissociation of the MH^+ -H₂O bond, it is also likely to be sufficient to bring about dissociation of a portion of all $H_{3}O^{+}$. $(H_{2}O)_{n}$ cluster species. Hence, as has already been discussed, the ECC may mask the true distribution of reagent ions within the reactor. Also, an increase in E/N at the base of the drift cell may cause fragmentation of the analyte (as discussed above and in Chapter 3). Therefore the ECC energy must be optimised to best facilitate focusing and cluster ion removal at the same time as maximising sensitivity through limiting the degree of fragmentation.

Figure 8 given below shows the variation of the $MH^+.(H_2O)/MH^+$ ratio for hexan-3-one, benzaldehyde, acetaldehyde, ethanol and 1,4-pentanedione, with ECC *E/N*. Also shown is the concomitant variation of fragment ion/MH⁺ ratio in each case. The experiments were conducted at a fixed reactor *E/N* of 100 Td (pressure 6 mbar), and the compounds were delivered in a dry nitrogen carrier gas (purity 99.9999 %). The data presented in **Figure 8** have been fitted with a two parameter power law curve to aid visualisation of the trends.

Each of the selected compounds possess suitably large dipole moments such that they will undergo ligand switching with hydrated hydronium *via* reaction (R5.4). Consequently, adduct ions of the form MH^+ .(H₂O) were observed in each of their mass spectra. **Figure 8** shows that in each case, the relative abundance of the MH^+ .(H₂O) ion water cluster with respect to

its MH⁺ counterpart decreased dramatically as the ECC *E/N* was increased from ~ 110 Td. Above ~ 160 Td contribution from the water cluster (adduct) ion was minimal, it having been dissociated by CID in the ECC. In moving from 110 to 160 Td the ion kinetic energies (*KE*_{ion}) of the acetaldehyde (the smallest test compound) and benzaldehyde (the largest test compound) MH⁺.(H₂O) complexes increased from ~ 0.36 – 0.89 eV and ~ 0.58 – 1.47 eV, respectively, with overall collision energies (*KE*_{cm} with respect to the buffer gas) increasing from ~ 0.14 to 0.31 eV.



Figure 8: Variation of the MH^+ . H_2O /molecular ion and fragment ion/molecular ion ratios with ECC *E/N* for a selection of test volatile organic compounds

Figure 8 also shows that for hexan-3-one, benzaldehyde and acetaldehyde, the increase in fragmentation with respect to the MH^+ ion is minimal up to ~ 160 Td. No significant fragmentation products were observed for ethanol or 2,4-pentanedione.

To better judge the effect of ECC *E/N* on compound fragmentation and instrument sensitivity, a series of calibrations were conducted over a range of collision cell field strengths. Acetaldehyde, acetone, isoprene and pent-1-ene were selected for the study, representing both polar and non-polar species, with a range of proton affinities. The compounds were delivered to the CIR-TOF-MS in a dry nitrogen carrier gas as detailed in Section 5.3.2, and experiments

were conducted at a fixed reactor E/N of 100 Td. Sensitivities were determined in the standard manner.

Figure 9 given below shows the variation of instrument sensitivity to the test compounds with ECC *E/N*. A decrease in sensitivity to the two hydrocarbons was observed as *E/N* was increased above ~ 150 Td. This decrease was matched by a corresponding increase in sensitivity to the allyl ion (m/z 41), a fragmentation product of both isoprene and pent-1-ene. This finding suggests that the ECC may cause significant fragmentation of such hydrocarbon compounds as they exit the reactor.



Figure 9: Variation of instrument sensitivity for a selection of volatile organic compounds with ECC E/N. For (a) isoprene and pentene sensitivities are on the left axis and for (b) acetaldehyde and acetone sensitivities are on the left axis. Suffix CL denote MH⁺.(H₂O) ion.

As is evident in **Figure 9**, sensitivity to the OVOCs was observed to increase with increasing ECC *E/N*. This result can be partially explained by the corresponding sensitivity decrease observed for the protonated acetaldehyde and acetone water cluster adducts (*i.e.* $MH^+.(H_2O)$). The data presented in **Figure 9** seems to suggest that a substantial fraction of the OVOCs exist as protonated-water adducts within the reactor. As these ions pass through the ECC, the energy ramp breaks the MH^+-H_2O bond, thus increasing the observed MH^+ signal. Over the 110 - 190 Td range, the ECC collision energy for the acetaldehyde-water and acetone-water adducts increases from ~ 0.14 - 0.41 eV.

It is clear from **Figure 9**, that in each case, the conversion of $MH^+ \rightarrow$ fragments, for the hydrocarbons, and $MH^+.(H_2O) \rightarrow MH^+$, for the OVOCs, is not fully a direct translation in terms of sensitivity, *i.e.* the conversion is not 1:1. This is most likely due to a focusing effect of the ECC electric field.

As was stated above, the electric fields of the central reactor and ECC can be employed to aid compound identification. An example of this is shown below in **Figure 10**, where two unknown compounds, 'a' and 'b' have been formed following the photooxidation of isoprene in a moist air matrix (see Chapter 7 for full experiment details). As the two compounds exhibit similar temporal behaviour and as the mass difference between them is 18 amu, it is possible that compound 'a' is a water adduct of protonated compound 'b'. To verify that this was the case the ECC E/N was increased from 150 to 190 Td; **Figure 10** shows the result. The energy increase applied caused an 88 % fall in the monohydrated hydronium signal (not shown) and an 82 % fall in the signal of compound 'a' is indeed likely to be its water cluster counterpart.



Figure 10: Time series plot of two unknown compounds formed following photooxidation of isoprene. ECC E/N ramp employed to help identify compound 'a' as a water cluster of compound 'b'.

The information gained from such energy modulation experiments may also be useful in providing bond dissociation energy limits for a range of compounds and processes. For instance, in the above example, to effect 82 % fragmentation of the water cluster adduct 'a', an additional KE_{cm} of ~ 0.16 eV was required.

5.6 An Overview of CIR-MS Sensitivity

So far it has been shown within this chapter that when operating in PTR mode the sensitivity response of the CIR-TOF-MS varies significantly with the nature of the target compound and

the instrument operating conditions. **Table 1** presents a comprehensive compilation of CIR-TOF-MS sensitivity calibrations for a variety of species. The compounds were calibrated at various collision energies and under both humid and dry conditions. These data can be used to further highlight and reinforce species specific trends across a wider range of compounds.

Compound (<i>m/z</i>) ^a	Calibration Method ^b	Relative Humidity ^c / %	<i>E/N /</i> Td (Reactor / ECC ^d)	Sensitivity / ncps ppbV ⁻¹
acetaldehyde (45)	1	0	$125(190)^1$	74.9
	1	0	$140(190)^{1}$	62.2
	1 / 2	0 / 50	90 $(150)^2$	105.1 / 86.9
	1 / 2	0 / 50	$90(190)^2$	130.5 / 107.3
	1/2	0 / 50	$120(150)^2$	88 9 / 68 4
	2	50	$120(170)^2$	81.7
	1 / 2	0 / 50	$140(140)^2$	68.1 / 57.0
propenal (57)	1	0	$125(190)^1$	67.2
	1	0	$140(190)^1$	57.5
	1	0	$90(150)^2$	117.0
	1	0	$90(190)^2$	107.0
	1	0	$120(150)^2$	91.1
	1	0	$140 (140)^2$	61.0
methacrolein (71)	2	0	$126(173)^2$	27.5
	2	50	$90(150)^2$	19.3
	2	50	$90(190)^2$	16.9
	2	50	$120(150)^2$	14.4
	2	50	$120(170)^2$	14.9
	2	50	$140(140)^2$	9.5
benzaldehyde (107)	1	0	$125(190)^{1}_{1}$	92.9
	1	0	$140(190)^{1}$	80.6
	1	0	$90(150)^2$	205.4
	1	0	$90(190)^2$	263.5
	1	0	$120(150)^2$	162.3
	1	0	$140(140)^2$	120.1
acetone (59)	1	0	$125(190)^{1}$	92.2
	1	0	$140(190)^{1}$	79.2
	2	50	$90(150)^2$	84.7
	1/2	0 / 50	$90(190)^2$	91.7 / 104.0
	2	50	$120(150)^2$	67.8
	$\frac{1}{2}$	50	$120(170)^2$	76.5
	$\frac{1}{2}$	50	$140(140)^2$	55.6
pentan-2-one (87)	1	0	$90(150)^2$	173.5
	1	0	$90(190)^2$	125.8
	1	0	$120(150)^2$	140.3
	1	0	$140(140)^2$	88.2
hexan-2-one (101)	2	0	$126(173)^2$	156.3
MVK (71)	1	0	$125(190)^{1}_{1}$	70.3
	1	0	$140(190)^{1}$	54.6
	1	0	$90(150)^2$	122.2
	1	0	$90(190)^2$	132.6
	1	0	$120(150)^{2}$	98.8
	1	0	$140(140)^2$	74.2
methanol (33)	1	0	$130(170)^{1}$	56.1
	2	0	$126(173)^2$	38.9

Table 1: Summary of CIR-TOF-MS sensitivities for a range of VOCs using PTR from hydronium

Compound (<i>m/z</i>) ^a	Calibration Method ^b	Relative Humidity ^c / %	<i>E/N /</i> Td (Reactor / ECC ^d)	Sensitivity / ncps ppbV ⁻¹
	2 2	50 0 / 50	$90 (150)^2 90 (190)^2$	37.3 32.4 / 46.1
	2	50	$120(150)^2$	29.4
	2	50	$120(170)^2$	35.6
	2	50	140 (140) ²	22.3
formic acid (47)	2	50	$90(150)^2$	5.1
	2/2	0 / 50	$90(190)^2$	33.8 / 5.2
	2	50	$120(150)^2$ 120(170)^2	9.5
	2	50 50	$120(1/0)^{-1}$	8./
	2	30	140 (140)	1.8
acetic acid (61)	2	50	$90(150)^2$	38.1
	$\frac{2}{2}$	0 / 50	$90(190)^2$ 120(150) ²	84.7 / 45.9
	2	50	120(150) $120(170)^2$	25.7
	$\frac{2}{2}$	50	120(170) $140(140)^2$	20.0 17.4
	2	50		10.0.50
c_{1s} - 3 -hexanol (55, 83)	1	0	$125(190)^{1}$	18.8, 59
	1	0	140 (190)	28.0, 22.1
propene (43)	1	0	$125(190)^{1}_{1}$	11.0
	1	0	$140(190)^{1}$	11.3
	1	0	$90(150)^2$	9.9
	1	0	90(190) 120(150) ²	20.5
	1	0	120(130) $140(140)^2$	12.3
. ((0)	1	°	125 (100)	22.5
isoprene (69)	1	0	$125(190)^{1}$ 140(190) ¹	32.7 14.5
	1	0 50	$90(150)^2$	14.3
	2	50	$90(190)^2$	15.0
	2	50	$120(150)^2$	24.6
	2	50	$120(170)^2$	24.6
	2	50	$140 (140)^2$	17.1
pentene (71)	2	0	$126(173)^2$	12.0
1 ()	2	50	$90(190)^2$	2.2
	2	50	$120(150)^2$	14.8
	2	50	$120(170)^2$	3.1
	2	50	$140(140)^2$	3.3
α-pinene (81, 137)	1	0	$125(190)^{1}$	12.8, 8.8
	1	0	$140(190)^{1}$	15.4, 11.3
	2	60	$90(190)^2$	28.4, 19.7
toluene (93)	1	0	$125(190)^{1}$	30.2
	1	0	$140(190)^1$	37.6
1.3.5-TMB (121)	3	50	$140(190)^1$	26.0
<i>y-y-</i> ()	1	0 / 50	$90(150)^2$	130.5 / 49.6
	1	0 / 50	$90(190)^2$	179.0 / 86.2
	1	0 / 50	$120(150)^2$	97.1 / 45.4
	1	0 / 50	$140 (140)^2$	81.4 / 37.8
naphthalene (129)	2	50	$90(150)^2$	17.4
	2	50	$90(190)^2$	20.9
	2	50	$120(150)^2$	19.4
	2	50	$120 (170)^2$ 140 (140) ²	23.7
	L	50	140 (140)	17.0
dimethyl sulphide (63)	2	0	$90(190)^2$	88.8

 dimethyl sulphide (63)
 2
 0
 90 (190)⁻¹
 88.8

 ^a Protonated analyte mass or fragment ion employed for calibration
 ^b Calibration method: 1 = certified gas standard, 2 = permeation tube, 3 = liquid injection into PTFE bag
 ^c Humidity of the sample matrix

 ^d Superscript 1 = calibration with ECC Mk.1, superscript 2 = calibration with ECC Mk.2

In general the calibration results presented in **Table 1** are in line with those findings previously discussed within this chapter. In brief, it appears that the CIR-TOF-MS sensitivity for most oxygenated VOCs exhibits a negative reactor energy dependence and in most cases positive ECC energy dependence. The reasons for this have already been discussed. Some of the larger OVOCs did show some degree of negative ECC energy dependence, as for such heavy compounds collisions are more violent and fragmentation more likely. As was shown for pent-1-ene, the CIR-TOF-MS sensitivity for most hydrocarbons increases with reactor E/N up to a (presumably) compound specific threshold, before falling off again as fragmentation begins to dominate and residence/reaction time decreases. The CIR-TOF-MS sensitivity to most compounds showed at least some degree of fall off with increasing humidity.

Finally, to conclude this section regarding sensitivity, a short investigation is made into the ability of the CIR-TOF-MS technique to quantify VOCs using ionisation reagents other than hydronium. It was shown within Chapter 3 that a number of different reagent ions can be employed within the CIR-TOF-MS instrument to ionise a host of VOCs. Here a standard calibration experiment was conducted using one of those species, NO⁺ rather than H₃O⁺, as the primary reagent ion. The experiment was conducted at reactor and ECC *E/N* values of 110 and 170 Td, respectively, and the findings are presented in **Table 2**.

Compound	Data Ion ^a	m/z	Sensitivity / ncps ppbV ⁻¹
ammonia	M^+	17	0.46
allyl ion ^b	$\mathrm{CH_2CHCH_2}^+$	41	2.04
acetaldehyde	$M^{+} / M(-H)^{+}$	44 / 43	14.34 / 28.04 ^c
acetone	$M^+ / M.NO^+$	58 / 88	0.08 / 0.09
dimethyl sulfide	M^+	62	23.04
isoprene	M^+	68	8.51
pent-1-ene	$M^+ / M.NO^+$	70 / 100	0.31 / 18.7

Table 2: NO⁺ CIR-MS sensitivity to a selection of atmospherically significant VOCs at E/N = 90 / 190 Td.

^a Ion from which sensitivity was extracted.

^b Fragment ion of isoprene and pent-1-ene.

^c Potential contamination from other species.

The sensitivities determined for reactions of NO⁺ with dimethyl sulphide, isoprene and pent-1-ene were entirely comparable to the equivalent values achieved using H₃O⁺, and were even greater in the case of pent-1-ene (for the adduct ion). The favourable sensitivities obtained here for these compounds most likely results from their reaction efficiencies and rate constants with NO⁺ being similar to their equivalent values with H₃O⁺. Sensitivity for acetaldehyde using NO⁺ as the primary reagent ion was reasonably high compared to that of certain other analytes, however, it was somewhat smaller than with H₃O⁺. This disparity also results from the relative magnitudes of the rate constants involved; acetaldehyde possesses a lower reaction rate constant with NO⁺ than with H₃O⁺ (*i.e.* 0.6 ×10⁻⁹ versus 3.7×10^{-9} cm⁻³ s⁻¹ (Spanel and Smith, 1997)). The sensitivities obtained for acetaldehyde, dimethyl sulphide, isoprene and pent-1-ene with NO⁺ are sufficiently high to make its use as an alternative ionisation reagent entirely viable for quantitative monitoring of such species.

5.7 Statistical Performance of CIR-TOF-MS

5.7.1 Linearity of Response

For satisfactory and reliable quantitative analysis, it is vital that the signal response of an instrument be linear over the full concentration range at which compounds are to be measured. It was shown in Chapter 4 that the signal response of the CIR-TOF-MS instrument to each of the compounds investigated was linear over a concentration range of ~ 1 – 20 ppbV. CIR-TOF-MS linearity was also previously established in a preliminary publication for the compound H₂S over the range 5 – 50 ppmV (Blake *et al.*, 2004). The CIR-TOF-MS signal response was found to be linear for the CI reagents H₃O⁺ and NO⁺ in each of the sensitivity calibrations reported within this thesis. Also the CIR-TOF-MS signal response has been verified as linear for the CI reagents NH₄⁺ and O₂⁺⁺ in a recent publication (Blake *et al.*, 2006). For all analytes investigated thus far, the signal *versus* concentration correlation coefficients (r²) are typically \geq 0.95. As an example, **Figure 11** displays calibration lines obtained for methanol and 0.9996 for methacrolein, over the concentration ranges 4 – 90 and 25 – 600 ppbV, respectively.



Figure 11: Calibration lines for (a) methanol and (b) methacrolein showing response linearity. Experiment conducted under dry conditions with a reactor E/N of 126 Td. Error limits determined from the relative standard deviation within the data.

5.7.2 CIR-TOF-MS Precision, Signal-to-Noise and Detection Limits

The concept of instrument *precision* was introduced in Chapter 4; it was defined as the relative standard deviation (RSD) of a given data set, *i.e.* the ratio of the standard error of the mean to the specific mean, expressed as a percentage. The precision value provides information about the ability of an instrument to reproduce a given measurement. In order to provide a more detailed qualification of CIR-TOF-MS instrument precision and to characterise its variation with sample concentration, a series of calibration style experiments were conducted for a range of compounds. Calibration for each compound comprised signal measurements at twelve different concentrations, with each measurement comprising twenty separate one-minute scans. The one-minute RSD precision value was calculated for each concentration measurement. **Table 3** and **Figure 12** show the findings.

Compound	Concentration Range / ppbV	Precision Range / %	
acetaldehyde	4 - 87	11.6 - 3.8	
methacrolein	27 – 595	13.7 - 3.7	
hexan-2-one	16 - 360	6.5 - 1.8	
methanol	4 - 87	11.9 – 3.7	
pent-1-ene	10 - 228	29.6 - 7.5	

Table 3: Variation of instrument precision with concentration for a selection of compounds



Figure 12: Variation of CIR-MS instrument precision for methanol and acetaldehyde, with sample concentration.

The relationship between measurement precision and sample concentration is shown for methanol and acetaldehyde in **Figure 12**; the same non-linear behaviour was observed for each of the compounds. In each case the trend in the precision appears to obey a power law relationship (*i.e.* $y = Ax^b$), with RSD increasing as concentration falls. This behaviour is related to the signal-to-noise statistics of measurement, *i.e.* as concentration falls, the random instrumental noise will begin to have a greater impact on the measured signal.

Instrumental 'noise' is essentially defined as any unwanted signal measured by an instrument. The noise superimposed upon a measured signal is composed of three separate factors: *fundamental noise*, that which results from the electrical components of an instrument; *excess noise*, that which originates from the function of internal components of an instrument; and *interference*, noise that results from other external factors (Wayne, 1995). Instrumental noise is generally a non-systematic phenomenon, with events and their magnitude both random factors within some larger bounds. Clearly then, the random superposition of unwanted signal on top of a desired signal, will cause problems with respect to meaningful data extraction and in some cases may severely compromise measuring capability.

As the strength of a given signal becomes progressively weaker, its magnitude approaches that of the background noise of the measuring instrument. Eventually the measured signal will become indiscernible from that of the average baseline. When it no longer becomes possible to discriminate between measured signal and baseline noise, the detection limit of the instrument has been surpassed. A useful method of defining the minimal detectable signal of an instrument involves the use of the *signal-to-noise ratio* (*S/N*). The *S/N* ratio is defined as the average measured signal divided by the root mean square (rms) of the noise, *i.e.*:

$$\frac{S}{N} = \frac{S_{av}}{\left(\overline{S_n^2}\right)^{1/2}}$$
(E5.4)

In equation (E5.4), S_{av} = the average ion signal in a given mass channel taken over the entire measuring period and S_n = the ion signal (in the stated mass channel) obtained during the n^{th} measurement, hence $(\overline{S_n^2})^{1/2}$ = the root-mean-square noise (Wayne, 1995).

The detection limit of the CIR-TOF-MS for a given compound can be determined through calculation of the signal-to-noise ratio of each measurement of that target compound at a number of concentrations over a wide mixing ratio range. The signal-to-noise ratios achieved for the measurement of acetaldehyde at various concentrations are shown in Figure 13. The data presented demonstrates that, as with precision, for the CIR-TOF-MS there exists a power law relationship between S/N ratio and measured concentration. The limit of detection can be determined by extrapolating the curve backwards to a point where the S/N ratio is such that the signal is considered indiscernible. Generally, the integration time dependent detection limit for a given compound in a PTR-MS type instrument is defined as the point at which the S/N ratio reaches a value of 2:1 (Hanson et al., 2003). In the given example, acetaldehyde has a 60 s detection limit of 6.3 ppbV at S/N = 2:1. Table 4 contains further examples of 1minute detection limits for a range of VOCs. Detection limits vary markedly between the compounds and, naturally enough, are best for those which exhibit the greatest sensitivity. It should be noted however, that variation of the system E/N will change the compound sensitivity and hence the detection limit. For example, the pent-1-ene detection limit could easily be improved by changing the reactor E/N to 110 Td, under which conditions pent-1-ene sensitivity is optimum (see section 5.2.2).



Figure 13: Signal/noise ratio versus concentration for the OVOC acetaldehyde. Data fitted with a power law.

Compound	Sensitivity ^a / ncps ppbV ⁻¹	1-Min. Detection Limit / ppbV min ⁻¹	10-Min. Detection Limit ^b / ppbV min ⁻¹
acetaldehyde	132.5	6.3	0.5
methacrolein	27.5	25.5	1.1
hexan-2-one	156.3	4.2	0.4
methanol	38.9	15.0	0.9
pent-1-ene	12.0	58.5	9.8

Table 4: One-minute detection limit for a number of common atmospheric VOCs

^a At a reactor *E/N* of 126 Td.

^b 10-minute detection limits calculated using the $M^{1/2}$ rule.

The detection limit of an instrument can be improved through signal averaging. When two or more signals are summed together, the rate of increase of desired signal will be greater than that of the noise signal. Indeed, the *S/N* ratio will increase by a factor equal to the square root of the number of measurements summed together to comprise the final signal (*i.e.* × $M^{1/2}$) (Wayne, 1995). Generally, CIR-TOF-MS measurements are recorded on the 1-minute time scale and are subsequently summed into 10 minutes data sets. Consequently, using the $M^{1/2}$ rule, detection limits for the test compounds fall by a factor of ~ 10 – 20 following 10-minute integration (see **Table 4**).

5.8 Application of CIR-TOF-MS for *in situ* Tropospheric Measurements: the Leicester Air Monitoring Project (LAMP)

5.8.1 Introduction and Experimental

With a sound base of characterisation and validation, the CIR-TOF-MS was applied to the monitoring of VOCs in the 'real' urban atmosphere during the Leicester Air Monitoring Project (LAMP). The LAMP campaign would constitute a thorough test of the CIR-TOF-MS technique, which had previously been employed primarily under controlled laboratory

conditions. LAMP was based at the University of Leicester and was run for twelve weeks between 1st July and 16th September, 2007. The primary goal of LAMP was to determine, in detail the state of local air quality through a combination of measurements provided by a variety of different techniques. The various instruments employed during the campaign included NO_x/NO_y and ozone monitors, a peroxy radical chemical amplifier (PERCA, for Σ HO₂+RO₂), spectral radiometers and broad-band cavity enhanced and multi-axis differential absorption spectrometers (BBCES and MAX-DOAS, for NO₂). To support these instruments standard meteorology and off-line aerosol composition measurements were also made.

During LAMP the CIR-TOF-MS was deployed at two separate sites on the University of Leicester campus: (a) at the Space Research Centre, situated close to a ~ 0.28 km² public park and (b) at the Department of Chemistry, a city centre road-side location. The data reported here were recorded at site (b). At site (b) the CIR-TOF-MS was housed in an air conditioned laboratory (21 °C) and the analyte air was delivered to the instrument through a 20 m long, pumped ¹/₄" Teflon sample line. Sample and reagent gas flows into the instrument were set to 230 and 30 sccm, respectively, to give a reactor pressure of 6.1 mbar. Hydronium reagent ions were generated in the standard manner. As measurements of both oxygenated and nonoxygenated compounds were desired, the reactor and ECC (Mk.2) were operated at E/N ratios of 110 and 170 Td, respectively. These energy settings represent a compromise between the low reactor, high ECC energies favoured by OVOCs and the high reactor, low ECC energies favoured by hydrocarbons. The drift cell was held at a constant temperature of 40 °C throughout the exercise. 'Background' scans were recorded at regular intervals by diverting the analyte air through a hydrocarbon trap (Alltech, UK) before measurement. Mass spectra were recorded for an averaging period of 60 s and over the mass range 0 - 200 Da. Post experiment integration was performed to give 10 minute averaged data. Standard calibration procedures (detailed above and in Chapter 4) were employed for sensitivity determination, with calibrant gases produced in the usual manner from permeation tubes held in a gas dilution system.

5.8.2 Results and Discussion

Figure 14 summarises some key local meteorology parameters measured over the period $5^{\text{th}} - 16^{\text{th}}$ September, during which the CIR-TOF-MS was based at site (b). Overall the weather was fair with no rainfall, the average pressures and relative humidities were 1016 mbar and 45 %, respectively. During the day, temperatures typically reached maxima of ~ 25 - 30 °C, whereas at night lows of ~ 10 °C were experienced.



Figure 14: Temperature (red line), relative humidity (green line), pressure (pink line) and rainfall (blue line) from $5^{\text{th}} - 16^{\text{th}}$ September (pressure measurement off-line during 09/10/2007).

Eleven different VOCs and three species markers were observed in the CIR-TOF-MS mass spectrum on a daily basis at site (b). These compounds are listed in **Table 5** and their temporal profiles are given in **Figure 15**. The species of VOC measured were typical for a modern city atmosphere (Fortner *et al.*, 2008), and the maximum concentrations recorded were within the expected bounds for a moderately sized UK city (Rivett *et al.*, 2003).

Compound	m/z	Max. Conc. / ppbV	Compound	m/z	Max. Conc. / ppbV
ammonia	18	5 – 25	acetic acid	61	4 – 8
methanol	33	4 – 14	methacrolein + MVK	71	1 – 1.5
allyl ion	41	$50 - 200^{a}$	me. glyoxal	73	5 - 35
acylium ion ^b	43	$100 - 250^{a}$	benzene ^e	79	1 – 3
acetaldehyde	45	1.5 – 2	toluene	93	3 – 6
acylium ion ^c	57	$100 - 200^{a}$	C2 benzenes (inc. xylene ^e)	107	3 – 10
acetone ^d	59	10 – 25	C3 benzenes (inc. trimethyl benzene ^e)	121	2-4

 Table 5: Significant compounds measured at site (b) during LAMP and approximate maximum measured concentrations

^a Signal in ncps.

^b Acylium ion = CH_2CHO^+ , although possible contributions from the *n*-propyl alkyl ion ($CH_3CH_2CH_2^+$).

^c Acylium ion = $CH_2CH_2CHO^+$, although possible contributions from the 1-butyl alkyl ion ($CH_3CH_2CH_2CH_2^+$).

^d Possible contributions from propanal and glyoxal.

^e Concentration determined using toluene sensitivity.



Figure 15: Temporal evolution of a selection of VOCs measured by CIR-TOF-MS during LAMP

Over the observation period all of the measured compounds generally followed some repetitive diurnal pattern, as exemplified in **Figure 15** for a selection of analytes. The aromatic species, *i.e.* benzene, toluene, the xylenes and trimethylbenzenes, appeared

simultaneously on weekday mornings between ~ 06:00 - 09:00 hrs. After their early appearance, the aromatic signals decayed to relatively low levels which were maintained throughout the day, until a second minor peak occurred between late afternoon and early evening. The aromatic signature was considerably weaker at weekends (*i.e.* 8th, 9th, 15th and 16th) than during week days. During the morning 'plumes' the abundance of C2 and C3 benzenes increased with respect to toluene, whereas the benzene-to-toluene ratio remained largely unchanged. Considering these findings and the known atmospheric lifetimes of such molecules (*i.e.* for reaction with OH, 9.4 days, 1.9 days, 5.9 hours and 4.3 hours for benzene, toluene, *m*-xylene and 1,2,4-trimethylbenzne, respectively (Atkinson, 2000)), it would appear that the aromatic VOCs measured had their origin in local traffic emissions, with the early morning and afternoon commuter 'rush hours' accounting for the enhanced weekday signals.

The highest measured aromatic signals showed some level of anti-correlation with temperature, which highlights the influence of the low nocturnal boundary layer 'trapping' such primary emissions close to the surface during the early morning period, indeed those mornings with highest VOC signals were amongst the coldest experienced during the campaign (see **Figure 15(e)**). As each morning evolved, the concentrations of the aromatic compounds were observed to fall, presumably due to dilution effects, which resulted from rising temperatures lifting the boundary layer height (Houghton, 2002). The fall in concentration of the aromatic species observed during the morning period would also have been partially due to the photochemistry which became initiated as the levels of actinic flux increased.

The observed early morning rise in concentration of the aromatic species was generally matched by a corresponding increase in the signals measured at m/z 41, 43 and 57, which correspond to the allyl, acylium and alkyl ions. As was shown in Chapter 3, these daughter ions result from fragmentation of a number of VOCs, including various hydrocarbons and carbonyls. The early morning signals measured for m/z 41, 43 and 57 most likely resulted from the primary uncombusted hydrocarbon species which are emitted alongside the aromatics from traffic sources. The allyl, acylium and alkyl signals also presented a second day time peak, which was generally coincident with the second peak in the aromatic signal; however, on certain days it began around midday prior to the second peak of the aromatics. The timing of the secondary peaks in m/z 41, 43 and 57 suggests that they may result from the presence of both primary and secondary VOC pollutants in the Leicester atmosphere. The measured signals of acetaldehyde and acetic acid were generally similar in diurnal behaviour

to those of the allyl, acylium and alkyl ions, and hence similar conclusions can be drawn regarding their origin, *i.e.* both acetaldehyde and acetic acid have some primary sources, but they may also be synthesised by photochemistry during the day. It should be noted here that a number of other compounds are able to make minor contributions to the m/z 61 channel (which has been attributed to acetic acid), and hence true acetic acid concentrations may have been lower than those reported here.

Finally, methanol, acetone and ammonia showed less evidence for primary emission from urban traffic. Both methanol and acetone generally appeared after the aromatics and were observed to rise to a concentration peak roughly between midday and early evening. The methanol and acetone signals are most likely secondary in nature, such compounds being formed *via* the oxidation of primary VOCs. As with the aromatics, the measured signals for all other VOCs were smaller during weekends.

None of the signals observed during the discussed period appear to correlate with wind speed and direction data; indeed wind speed was generally minimal throughout. Hence it would appear that all primary 'plume events' observed, resulted from local emissions rather than those brought in from outside of the vicinity. Moreover, rather than transporting VOCs to the area, findings suggest that certain wind events induce boundary layer mixing sufficient to facilitate dilution of the VOC loading of the local area, as exemplified for acetaldehyde in **Figure 16**.



Figure 16: Diurnal variation of acetaldehyde as measured at site (b) on 13th September 2007. Upper panel shows the concomitant wind speed and direction.

5.8.3 Conclusions for LAMP

During the LAMP campaign the CIR-TOF-MS was able to measure a variety of common atmospheric VOCs down to the ppbV level with good temporal resolution. Moreover, it was found that such measurements are sufficient to help identify the major sources of VOC pollution on the local scale. Here it was found that the dominant (measurable) primary VOCs present in the Leicester city centre boundary layer during the observation period were various aromatic compounds, which were most likely emitted from traffic sources. Common secondary OVOC oxidation products were also identified, including methanol, acetone, acetaldehyde and acetic acid. During the working week, the temporal profiles of methanol and acetone generally lagged those that pertained to primary emissions. Unsurprisingly, all measured VOC signals were stronger during week days than at the weekend. In essence the Leicester Air Monitoring Project has proven that CIR-TOF-MS can be used for the measurement and monitoring of VOCs (with rapidly fluctuating concentrations) in the contemporary atmosphere. The information provided by CIR-TOF-MS can be employed for the interpretation of atmospheric organic gas phase composition and behaviour.

5.9 Conclusions

This chapter has brought together a host of work conducted to characterise the CIR-TOF-MS. The findings that have been presented have proved critical in advancing our understanding of the processes involved in the detection of trace VOCs using the CIR-TOF-MS technique, and as such will be highly useful for all users within the field. The characterisation work was undertaken primarily on ionisation using the hydronium ion, as it proved by far to be the most successful ioniser during initial testing. The work presented here introduced hydrated hydronium as an ionisation reagent and its impact within the CIR-TOF-MS technique has been assessed.

Within this chapter extensive investigations were conducted to evaluate the sensitivity of the CIR-TOF-MS technique to a variety of different compounds utilising H_3O^+ as the primary reagent ion. Species specific trends in the variation of sensitivity as a function of reactor energy and sample humidity have been identified, mapped and justified. Also, the role of the exit/collision cell was investigated and its impact upon compound sensitivity and observed hydronium levels has been determined. Results obtained from ion fragmentation studies within both the reactor and the ECC were also presented. The statistical performance of the

CIR-TOF-MS was assessed here, the linearity of response was confirmed and detection limits were established.

The findings obtained from the detailed characterisation described within this chapter, indicate that CIR-TOF-MS operating conditions should be tuned to best suit the target analyte. For example, from the data presented it appears that for optimum sensitivity to hydrocarbons a reactor E/N of ~ 100 – 110 Td is desirable, coupled to a low ECC E/N of ~ 150 Td. In order to increase sensitivity to polar compounds, such as OVOCs and NVOCs, the reactor should be operated at an E/N of ~ 80 – 90 Td, with a high ECC E/N of ~ 170 – 190 Td. As both polar and non-polar compounds are likely to be found in any given atmospheric analyte matrix, a compromise in operating conditions must be reached in order to obtain the most information.

Chapter 6

Gas Phase Precursors to Anthropogenic Secondary Organic Aerosol: Detailed Observations of 1,3,5-trimethylbenzene Photooxidation

6.1 Summary

A series of photooxidation experiments were conducted in an atmospheric simulation chamber in order to investigate the oxidation mechanisms and secondary organic aerosol (SOA) formation potential of the model anthropogenic gas phase precursor, 1,3,5-Alongside specific aerosol measurements, comprehensive gas phase trimethylbenzene. measurements, primarily by Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS), were carried out to provide detailed insight into the composition and behaviour of the organic components of the gas phase matrix during SOA formation. An array of gas phase organic compounds was observed during the oxidation process, including several previously unmeasured primary bicyclic compounds possessing various functional groups. Analysis of results obtained during this study implies that these oxygen-bridged bicyclic species, along with a series of ring opening products and organic acids contribute to SOA growth. The effect of varying the VOC/NO_x ratio on SOA formation was explored, as was the effect of acid seeding. It was found that low NO_x conditions favour more rapid aerosol formation and a higher aerosol yield, a result that implies a role for organic peroxides in the nucleation process and subsequent SOA growth.

6.2 Introduction

Secondary organic aerosol (SOA) is formed in the atmosphere from the oxidation products of certain biogenic and anthropogenic volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts Jr., 2000). One important class of such compounds known to be precursors to SOA are

aromatic hydrocarbons (Stern *et al.*, 1987; Odum *et al.*, 1997). Possessing complex and extensive atmospheric reaction pathways, aromatic VOCs (AVOCs) have the ability to yield a wide array of secondary oxygenated and nitrated volatile, semi-volatile and non-volatile organic products which contain a multitude of different functional groups (Atkinson, 2000; Hamilton *et al.*, 2003; Johnson *et al.*, 2005; Sax *et al.*, 2005; Bloss *et al.*, 2005b).

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Released principally from automobile exhaust emissions, industrial scale combustion and the evaporation of fuels and solvents (Friedrich and Obermeier, 1999), AVOCs make up as much as 40 % of the total mass of anthropogenic hydrocarbon emissions in the city environment (Smith *et al.*, 1999). On the global scale total aromatic emissions are of the order 15.8 Tg y⁻¹ (Tsigaridis and Kanakidou, 2003), which account for ~ 15 % of the annual anthropogenic non-methane hydrocarbon (NMHC) budget (Bloss *et al.*, 2005a). As well as constituting precursors to SOA production, AVOCs generally have high photochemical ozone creation potentials and hence contribute significantly towards tropospheric ozone pollution (Calvert *et al.*, 2002; Derwent *et al.*, 2003; Derwent *et al.*, 2007a; Derwent *et al.*, 2007b).

As was discussed in Chapter 1, SOA mass comprises a major fraction of total atmospheric particulate matter, the presence of which within the atmosphere has a range of wide reaching negative effects. As highlighted in recent reviews (*e.g.* (Seinfeld and Pankow, 2003; Kanakidou *et al.*, 2005; Holmes, 2007)), despite its crucial impact upon the Earth-atmosphere system, there currently remains a certain lack of understanding regarding the physical and chemical properties of SOA, its chemical composition and crucially the atmospheric processes by which it is formed.

Over the last decade much research and many state of the art techniques have been applied to the critical problem of determining SOA chemical composition, with off-line GC-MS analysis of filter samples often providing the foundation. However, such studies have supplied limited molecular level classification, with generally no more than 30 % of the total SOA mass being identified (*e.g.* (Forstner *et al.*, 1997; Kleindienst *et al.*, 1999; Cocker III *et al.*, 2001; Hamilton *et al.*, 2003; Edney *et al.*, 2005; Surratt *et al.*, 2006)).

A series of recent discoveries have allowed significant advancement to be made in our understanding of SOA composition and the role of relatively low molecular mass species in aerosol growth. It has been proposed that between 20 and 50 % of SOA mass could be comprised of large multi-functional macromolecular compounds known as 'humic-like substances' (HULIS) (Havers *et al.*, 1998), which would go undetected using standard GC-

MS techniques. Research has suggested that such compounds are secondary in nature, being formed by heterogeneous polymerisation/oligomerisation reactions in the aerosol. For example, Jang and Kamens (Jang and Kamens, 2001) witnessed an increase in SOA yield when various gas phase aldehyde compounds were injected into a synthetic air matrix impregnated with acidic seed particles. The authors attribute the increase in SOA mass to heterogeneous hydration and polymerisation reactions of low molecular mass aldehydes following their transfer from the gas phase. Their findings also indicated that hemiacetal/acetal formation is also an important contributing pathway to increased SOA yields when alcohols were also present.

Numerous investigations have since confirmed the existence of polymeric/oligomeric compounds in various SOA systems of both anthropogenic (Gross *et al.*, 2006) and biogenic (Surratt *et al.*, 2006) origin, both in simulation chamber studies (Baltensperger *et al.*, 2005) and in the 'real' atmosphere (Kalberer *et al.*, 2006), with molecular masses as large as 1,600 Da (Gao *et al.*, 2004). One such study by Kalberer *et al.* demonstrated that as much as 50 % of the SOA mass formed during the photooxidation of 1,3,5-trimethylbenzene was composed of polymers (Kalberer *et al.*, 2004). The authors proposed that the polymers, which were detected with masses as high as 1000 Da, were formed primarily through acetal polymerisation involving the known trimethylbenzene photooxidation product methyl glyoxal, in the presence of water.

With a large portion of current research into SOA formation geared towards investigation of the aerosol phase, there exists a distinct lack of detailed understanding of the concomitant gas phase organic components of the system. Indeed limited work has been conducted to help illuminate the actual mechanisms of SOA formation from the view point of the gas phase. Recently, research has shown that the SOA forming capacity of aromatic systems is strongly related to the gas phase [NO_x], with greater SOA yields obtained under low NO_x conditions (Izumi *et al.*, 1988; Stroud *et al.*, 2004; Song *et al.*, 2005; Ng *et al.*, 2007). Conclusions drawn from such work infer an important role for gas phase organic peroxides in initiating the formation of SOA (Johnson *et al.*, 2004), but no direct evidence is available to support this.

The present study begins to address these issues by presenting findings from a series of comprehensive photooxidation experiments conducted in an atmospheric simulation chamber. The main aim of the study was to monitor, in detail and with good temporal resolution, the complex array of gaseous organic oxidation products derived from known SOA precursors, and in doing so elucidate underlying degradation mechanisms and identify potential species

contributing to incipient aerosol formation and growth. In this instance the common, but less well studied anthropogenic AVOC, 1,3,5-trimethylbenzene (TMB) was chosen as a model anthropogenic SOA precursor. The effect of variation of the initial VOC/NO_x ratio on SOA formation was explored, as was the potential role of acid-catalysed heterogeneous chemistry. As well as presenting information that provides insight into the mechanisms of TMB oxidation and the identity of SOA forming species, this work presents the first measurements of a set of previously undetected high mass oxygen-bridged bicyclic compounds, which are formed during aromatic oxidation.

Finally, the gas phase measurements presented here are compared with the output of a box model employing data extracted from the Master Chemical Mechanism (MCMv3.1; http://mcm.leeds.ac.uk/MCM). The evaluation of the MCM *via* the comparison of model simulations with chamber measurements, conducted under various controlled and well defined conditions is crucial for advancement to be made in the understanding of atmospheric chemistry. Furthermore, results obtained from concomitant theoretical and experimental work can provide important information to drive the direction of future science. In the context of this thesis, the comparison of modelled and measured data helps to support current theories regarding the atmospheric oxidation of aromatic compounds, as well as providing further insight into the identity of potential SOA forming species.

6.3 Experimental

6.3.1 The Paul Scherrer Institut Aerosol Chamber

Experiments were carried out at the Paul Scherrer Institut aerosol chamber facility (Ch.), a diagram of which is given in **Figure 1**. The chamber comprises a single-lined collapsible bag constructed from DuPont[®] fluorinated ethylene propylene (FEP) film, with a wall thickness of 125 µm and a volume of 27 m³ (3 x 3 x 3 m³). The chamber surface area to volume ratio (2 m⁻¹) is relatively small when compared to most environment chambers, allowing wall effects to be minimised. The chamber bag is held by a large metal frame inside a temperature-controlled wooden housing, which was maintained at 20 °C (\pm 1 °C) during all experiments. Four 4 kW xenon arc lamps, deployed at various points inside the housing were employed to simulate the solar spectrum. Spectral radiometry measurements indicate that in the λ range 290 – 800 nm, > 90 % of the incident light is transmitted to the interior of the bag. Spectral filtering is employed to ensure the removal of radiation of λ < 290 nm (Paulsen *et al.*, 2005).

The chamber sample gas comprised purified ambient air, which was produced by a clean air

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generator (AADCO Instruments Inc., USA). Chamber humidification was facilitated by bubbling the bulk matrix gas through a heated glass vessel containing high purity deionised water (15 M Ω) prior to the injection of other gases and the precursor VOC. The chamber humidity was typically near 50 % during each experiment.

Delivery of the VOC SOA precursor to the chamber took place *via* syringe injection of the liquid compound into a heated injector port, which facilitated compound volatilisation before entry into the bag. A period of 30 minutes was allowed for mixing to create a homogeneous sample matrix before any measurements were made.



Figure 1: Diagram of the Paul Scherrer Institut aerosol chamber (Paulsen et al., 2005)

In order to remove any potential organic impurities from the chamber and hence to eliminate unwanted artefacts from the data (in the form of SOA formed from species other than the TMB), the chamber bag was scrubbed with ozone (2 - 7 ppmV) for 5 hours, before being flushed thoroughly with purified ambient air for approximately 30 hours prior to each experiment.

On-line measurements of chamber nitric oxide (NO) and NO_x concentrations were made throughout each experiment using a Monitor Labs 9841A NO_x analyser (for NO_x concentrations: 50 - 2000 ppbV) and a Thermo Environmental Instruments 42C trace level NO_x photolytic converter (for NO_x concentrations: 0 - 200 ppbV). Ozone measurements were also conducted in *real-time* using an ozone analyser (Environics model S300). The aerosol phase was monitored using two TSI (3025 and 3022A) condensation particle counters (CPC, size range: particle diameter (D_p) \geq 3 nm) and a Scanning Mobility Particle Sizer (SMPS, size range: $15 \le D_p \le 690$ nm), providing information on the total number density of particles in the chamber along with particle geometric mean diameter and volume concentration (see (Dommen *et al.*, 2006) for further instrument details).

6.3.2 Experiment Design

In order to explore the effect of NO_x on the TMB-SOA system, experiments were conducted with various initial VOC/NO_x ratios. For the first part of the study chamber experiments were conducted with high concentrations of VOC (> 500 ppbV) and NO_x (> 250 ppbV). For these 'high NO_x' experiments nitric oxide and nitrogen dioxide (NO₂) gases (Air Liquide, Ch., grade N6.0) were added to the chamber *via* an inlet injection system prior to introduction of the VOC. Experiments with initial VOC/NO_x ratios of approximately 2:1, 2:1 (with NO only) and 1:2 were carried out during the high NO_x part of the study.

As well as conducting high NO_x style experiments, with input of all gases to the chamber before initiation of the photochemistry, two 'low NO_x' concentration experiments were conducted in order to simulate more realistic atmospheric conditions. In these experiments a constant low level source of nitrous acid (HONO) was used to supply NO to the system in place of NO and NO₂ gases. HONO was produced by the reaction of a sodium nitrite solution with sulphuric acid in a flow system. A nitrogen carrier gas was passed through the mixture continuously in order to purge nitrous acid vapour out and into the chamber bag (Taira and Yukio, 1990). This process provided a constant HONO mixing ratio of roughly 10 ppbV throughout each low NO_x experiment. Consequently, the low concentration experiments had high initial VOC/NO_x ratios of ~ 16:1. In order to provide a brief exploration into the effect of an inorganic seed, for experiment 7 (see below), 400 pptV sulphur dioxide (SO₂) gas was added to the chamber in order to generate sulfuric acid (H₂SO₄) particles. **Table 1** lists the specific starting conditions used for each experiment performed.

Exp. No.	Initial [VOC] / ppbV	Initial [NO] / ppbV	Initial [NO ₂] / ppbV	VOC/NO _x Ratio	Relative Humidity / %	Exp. Duration ¹ / Mins.	Peak OH ² / pptV	Average [OH] ² / pptV	CIR-MS Conditions ³ (E/N)/Td
-	560	129	141	2.07	52	539	0.06	0.04	120/170
7	1,180	535	0	2.21	49	521	0.04	0.02	120/170
ю	143	134	129	0.54	48	596	0.08	0.06	140/140
4	554	135	129	2.1	52	521	0.04	0.02	120/150
5	151	Continuous F	HONO input ⁴	~ 15.10	62	488	0.06	0.05	90/150
9	597	135	130	2.25	53	462	0.04	0.03	90/190
٢	166	Continuous H	HONO input ⁴	$\sim\!16.60$	50	549	0.08	0.06	90/190

⁴ HONO injected continuously throughout experiment, chamber concentration ~ 10 ppbV

Table 1: Summary of the major gas phase parameters for experiments 1 - 7 along with specific CIR-TOF-MS conditions employed for VOC monitoring

6.3.3 VOC/OVOC Measurement with Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry

The gas phase organic compounds within the chamber were monitored using Chemical Ionisation Reaction Time-of-Flight Mass Spectrometery (CIR-TOF-MS). TOF-MS comes into its own when dealing with such complex mixtures since the entire spectrum is captured in any one instant. Furthermore, the technique is not constrained by upper mass limits and its standard resolution is usually far higher than more conventional quadrupole mass spectrometers. Therefore, important advantages of CIR-TOF-MS in this instance include the ability to detect a comprehensive set of organic compounds, including oxygenated VOCs (OVOCs) and species of relatively high molecular mass, and the ability to assist compound identification through accurate (*i.e.* exact) mass measurements.

The CIR-TOF-MS instrument employed during this study was as described in Chapter 2, and experiments were conducted using both versions of the exit/collision cell (ECC). In the current study proton transfer was used as the means of ionisation and the proton donor was the hydronium ion (H_3O^+) (Lindinger *et al.*, 1993). In order to generate the primary reagent ions, water vapour was delivered to the ion source by bubbling a high purity nitrogen carrier gas (Air Liquid, Ch, grade 7.0) through a glass vessel containing ultra-pure deionised water $(15 \text{ M}\Omega)$ at a rate of 30 - 52 sccm. Sample air from the PSI aerosol chamber was delivered to the CIR-TOF-MS at a rate of 200 - 275 sccm via an insulated 2 m long Teflon tube and a PTFE critical orifice. Both the sample line and critical orifice were heated to 40 $^{\circ}C$ (± 1 $^{\circ}C$) in order to limit wall losses. For brief intervals during certain experiments a particle filter was placed in the sample line to verify that all measured signals were due to gas phase species. The combined reagent and sample gas flows led to drift cell operating pressures in the range 6 - 9 mbar. The drift cell electric field (and therefore internal energy) was varied for certain experiments in order to enhance sensitivity to certain VOCs (see Table 1). The potential difference over the exit/collision cell was varied to facilitate collision-induced dissociation of the ionised sample and hence to allow controlled removal of unwanted water cluster ions, *i.e.* MH^+ .(H₂O)_n (where M represents the target VOC and $n \ge 1$). The experiment specific drift cell E/N ratios (where E is the electric field strength and N is the gas number density) are provided in Table 1.

As stated earlier, an important feature of time-of-flight mass spectrometry is the ability to achieve a much higher mass resolution than alternative techniques, notably quadrupole mass spectrometry. The mass resolution attained in the current study was in the region of 0.01 Da,

which has proved useful in confirming the assignment of various spectral features.

The sum of hydro and organic peroxy radicals (*i.e.* $\sum(HO_2 + \Sigma_i R_i O_2))$ present in the chamber was also measured during low NO_x experiments using a dual channel Peroxy Radical Chemical Amplifier (PERCA). The PERCA deployed during this work was similar to that described by Green *et al.* (Green *et al.*, 2006), but with inlet systems as per Monks *et al.* (Monks *et al.*, 1998).

6.3.4 Calibration Issues

A wide array of species was detected using the CIR-TOF-MS and it was therefore impractical to carry out independent calibrations for all measured compounds. Consequently, where no calibration standard was available for a given compound, the calibration factor determined for a structurally and kinetically similar surrogate was utilised (see **Table A6.1** of Section A6 of the Appendix). If no appropriate surrogate could be found, measurements are reported in terms of instrument signal (*i.e.* normalised ion counts per second (ncps)). VOC concentrations and yields quoted in the following discussion therefore act only as a guide for those compounds where surrogates have been employed for calibration. **Table A6.1** of Section A6 of the Appendix provides comprehensive details of all VOC calibrations employed in the current study. Considering all instrument and calibration associated uncertainties (see Chapter 4 for further details), the overall CIR-TOF-MS potential measurement errors lay within the range 2.9 - 27.6 % (**Table A6.1**).

Owing to experimental time constraints, a PERCA *chain length calibration* (see for example (Green *et al.*, 2006; Parker, 2007)) was not carried out following all experiments. Consequently, a typical chain length of 109 (obtained from previous work (Parker, 2007) was assumed to provide reasonable estimates of the peroxy radical concentrations. The amplification chain length of the PERCA varies between ~ 80 and 150. When combined with instrument uncertainties this gives an estimated peroxy radical uncertainty of 42 % (Fleming *et al.*, 2006a; Fleming *et al.*, 2006b).

6.3.5 Chamber Model Construction

The composition and evolution of the gas phase components of the TMB-SOA chamber system were simulated using a chamber optimised photochemical box model incorporating the comprehensive 1,3,5-trimethylbenzene atmospheric oxidation scheme extracted from the Master Chemical Mechanism website (Jenkin *et al.*, 1997; Jenkin *et al.*, 2003; Saunders *et al.*,

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2003; http://mcm.leeds.ac.uk/MCM, v3.1)^a. The TMB mechanism employed (along with an appropriate inorganic reaction scheme) contained approximately 145 species and almost 390 different reactions.

The box model used in this study also included a series of 'chamber specific' auxiliary reactions adapted from Bloss *et al.* (Bloss *et al.*, 2005a) and (Zador *et al.*, 2006) in order to take into account the background reactivity of the chamber. The original auxiliary mechanism of Bloss *et al.* was experimentally optimised for use in MCM model simulations of a comprehensive series of aromatic photooxidation experiments similar to those described here, yet conducted at the outdoor EUropean PHOto REactor (EUPHORE) in Valencia (It.). The chamber auxiliary mechanism employed by Bloss *et al.* and adapted for use within this work, contains a number of specific of features to account for the effects of the experimental conditions of an atmospheric simulation chamber; specifically the effects of the chamber walls. Primarily, these features consider:

- 1. (Photochemical) heterogeneous wall chemistry in the production (and supply to the chamber) of free radicals.
- 2. Removal of NO_y species (including HONO) from the gas matrix to the chamber walls.
- 3. Heterogeneous wall chemistry of various reactive species (including NO_y species such as HONO) and their subsequent liberation to the gas matrix.
- 4. Dilution of chamber trace constituents as bulk gas is added to the matrix in order to compensate for gas removed by instruments.
- 5. Use of xenon arc lamps to simulate the solar spectrum.

(For further information, see Bloss et al. (2005a and b))

In order to replicate the photolytic conditions inside the PSI aerosol chamber, key measured photolysis rates, made by spectral radiometry, were employed to tune the model photolysis rate parameterisations (Metzger *et al.*, 2008a). The calculated photolysis rates employed within the model have been adapted in order to account for the wavelength dependent light transmission through the FEP film of the chamber bag. The photolysis rate of NO₂ (j(NO₂)) was measured during each experiments using filter radiometry. j(NO₂) measurements were employed to account for possible inter-experimental variability in the Xe arc lamp spectrum, which may result from degradation of, and temperature effects on the chamber lights.

^a Chamber box model constructed by, and supplied with permission of Andrew R. Rickard (Univ. Leeds, UK).
In order to simulate the high NO_x experiments, the model simulations were run using experiment specific initial concentrations of NO, NO_2 and TMB. Similarly, for the low NO_x experiments, the initial TMB concentration was set according to experiment conditions, however, initial NO and NO_2 concentrations were set to zero and the value of HONO was constrained to 10 ppbV throughout the experiment. Each model simulation was run at the measured average experiment specific chamber temperature and relative humidity.

6.4 **Results and Discussion**

As has been discussed, the chamber conditions in this work can be broadly divided into two groups, high NO_x and low NO_x. In the high NO_x experiments the initial NO_x concentration was > 250 ppbV, whereas low NO_x conditions corresponded to NO_x at \leq 5 ppbV. The results from the high and low NO_x experiments are reported separately in the following sections. Comparisons of gas and aerosol phase measurements carried out under different VOC/NO_x regimes are utilised during the present study to help elucidate the underlying SOA formation mechanisms.

6.4.1 Chamber Inorganic Species and the SOA Precursor under High NO_x Conditions

Figure 2(a) - (d) displays the temporal evolution of the major inorganic gas phase components of the chamber system^b and the 1,3,5-trimethylbenzene precursor in several different experiments (listed in **Table 1**). In all instances the experiment start time is taken from the point at which chamber lights were switched on and hence the photochemistry initiated. On average the duration of each experiment was of the order of 8 – 10 hours.

The majority of experiments (experiments 1 - 4 and 6; see **Table 1**) were carried out under high NO_x conditions. During these experiments the initial VOC/NO_x ratio was varied between 0.54 and 2.25. **Figure 2(a)** summarises the findings for experiment 6, which constitutes a typical example of a high NO_x experiment with VOC/NO_x ~ 2:1; hence it is used as a focus for discussion. The experiment essentially begins with the production of atomic oxygen in the (ground) O(³P) state from the photolysis of NO₂ (reaction (R6.1)). The generation of O(³P) results in the subsequent production of ozone, photolysis of which in the presence of water yields OH:

$$NO_2 + hv \ (\lambda \le 420 \text{ nm}) \to NO + O(^{3}P)$$
(R6.1)

$$O(^{3}P) + O_{2} + B \rightarrow O_{3} + B$$
(R6.2)

^b NO, NO₂ and O₃ measurements supplied courtesy, and with permission of Axel Metzger (PSI, Ch.)

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$$O_3 + hv (\lambda \le 336 \text{ nm}) \rightarrow O(^1\text{D}) + O_2$$
(R6.3) $O(^1\text{D}) + H_2O \rightarrow 2OH$ (R6.4)

OH can also be generated in smog chamber systems from HONO photolysis, which is generally produced in all such systems following wall reactions involving NO₂ (*e.g.* (Metzger *et al.*, 2008a)). Following its production, OH reacts readily with TMB to generate a complex array of oxidation products, including organic peroxy radicals (RO₂), hydroperoxy radicals (HO₂) and oxygenated and nitrated VOCs (Calvert *et al.*, 2002).



Figure 2: Temporal evolution of the major gas phase components of the 1,3,5-TMB photooxidation system during (a) experiment 6 (VOC/NO_x ~ 2:1), (b) experiment 2 (VOC/NO_x ~ 2:1, NO only), (c) experiment 3 (VOC/NO_x ~ 1:2) and (d) experiment 7 (VOC/NO_x ~ 17:1). For (a) and (d) lights off for the 'dark phase' at 460 and 550 minutes, respectively, followed by NO injection (see text for details).

The oxidation profiles for TMB during all high NO_x experiments exhibited similar behaviour, with a short initial concentration plateau corresponding to the time required to initiate the OH chemistry, followed by a peak in oxidation rate at ~ 160 minutes after lights on. After this period, the TMB concentration profiles were characterised by a continual decay. For each experiment a plot of ln[TMB] *versus* time is approximately linear, with no distinct change in rate with accumulation of ozone (see **Figure 3**). This result verifies that as expected 1,3,5-TMB does not react appreciably with O₃. Consequently, with NO₃ oxidation of TMB negligible under the experimental chamber conditions employed, the major chemical loss of TMB would have resulted solely from its reaction with OH. Therefore, if the process is treated as pseudo first order (assuming sufficiently high oxidant levels such that reaction of the precursor VOC is rapid), OH concentrations can be inferred from the rate of decay of TMB, recorded by CIR-TOF-MS, using equations (E6.1) and (E6.2):

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$$\frac{d[TMB]}{dt} = [TMB](k_{OH}[OH])$$
(E6.1)

$$\ln[\text{TMB}] = -(k_{\text{OH}}[\text{OH}])t \qquad (E6.2)$$

For experiments with an initial VOC/NO_x ratio of ~ 2:1, peak OH concentrations inferred from the TMB decay profile were ~ 0.04 pptV, and experiment average concentrations were ~ 0.03 pptV (using $k_{\text{OH+1,3,5TMB}} = (5.67 \pm 1.13) \times 10^{-11} \text{ cm}^3$ molecules⁻¹ s⁻¹ at T = 298 K (Calvert *et al.*, 2002)). As an example, the inferred OH temporal profile for experiment 6 is given in **Figure 3**.



Figure 3: Temporal variation of OH concentration inferred from CIR-TOF-MS measurements of the precursor TMB during experiment 6 (solid black line). Also shown is the profile of $\ln[TMB]$ for experiments 6 (high NO_x) and 7 (low NO_x).

With the production of both HO₂ and RO₂ radicals within the chamber, NO became oxidised to NO₂, leading to the concentration peak seen in **Figure 2(a)** – (c). Due to the presence of the VOC (and hence RO₂), the NO/NO₂ partitioning was such that there was a positive deviation from the photostationary state resulting in net initial ozone production (Monks, 2005). As noted in other chamber studies (*e.g.* (Bloss *et al.*, 2005a; Dommen *et al.*, 2006)), the peak in [NO₂] and the initial accumulation of O₃ roughly coincide with the observed maximum rate of loss of the VOC and the peak in [OH]. Eventually, NO₂ was removed from the gas phase through the production of nitric acid (HNO₃), reactions on the chamber walls and incorporation into organic nitrates and the aerosol phase (Monks, 2005). As NO₂ chemistry constitutes the sole route to O₃ formation within the chamber, the removal of NO_x from the system was followed by a fall in the concentration of O₃. At the conclusion of experiment 6, ~ 70 % of the VOC precursor had been consumed and the concentrations of NO and NO₂ had fallen to negligible levels (**Figure 2 (a)**). Isopleth plots displaying the relationship between [TMB], [NO_x] and [O₃] under high NO_x chamber conditions are given in **Figure A6.1** of the Section A6 of the Appendix.

Figure 2(b) provides the corresponding system overview for experiment 2, during which a VOC/NO_x ratio of ~ 2:1 was again employed but this time with initial NO_x being introduced solely in the form of NO. In order to initiate the oxidation chemistry in this instance, the OH radical precursor, HONO, had first to be liberated from the illuminated chamber walls along with NO₂, following known heterogeneous chemical mechanisms (Stroud *et al.*, 2004; Metzger *et al.*, 2008a). Subsequent reactions involving OH (including with the precursor VOC) would have resulted in the formation of HO₂ and RO₂ species, which proceeded to react with NO to produce NO₂. Inspection of **Figure 2(b)** demonstrates this, with a steady rise in NO₂ to a slightly later peak than was observed when the initial NO_x consisted of both NO and NO₂ (**Figure 2(a)**). With this exception, the temporal evolution of the inorganic components of the chamber was broadly in line with findings from other experiments where the initial VOC/NO_x ratio was ~ 2:1.

Experiment 3, the final variant of the high NO_x system, involved a reversal of the VOC/NO_x ratio to a value of roughly 1:2. As can be seen in Figure 2(c) the NO_x, O₃ and TMB components of the system exhibited similar profiles to those observed during the other high NO_x experiments, but with a number of key exceptions. When the VOC/NO_x ratio was decreased to ~ 0.5 , the rate of decay of TMB appeared enhanced, suggesting higher levels of oxidant. In this instance inferred OH radical levels were on average ~ 0.06 pptV (peak ~ 0.08 pptV), *i.e.* twice as high as levels observed in the other high NO_x experiments. This finding is most likely a result of balancing of the OH/HO₂ ratio in the hydroxyl radical cycle, where a relatively higher proportion of NO (with respect to that of the VOC) will force a shift towards OH in the chamber HO_x balance. The impact of an elevated OH density is reflected in the amount of VOC consumed by the conclusion of the experiment, *i.e.* after 600 minutes less than 10 % of the initial TMB remained. In addition to this, a lower RO₂/NO_x ratio will slow the cycling of NO to NO_2 and hence delay subsequent O_3 production (see Section 6.4.3). This effect can be seen in the data presented in Figure 2(c), where a significant delay is evident in the times at which NO₂ and O₃ reached their respective peaks, and at which NO reached negligible concentrations (when compared to experiments with VOC/NO_x \sim 2:1).

6.4.2 Chamber Inorganic Species and the SOA Precursor under Low NO_x Conditions

The second component of the chamber study comprised two low NO_x experiments, experiments 5 and 7, during which $[NO_x]$ was kept below ~ 5 ppbV. For experiment 7, SO_2 gas was added to the chamber in order to generate sulfuric acid (H₂SO₄) seed particles. The

presence of H_2SO_4 during experiment 7 would give insight into the effect of an acid seed on SOA formation from TMB.

As discussed in Section 6.3.2, during the low NO_x experiments the chamber was supplied with a continuous source of NO (from HONO) at a rate greater than the sum of its removal pathways. Consequently, the chamber remained in a state of *net* ozone production throughout the experiment and therefore no distinct peak and fall was observed in the ozone concentration profile (see **Figure 2(d)**). Isopleth plots displaying the relationship between [TMB], [NO_x] and [O₃] under low NO_x chamber conditions are given in **Figure A6.2** of Section A6 of the Appendix.

In addition to supplying the chamber with NO, HONO photolysis constituted an additional source of OH. The photolysis rate of nitrous acid (*j*(HONO)) for the PSI chamber has been measured as 2.7×10^{-4} s⁻¹, which yields an OH production rate (P(OH)) of 2.7 pptV s⁻¹ for a constant HONO value of 10 ppbV. As P(OH) from the photolysis of HONO was several times larger than P(OH) from ozone at any instant during the low NO_x experiments, the level of OH in the chamber was roughly constant. Evidence for this can be seen in **Figure 2(d)**, where the rate of decay of TMB during experiment 7 remained roughly constant during the majority of the experiment. Using the rate of oxidation of TMB (as described in Section 6.4.1), the average OH concentrations in the chamber for the two low NO_x experiments (5 and 7) were estimated to be ~ 0.05 and 0.06 pptV.

Tables 1, **2** and **3** provide a summary of various important measured parameters which describe the evolution of the inorganic species and TMB during each experiment. From a comparison of the peak NO_2 and O_3 concentrations achieved across experiments with similar initial conditions, and from the times at which those peaks occurred, it can be seen that there was a high level of experimental reproducibility within this work.

Exp. No.	TMB consumed / %	Peak d[TMB]/d <i>t</i> / mins.	Peak [O ₃] time / mins.	Peak [O3] / ppbV	Peak [NO ₂] time / mins.	Peak [NO2] / ppbV
1	89.4	130	278	274.1	103	212.7
2	44.3	120	259	365.2	137	446.2
3	91.5	120	600	199.1	188	187.4
4	63.5	110	287	230.8	104	196.4
5	82.2	-	489	43.8	-	-
6	62.1	110	284	226.3	110	200.9
7	92.5	-	551	58.9	-	-

Table 2: Quantity of organic precursor consumed and peak inorganic concentrations

(a) $[NO] - 0$ fion T^3 V / mins.	$\begin{array}{cccc} & 152 \\ 152 - 169^4 \\ 325 \\ 157 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{array}$	eached 2 ppbV	below 2 ppbV V throughout
MPS [NO] k. [No.] ² nucleat #cm ⁻³ / ppb	580 16.2 1099 6.2 406 1.4 491 1.2 491 1.2 407 0.4 494 1.4 2216 0.4	om CPC acter ≥ 3 nm) rom SMPS acter ≥ 15 nm) time at which [NO] r	f line, [NO] dropped riment, [NO] < 1 ppt
CPC S Max. [No.] ¹ Ma: /#cm ⁻³ /-	620 1180 337 392 323 361 1752	¹ Data obtained fi (particles of dian ² Data obtained f (particles of dian ³ Defined as the	⁴ NO analyser of during this time ⁵ Low NO _x expe experiment
Max. [No.] T ² / mins.	225 228 228 609 256 163 257 76	SOA Yield / %	1.94 7.47 0.29 6.36 1.79
Half Max. [No.] T ² / mins.	183 167 543 226 94 218 43	Aerosol ((Time) ³ (Mins.)	(465) (433) (433) (413) (415) (502) (358)
SMPS nucleation T ² / mins.	108 149 420 193 58 182 28	sol Max. ime) Mass s.) /μg m	182 182 182 182 182 182 182 182
CPC nucleation T ¹ / mins.	108 145 400 188 50 184 22	. Max. Aerc diameter (T / nm (Min	387 (357 663 (505 155 (618 507 (484 462 (513 484 (487
Exp. No.	- 9 6 4 6 9 5	Exp. No.	- 0 0 4 0 0 1

6.4.3 Chamber Aerosol Formation under High NO_x Conditions

Figure 4(a) – (d) summarises the key aerosol phase parameters for the four variants of the TMB photooxidation study, *i.e.* the total aerosol number density, total aerosol volume and mean geometric particle diameter^c.



Figure 4: Temporal evolution of the aerosol number density (ND), geometric mean diameter (GMD) and volume concentration (Vol) within the chamber during (a) experiment 6 (VOC/NO_x ~ 2:1), (b) experiment 2 (VOC/NO_x ~ 2:1, NO only), (c) experiment 3 (VOC/NO_x ~ 1:2) and (d) experiment 7 (VOC/NO_x ~ 17:1). For (a) and (d) lights off for the 'dark phase' at 460 and 550 minutes, respectively, followed by NO injection (see text for details). ND taken from CPC measurements, GMD and Vol taken from SMPS measurements.

For experiments 1 - 6 no seeding was employed in the simulation chamber and hence new aerosol formation occurred *via* homogeneous nucleation involving certain key semi-and non-volatile oxidation products of the precursor VOC (Seinfeld and Pankow, 2003; Holmes, 2007). That is, following oxidation of the precursor, the concentration of the nucleating species eventually reached the point at which their gas phase saturation limit was achieved and transfer to the particle phase transpired (Pandis *et al.*, 1992).

The nucleation event observed during experiment 6 (high NO_x experiment, VOC/NO_x ~ 2:1) is clearly evident in **Figure 4(a)**, seen as a dramatic increase in the total number density of particles in the chamber at ~ 185 minutes. In this study nucleation is deemed to have occurred once the differential of the particle number density (with respect to time) exceeds a value of one for three consecutive measurements (*i.e.* when the particle count tends away from the baseline). Nucleation times are given for the CPC and the SMPS instruments in

^c Aerosol phase measurements supplied courtesy, and with permission of Axel Metzger (PSI, Ch.)

Table 3. However, as the CPC measures particles closer in size to the nucleating cluster (*i.e.* ~ 1.5 nm), it is the CPC derived nucleation times that are employed during the following analysis and discussion.

In experiment 6 new SOA formation continued for approximately 100 minutes, by which time a maximum (measured) number density of ~ 490 particles cm⁻³ was reached (in the size range 15 - 690 nm). During this time, *via* condensation and then coagulation mechanisms, the particles grew in size to possess a maximum mean diameter of ~ 480 nm at ~ 490 minutes. The total volume of chamber SOA followed a similar trend to that of particle diameter. Ultimately the number density of SOA particles and the total suspended chamber mass began to decrease owing to coagulation and deposition to the chamber walls.

Table 3 highlights the reproducibility of aerosol phase parameters between the three high NO_x experiments carried out at VOC/NO_x ~ 2:1 (*i.e.* experiments 1, 4 and 6). The number density of aerosol particles formed in the chamber matrix during all high NO_x experiments of VOC/NO_x ~ 2:1 was highly reproducible between repeat studies, with maxima of ~ 580, 490 and 490 particles cm⁻³ (in the size range 15 – 690 nm) formed during experiments 1, 4 and 6, respectively (relative standard deviation = 9.7 %). The time at which the maximum number density was reached was equally consistent between repeat experiments 1, 4 and 6, respectively. The particles formed grew to possess maximum average diameters of around 390, 480 and 510 nm between 360 and 490 minutes after the start of each experiment.

Following the analysis performed by Baltensperger and colleagues (Baltensperger *et al.*, 2005), total SOA mass has been determined from the measured SOA volume by assuming an aerosol density of 1.4 g cm⁻³. In the case of experiment 6, a maximum SOA mass of ~ 31 μ g m⁻³ was reached. As no *wall loss* corrections have been applied to the aerosol phase data, this value constitutes a lower limit and should be treated with care (for details regarding wall loss correction methodology and example wall loss corrected SOA mass data, the reader is referred to Section A6 of the Appendix). Using the methods developed by Odum *et al.*, a 'relative' SOA yield (Y) was subsequently calculated according to equation (E6.3) (Odum *et al.*, 1996):

$$Y = \frac{M_0}{\Delta VOC} \times 100$$
 (E6.3)

In the above expression M_0 corresponds to the peak mass of SOA produced and ΔVOC is the amount of the precursor VOC consumed by the time that the point of peak SOA mass is 210

reached (both expressed in units of μ g m⁻³). Yields for the three repeat experiments with a VOC/NO_x ratio ~ 2:1 (*i.e.* experiments 1, 4 and 6) were 1.9, 2.3 and 1.8 %, respectively.

The temporal behaviour of the measured aerosol parameters for experiment 2 (VOC/NO_x ~ 2:1, NO only) was similar to those of experiments 1, 4 and 6. However, as the initial concentration of both TMB and NO was set to twice that of the other high NO_x (VOC/NO_x ~ 2:1) experiments, an approximate two-fold increase in the maximum number density of particles was observed (~ 1100 particles cm⁻³ in the size range 15 – 690 nm). Also, particles grew to larger maximum mean diameters (~ 660 nm) and the ultimate experiment SOA yield was roughly four times greater than that of the other high NO_x experiments (1, 4 and 6), being ~ 7.5 %. The findings described here for an enhanced level of starting material are consistent with reports from previous studies (Paulsen *et al.*, 2005; Song *et al.*, 2005; Gross *et al.*, 2006).

When the starting VOC/NO_x ratio was reversed to ~ 1:2 for experiment 3, SOA formation was significantly delayed, with nucleation occurring around 215 minutes later than in experiment 6. By the conclusion of experiment 3 (~ 600 minutes) the chamber aerosol appeared to still be in a state of growth and no distinct peak in either size or mass had been reached. Consequently, the SOA yield was determined from the aerosol mass produced at the conclusion of the experiment. With a VOC/NO_x ratio of ~ 1:2, a SOA yield of 0.3 % was achieved, *i.e.* roughly an order of magnitude lower than for the larger VOC/NO_x ratios. With more than 90 % of the precursor VOC consumed by termination of the experiment and with primary and secondary oxidation products having reached their concentration peaks, it may be assumed that further aerosol growth after this point would have been minimal.

From the above discussion and from inspection of **Table 3** it is clear that for each experiment conducted under high NO_x conditions a significant delay, or 'incubation' period, was witnessed before the nucleation event. For experiments 1, 2, 4 and 6 (VOC/NO_x ~ 2:1) this period lasted for approximately 110, 145, 190 and 185 minutes, respectively, and for experiment 3 (VOC/NO_x ~ 1:2) it was over twice as long at 400 minutes. Evidence for this incubation period has been reported for several other aromatic oxidation systems, including benzene, toluene, *o*-xylene and *m*-xylene in a number of different simulation chambers (Izumi *et al.*, 1988; Johnson *et al.*, 2004; Johnson *et al.*, 2005; Song *et al.*, 2005; Ng *et al.*, 2007).

It has been proposed that the existence and duration of the incubation period are directly related to the presence of NO in the gas phase (Johnson *et al.*, 2004; Johnson *et al.*, 2005). Results obtained by Johnson *et al.* (2005) from a gas phase oxidation model coupled to an

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absorptive aerosol transfer scheme showed that the less volatile organic hydroperoxides, formed from the self-reactions of hydro and organic peroxy radical species (R6.8), were significant contributors to SOA mass. Consequently, new particle formation and growth would be closely linked to the ambient level of NO, which may react with HO₂ and RO₂ *via* reactions (R6.5) and (R6.6) in the scheme below, limiting the capacity of the system to form peroxides:

$$NO + HO_2 \rightarrow NO_2 + OH$$
 (R6.5)

$$NO + RO_2 \rightarrow NO_2 + RO$$
 (R6.6a)

$$\rightarrow \text{RONO}_2$$
 (R6.6b)

$$RO_2 + RO_2 \rightarrow Products$$
 (R6.7)

 $RO_2 + HO_2 \rightarrow ROOH + O_2$ (R6.8)

Note, as was discussed within Chapter 1 (Sections 1.4.2 and 1.4.4.3), the $RO_2 + RO_2$ selfreaction (R6.7) will proceed *via* one of three different pathways, the relative importance of which depends on the structure of the reacting RO_2 radicals. Generally, the $RO_2 + RO_2$ reaction will produce either (i) an equivalent alkoxy radical pair (RO), (ii) a carbonyl compound and an alcohol, or (iii) an organic peroxide (ROOR). Although reaction (R6.7) can lead to the formation of low volatility ROOR compounds, it proceeds at a considerably slower rate than reaction (R6.8), hence ROOH species are expected to be of greater importance in SOA formation (see discussion below).

Johnson and co-workers (Johnson *et al.*, 2005) proposed that once in the aerosol phase, the organic peroxides are able to take part in heterogeneous chemistry with certain aldehyde compounds to form peroxyhemiacetals. This hypothesis supports results from previous studies of various workers demonstrating the importance of heterogeneous chemistry within the aerosol, and in particular acetal and hemiacetal reactions involving carbonyl oxidation products (Jang and Kamens, 2001; Jang *et al.*, 2003).

Following the method detailed by Ng *et al.* (Ng *et al.*, 2007), an examination of the kinetics involved in reactions (R6.6) – (R6.8) enables us to infer the influence of the NO concentration on gas phase organic hydroperoxide formation during the current experiments. Equation (E6.4) below accounts for reactions (R6.6) – (R6.8) to determine the fraction of RO₂ (Φ) that forms organic hydroperoxides:

$$\Phi = \frac{k_{6.8}[\text{RO}_2][\text{HO}_2]}{k_{6.8}[\text{RO}_2][\text{HO}_2] + k_{6.7}[\text{RO}_2]^2 + k_{6.6}[\text{RO}_2][\text{NO}]}$$
(E6.4)

For this simple model the overall rate constant k_6 has been used to account for the fate of RO₂ *via* reaction with NO by both pathways (R6.6a) and (R6.6b). Rate constants $k_{6.6}$, $k_{6.7}$ and $k_{6.8}$ taken from MCMv3.1; http://mcm.leeds.ac.uk/MCM.

Figure 5 shows the variation of Φ with NO concentration taken from experiment 6 for a series of HO₂ and RO₂ concentrations obtained from the chamber box model described in Section 6.3.5 (see Section 6.4.9 for modelled HO₂ + RO₂ temporal profiles). **Figure 5** clearly demonstrates that for the self-reaction route involving both hydro and organic peroxy radical species to become significant, either high radical levels are required (*i.e.* tens of pptV) or the concentration of NO must approach zero. For Φ (hence organic hydroperoxide formation) to reach as much as 5 % in this model, the concentration of NO must fall to ~ 2 ppbV (with ~ 40 and 50 pptV HO₂ and RO₂, respectively) and for 10 %, ~ 1 ppbV (with ~ 50 and 70 pptV HO₂ and RO₂, respectively). Similar results have been obtained here using a simple linearly increasing radicals profile with time (not shown).



Figure 5: Theoretical variation in partitioning of RO_2 with evolving chamber NO under high NO_x conditions. Φ gives the percentage of RO_2 species forming organic hydroperoxides (see Equation (E6.4) and text for further details). Graph number markers give the time after lights on.

During experiments 1, 2, 4 and 6 (VOC/NO_x ~ 2:1), the time required for the NO concentration in the chamber to reach 2 ppbV (*i.e.* to approach zero) ranged from ~ 150 to 170 minutes (see **Table 3**). Contrasting these times with those of the nucleation event in each case, we see that SOA formation does occur only as [NO] drops towards zero, adding support to the proposal that peroxide chemistry is involved in SOA formation. However, during experiments 4 and 6 there is a further time delay (of ~ 30 and 20 minutes, respectively) before particle formation occurs, implications of which are discussed in Section 6.4.6. The concentrations of NO at nucleation for the high NO_x experiments 1, 2, 4 and 6 were 16.2, 6.2,

1.2, and 1.4 ppbV, respectively. Particle growth during experiment 1 was slower than other repeat experiments, an observation in line with the slightly higher [NO] observed at the point of SOA formation. Using the partitioning theory of equation (E6.4), at the time of nucleation during experiment 6, $\Phi = 5$ %.

The hypothesis suggesting that the NO concentration in the chamber must reach a minimal value before nucleation can occur is supported by results obtained from varying the VOC/NO_x ratio. When the VOC/NO_x ratio was changed from 2:1 to 1:2 (experiment 3), a considerably longer time was required for the system chemistry to reduce the concentration of NO to negligible levels (see **Table 3**). Correspondingly, a delay was observed in the timing of the nucleation event. In addition to this, nucleation did not occur until approximately a further 75 minutes after [NO] had reached minimal levels.

Despite occurring at a significantly slower rate than the HO₂ + RO₂ reaction, the RO₂ + RO₂ pathway may also be significant in the formation of SOA on account of the low volatility reaction products that it can yield, *i.e.* the RO₂ + RO₂ self reaction may produce a molecule of greater carbon and oxygen number, and substantially lower volatility than either of the reactants (*i.e.* ROOR). Equation (E6.4) can be modified to estimate the fraction of RO₂ radicals which reacted *via* the RO₂ + RO₂ route during the current experiments. Using this partitioning theory it is estimated that at the time of nucleation during experiment 6 approximately 0.2 % of RO₂ species were reacting *via* reaction (R6.7), a fraction of which would have yielded ROOR. Consequently, under high NO_x conditions ROOR species are likely to have played only a minor role in the nucleation process, however, their contribution to the formation of SOA mass most probably increased with time, with the fraction of RO₂ reacting *via* pathway (R6.7) (and potentially forming ROOR) rising (theoretically) to ~ 3 % by 375 minutes (with ~ 58 and 93 pptV HO₂ and RO₂, respectively). Detailed, concomitant gas and aerosol phase ROOH and ROOR measurements are still required to illuminate the role of such species in SOA formation and growth.

6.4.4 Chamber Aerosol Formation and Peroxy Radical Behaviour under Low NO_x Conditions

Figure 4 and Table 3 demonstrate the clear difference between the nucleation times of the high and low NO_x experiments. During the low NO_x experiments a distinctly shorter incubation period was observed before the onset of aerosol formation, *i.e.* ~ 50 and 20 minutes for experiments 5 and 7, respectively, compared to an average of ~ 155 minutes for

the typical high NO_x experiments (see **Figure 4(d)**). During the low NO_x (constant HONO) experiments the concentration of NO up to the point of nucleation was no greater than ~ 1 ppbV and an additional radical source was present to supply OH and (therefore HO₂) to the chamber matrix. Consequently, it is highly likely that radical-radical self-reaction routes (R6.7 and R6.8) dominated the fate of the RO₂ species from the start of the experiment. It should be noted that the length of the incubation period of each low NO_x experiment (*i.e.* 5 and 7), was comparable to the length of the time delay between NO falling to negligible concentrations and nucleation during high NO_x experiments 4 and 6.

The SOA yields obtained during low NO_x experiments 5 and 7 were 6.4 and 6.2 % respectively, *i.e.* roughly 3.5 and 22 times larger than those achieved under high NO_x conditions of VOC/NO_x ~ 2:1 and 1:2, respectively. It should be noted that in the latter instance (experiment 3, VOC/NO_x ~ 1:2), the experiment was conducted with the same initial TMB concentration as the low NO_x experiments, and thus it is unlikely that enhanced yields under low NO_x conditions are an artefact of the initial precursor concentration (Ng *et al.*, 2007). Ng *et al.* (2007) saw roughly 3 and 6 fold increases in SOA yields in the toluene and *m*-xylene systems, respectively, when moving from high to low NO_x conditions, comparable to observations made here.

As discussed earlier, recent reports attribute the production of a greater aerosol yield in low NO_x systems to chamber conditions favouring the formation of low volatility peroxides from reactions (R6.7) and (R6.8) (Stern *et al.*, 1987; Jenkin *et al.*, 2003; Johnson *et al.*, 2004; Song *et al.*, 2005; Ng *et al.*, 2007). However, as will be discussed below, the conditions of low NO_x experiments 5 and 7 also allowed the early production of a variety of other organic oxidation products which may have further contributed to SOA formation and facilitated enhancement of SOA yield.

Elevated NO_x concentrations, such as those employed during the high NO_x experiments of this study, lead to interference problems in the inlet chain length chemistry when measuring peroxy radical species using the PERCA technique (Green *et al.*, 2006; Parker, 2007). Consequently, peroxy radical data are presented only for experiments conducted under low NO_x conditions. **Figure 6** displays the temporal evolution of the sum of both hydro and organic peroxy radicals during experiment 5, during which a rapid rise in peroxy radical concentration was observed from lights on to a concentration plateau of ~ 175 pptV by ~ 400 minutes.



Figure 6: Temporal evolution of the sum of hydro and organic peroxy radicals (*i.e.* Σ (HO₂+RO₂)) recorded by the PERCA during low NO_x experiment 5 (VOC/NO_x ratio ~15:1).

The temporal behaviour of the peroxy radicals during the low NO_x experiments can be attributed to the constant HONO input and the constant photolysis rate within the chamber. Upon being introduced into the chamber, HONO was photolysed to yield OH and NO. Once formed the OH would have reacted rapidly with CO and the precursor 1,3,5-TMB leading to the production of HO₂ and RO₂ radicals, respectively. Within the chamber matrix the hydro and organic peroxy radicals would have resided in steady state, being formed and then reacted rapidly. Consequently, the rise in radical concentration observed in **Figure 6** during the early stages of the experiment indicates that up to ~ 400 minutes HO₂ and RO₂ species were produced at a faster rate than they were consumed. The subsequent onset of plateau behaviour in radical concentration highlights the point at which the HO₂ + RO₂ loss rate became constant.

Using the partitioning theory outlined in Section 6.4.3 (equation (E6.4)) along with total peroxy radical and NO measurements, it is possible to demonstrate how hydroperoxide production may have proceeded within the chamber under low NO_x conditions. **Figure 7** shows the variation of Φ with [RO₂] and [NO], using measured data and assuming the same [HO₂]/[RO₂] ratio as produced in the chamber box model, *i.e.* 0.45 (see Section 6.4.9). With the NO concentrations no greater than 1 ppbV, formation of peroxides within the chamber becomes efficient as soon as the photochemistry is initiated and peroxy radicals are formed (see **Figures 2(d)** and **6**). Under low NO_x conditions equation (E6.4) predicts that partitioning of RO₂ to organic hydroperoxides is as efficient as ~ 5 % after only the first 10 minutes of experiment, a result that contrasts strongly with findings from the high NO_x cases. Furthermore, equation (E6.4) predicts that partitioning of RO₂ to peroxides that partitioning of RO₂ to peroxides that partitioning of RO₂ to peroxide that contrasts strongly with findings from the high NO_x cases.

18 % by the time of the nucleation event of experiment 5. These experimental findings further strengthen theories regarding the crucial role possibly played by organic hydroperoxides during the SOA formation process.



Figure 7: Theoretical variation in partitioning of RO₂ species with evolving chamber [NO] under low NO_x conditions. Graph number markers give the time after lights on. Φ gives the percentage of RO₂ species forming hydroperoxides (see Equation (E6.4) and text for further details).

As was discussed in Section 6.4.3, equation (E6.4) can be modified to provide an estimate of the fraction of RO₂ radicals reacting *via* the RO₂ + RO₂ route (*i.e.* reaction (R6.7)). From this partitioning theory we find that by the point of nucleation during low NO_x experiment 5, ~ 0.8 % of RO₂ radicals were reacting *via* reaction (R6.7). Partitioning of organic peroxy radicals to the RO₂ + RO₂ route reached a maximum of ~ 1.6 % by 170 minutes. Combined with the larger aerosol yields obtained, this finding suggests that low volatility ROOR species, formed more readily in the absence of NO_x, may play some role in SOA formation and growth under low NO_x conditions.

6.4.5 Effect of Inorganic Seed

A comparison of the two low NO_x experiments (5 and 7) in **Table 3** shows that particle formation occurred ~ 30 minutes earlier when SO₂ gas was included in the matrix. This result could be due to the slightly higher OH levels which were measured during experiment 7 (owing to slight inaccuracies in the input of HONO to the chamber), but is most likely a consequence of H_2SO_4 nucleation, which subsequently supplied a condensation surface for the condensable organic oxidation products (Holmes, 2007). Additionally, seeding the chamber generated a larger number of particles than in other experiments. The peak particle number density during experiment 7 reached roughly 2200 cm⁻³, compared to only 410 cm⁻³ during experiment 5 (in the size range 15 – 690 nm). Due to the larger number of particles produced,

the mean geometric aerosol diameter of the seeded SOA was slightly smaller than that produced by homogeneous nucleation, *i.e.* \sim 400 compared to \sim 460 nm.

Various chamber studies have shown that SOA yields generated from a VOC precursor can become enhanced in the presence of an acidic seed (Jang and Kamens, 2001; Czoschke et al., 2003; Jang et al., 2003; Limbeck et al., 2003; Gao et al., 2004; Surratt et al., 2007; Verheggen et al., 2007). Further inspection of Table 3 shows that despite the production of a greater number of particles, the aerosol yield obtained in the presence of H₂SO₄ was no greater than the yield obtained during the companion low NO_x homogeneous nucleation experiment (5). However, the SO_2 concentration employed during experiment 7 was somewhat small (0.4 ppbV compared to > 100 ppbV used by other workers (Edney et al., 2005; Kleindienst et al., 2006; Metzger et al., 2008b)); hence it is possible that the resultant $[H_2SO_4]$ (*i.e.* a limit of 1.5 µg m⁻³ assuming full conversion of SO₂ to SO₄²⁻) was too low to facilitate an acid seed effect. Therefore, with this in mind and with a lack of repeat seed experiments, the result of 'no yield enhancement' for TMB-SOA in the presence of H₂SO₄ is not conclusive, but is in line with findings presented by Ng et al. for two other aromatic systems: toluene and *m*-xylene (Ng et al., 2007). A more exhaustive study investigating the effect of acid seeding on TMB-SOA has been produced recently by Metzger et al. (Metzger et al., 2008b). Metzger et al. observed no effect on SOA yield with initial [SO₂] as high as 20 ppbV.

6.4.6 Time-Dependent SOA Growth Curves

In order to help elucidate the mechanisms underlying SOA formation in the TMB system, a series of time-dependent SOA growth curves have been generated following methods employed by Song, Ng and co-workers (Song *et al.*, 2005; Ng *et al.*, 2007). The time-dependent growth curves essentially comprise a plot of SOA mass formed *versus* the amount of VOC reacted. **Figure 8(a)** presents the growth curve for experiment 6, a typical example of the high NO_x system (VOC/NO_x ~ 2:1). Initial inspection reveals the significant incubation period noted previously as the chamber concentration of NO \rightarrow 0. The incubation period is followed by a linear increase in SOA mass with consumption of the TMB. The growth curves for all high NO_x experiments with VOC/NO_x ~ 2:1 exhibit similar behaviour, with all profiles displaying similar slopes and with all nucleation events occurring within a narrow band of reacted TMB (see **Figure A6.4** of Section A6 of the Appendix). The time-dependent growth curves for the low NO_x experiments are also linear following nucleation but, as noted earlier, are preceded by a much shorter incubation period than those of the high NO_x systems. As an

example, **Figure 8(b)** displays the growth curve for experiment 7 (also see **Figure A6.5** of Section A6 of the Appendix).



Figure 8: SOA time-dependent growth curves for (a) experiment 6 (high NO_x experiment, VOC/NO_x ~ 2:1) and (b) experiment 7 (low NO_x experiment, VOC/NO_x ~ 17:1). Δ [TMB] = reacted mass of TMB following initiation of the oxidation chemistry

As noted in Sections 6.4.3 and 6.4.4 a time delay was observed between $[NO] \rightarrow 0$ and the nucleation event in high NO_x experiments 4 and 6, which was comparable in duration to the incubation period clearly evident in the growth curves of the low NO_x experiments (*e.g.* **Figure 8(b)**). As shown above, the formation of hydroperoxides in the low NO_x system is likely to be extremely efficient even very early into the experiment. Consequently, if organic hydroperoxides are indeed pivotal in TMB-SOA formation, the incubation period observed under low NO_x conditions (and the further time delay under high NO_x conditions) could be indicative of the time required for their gas phase concentrations to build to sufficient levels such that their saturation vapour pressure relative to the particle phase is exceeded. It is also possible that the presence of the time delay in the high NO_x experiments and the incubation zone in the absence of NO_x, are a consequence of the SOA forming species consisting of later stage oxidation products which form further down the oxidation chain, *i.e.* from further reaction of primary products (including certain peroxides, see discussion in Section 6.4.10 for further details). Growth curves displaying similar behaviour to those derived from the current study were presented by Song *et al.* for the *m*-xylene system (Song *et al.*, 2005).

6.4.7 The Gas Phase Organic Compounds

6.4.7.1 The 1,3,5-trimethylbenzene Atmospheric Oxidation Mechanism

Before reporting the findings obtained from the CIR-TOF-MS measurements, the current known atmospheric oxidation processes of TMB are first outlined. Atmospheric oxidation of

TMB occurs primarily by reaction with the OH radical, and may essentially be separated into two distinct pathways. One pathway is reaction *via* OH addition to the aromatic ring, which may ultimately lead to ring cleavage (pathway *Pi*), while the other involves hydrogen abstraction from a methyl group (pathway *Pii*) (Seinfeld and Pandis, 2006). In general, the more substituted the aromatic ring, the more important the ring fragmentation route (Johnson *et al.*, 2005; Bloss *et al.*, 2005b). A simplified mechanism for the photochemical degradation of TMB, highlighting the most important atmospheric oxidation routes, is displayed in **Figure 9**. This scheme has been constructed through an amalgamation of previous descriptions of the benzene and toluene oxidation systems (Yu *et al.*, 1997; Atkinson, 2000; Bohn, 2001; Calvert *et al.*, 2002; Johnson *et al.*, 2004; Johnson *et al.*, 2005), the MCMv3.1 TMB subset (extracted from the MCM website (http://mcm.leeds.ac.uk/MCM), (Bloss *et al.*, 2005a; Bloss *et al.*, 2005b)) and measurements made by CIR-TOF-MS during this study:

(Pi) OH Addition to the aromatic ring. The principal atmospheric oxidation route for TMB involves the addition of OH to the aromatic ring (branching ratio of 0.97 in MCMv3.1), initially forming an OH-aromatic adduct (a trimethyl hydroxycyclohexadienyl radical; compound (B) in Figure 9). In the presence of atmospheric levels of O_2 this radical is in equilibrium with its equivalent OH-aromatic-O₂ adduct (a trimethyl hydroxycyclohexadienyl peroxy radical) (C). The OH-aromatic-O₂ adduct (C) can either subsequently decompose to yield HO_2 and the ring retaining product 2,4,6-trimethylphenol (D), or most likely will undergo internal rearrangement to generate an O₂-bridged trimethyl peroxide bicyclic radical (E) (branching ratio of 0.96 in MCMv3.1). The O₂-bridged trimethyl peroxide bicyclic radical (E) can subsequently degrade through various stages of isomerisation, decomposition and scission to form the epoxy-oxy species (H) (yield ≈ 0.15 in MCMv3.1). The epoxy-oxy compound can decompose to give a variety of lower molar mass oxygenates (e.g. compounds I and J). However, in the atmosphere the bicyclic peroxide radical (E) will most likely undergo reaction with O_2 to form the peroxy radical equivalent (K) (yield ≈ 0.85 in MCMv3.1). The yields of initial products formed after addition of OH to the aromatic ring of TMB in MCMv3.1 are 0.79, 0.14, and 0.04 for the trimethyl peroxide bicyclic peroxy radical (K), the epoxy-oxy species (H) and 2,4,6-trimethylphenol (D), respectively. Depending on the amount of NO_x present, the peroxide bicyclic peroxy radical (K) will degrade via a number of intermediary steps to produce a range of O₂-bridged oxygenated and nitrated compounds (compounds L - P). Some of the larger oxygenated and nitrated ring-retaining products, including the multi-functional O₂-bridged species shown in Figure 9, are likely to be sufficiently non-volatile to partition into the organic aerosol phase (Johnson et al., 2004;

Johnson *et al.*, 2005). Once inside the particle phase, these types of multi-functional compounds can take part in certain association reactions (Johnson *et al.*, 2005).



Figure 9: Mechanism summary of OH radical-induced photooxidation of 1,3,5-trimethylbenzene. Key primary and secondary product formation shown, branching ratios/route yields are taken from MCMv3.1(http://mcm.leeds.ac.uk/mcm) (see text for details).

Further oxidation and ring opening processes (mainly through the oxy radical (N)) will yield an array of lower molecular mass carbonyl (including methyl glyoxal), unsaturated γ dicarbonyl, acid and furanone species, some of which are shown in **Figure 9** (*e.g.* compounds Q - S). These low molecular mass ring fragmentation products have a tendency to be multifunctional and can be unsaturated, and therefore are often relatively reactive and hence can be oxidised further through reactions with OH, O₃ and NO₃. A selection of likely, further reaction products are shown in **Figure 9**. Some of these products, *e.g.* 3-methyl maleic anhydride (citraconic anhydride) (AB) and 3,5-dimethyl-5(2H)-2-furanone (S), can be highly polar and less volatile, and hence may be able to transfer into the organic aerosol phase (Kleindienst *et al.*, 1999; Johnson *et al.*, 2005).

(*Pii*) Hydrogen abstraction from a pendant methyl group. OH initiated hydrogen abstraction from a pendant methyl group constitutes the alternative oxidation route for TMB in the atmosphere, and represents the major ring retaining pathway (other than the formation of 2,4,6-trimethyl phenol as described above). Eventually, following hydrogen abstraction, reaction with O_2 , and subsequent radical reactions (*e.g.* with NO, RO₂ and HO₂), 3,5 dimethyl benzaldehyde (W) is formed with a yield of ~ 0.03 according to MCMv3.1 (Bloss *et al.*, 2005b).

6.4.7.2 Measurements of the Gas Phase Organic Compounds

Figures 10(a) – (d) display the CIR-TOF-MS mass spectra recorded after 400 minutes of irradiation during experiments 6, 3, 2 and 7, with VOC/NO_x ratios of around 2:1, 1:2, 2:1 (NO only) and 17:1, respectively. All of the CIR-TOF-MS data presented within this work have been normalised to 10^6 primary reagent ion counts (*i.e.* the sum of the H₃O⁺ and H₃O⁺.(H₂O) signals) and have been background subtracted. Consequently, all signals stated here are quoted in units of normalised counts per second *i.e.* ncps (de Gouw *et al.*, 2003). In order to show the relative contributions of the various peaks to the total mass spectra, for **Figures 10(a)** – (d) the *m/z* 121 peaks (*i.e.* 1,3,5-TMB) have each been assigned a nominal value of 100 % and all other peaks have been scaled accordingly.



Figure 10: Comparison of CIR-TOF-MS mass spectra recorded 400 minutes after 'lights on' for (a) experiment 6 (VOC/NO_x ~ 2:1), (b) experiment 3 (VOC/NO_x ~ 1:2), (c) experiment 1 (VOC/NO_x ~ 2:1, NO only) and (d) experiment 7 (low NO_x, VOC/NO_x ~ 17:1). Each mass spectrum corresponds to data accumulated over a ten-minute period, see text for details.

During a typical high NO_x chamber experiment (and depending on the drift cell conditions employed) around sixty peaks were recorded in the mass spectra between m/z 0 and 300, with around thirty peaks possessing a mass greater than that of the precursor VOC (m/z 121). In contrast, roughly fifty significant features were recorded during the low NO_x experiments, with around twenty of those possessing a mass greater than that of the precursor. It should be noted, however, that this difference could be attributed to the use of a lower precursor concentration during the low NO_x studies, where detection limits of the instrument may have become an issue for certain low concentration oxidation products (see Chapter 5 for further information regarding detection limits). The number of spectral features quoted here includes features present due to fragment ions as well as parent ions, and hence the number of peaks recorded does not necessarily represent the total diversity of organic species in the chamber. For brief periods during certain experiments, the electric field applied over the exit/collision cell in the CIR-TOF-MS drift tube was increased to produce more energetic collisions, and thus to identify and help exclude any possible molecular ion water cluster products (*i.e.* MH⁺.(H₂O)_n).

The major spectral features common to all experiments are listed in **Table 4** along with, where possible, a tentative compound assignment. **Table 4** also gives a chamber *appearance time* for each compound, defined as the time at which the signal for a given spectral feature exceeds the mean background signal plus three times its standard deviation. All compound assignments have been made using a combination of information, namely TOF-MS accurate

mass measurements, appearance time, subsequent temporal profile, and data available from the MCMv3.1 box model simulations (see Section 6.4.9).

Table 4: Most major VOC contributors to the gas phase as measured by CIR-TOF-MS. Measured m/z, actual 'unprotonated' compound mass, approximate peak signal intensity, appearance time and tentative assignments are included (MCM designations are given in parentheses where applicable).

Mass	Peak Signal / ncps	Tentative Assignment Name (MCM designation) /(Figure 6 identifier)	Appearance Time / Minutes							
Measured <i>m/z</i> .					Ex	perime	ent			
(Actual / Da)	.1.		1	2	3	4	5	6	7	
232.20 (231.20)	200	1,3,5-trimethyl-4-nitrooxy- 6,7-dioxa-bicyclo[3.2.1]oct- 2-en-8-ol (TM135BPNO3)/(L)	120	90	n/m	51	36	51	3	
214.15 (214.20)	200	TM135BPNO3 Fragment: MH ⁺ [- H ₂ O]	96	100	87	81	33	12	3	
185.20 (184.19)	300	 8-hydroxy-1,3,5-trimethyl- 6,7-dioxa-bicyclo[3.2.1]oct- 3-en-2-one (TM135OBPOH)/(P) 2-methyl-3-(1-methyl-3-oxo- but-1-enyl)-oxirane-2- carboxylic acid (TM135MUO2H) 	130	130	288*	108	24	60	15	
169.22 (169.20)	70	1,3,5-trimethyl-6,7-dioxa- bicyclo[3.2.1]oct-3-ene-2,8- diol (TM135BP2OH)/(O) Fragment: MH ⁺ [-H ₂ O]	36	93	n/m	69	36	42	3	
(168.19)		2-methyl-3-(1-methyl-3-oxo- but-1-enyl)-oxirane-2- carbaldehyde (TM135OXMUC)								
167.18 (166.17)	120	3,5-dimethyl- benzenecarboperoxoic acid (TMBCO3H)	147	177	n/m	81	114	63	n/m	
157.20 (156.18)	150	5-hydroxy-4-methyl-hept-3- ene-2,6-dione (C7M2CO5OH)	150	126	240	99	102	66	24	
155.18 (154.16)	120	4-methyl-hept-4-ene-2,3,6- trione (C7M3CO)	453*	171	n/m	111	183	129	30*	
153.22 (152.19)	100	(3,5-dimethyl-phenyl)- methyl-hydroperoxide (TMBOOH)	72	120	n/m	102	120	120	120*	
151.17 (150.17)	160	3,5-dimethylbenzoic acid (TMBCO2H)	105	84	465*	72	135	60	39*	
145.17	50	2-methyl-4-oxo-pent-2-	309	180*	n/m	141	81	249*	n/m	

Chapter 6				Anthropogenic Secondary Organic Aeroso							
Mass Massured	Peak Signal /	Tentative Assignment		Ap	opearan	ce Time	e / Minu	tes			
m/z	ncps	cps /(Figure 6 identifier)			Ex	perime	ent				
(Actual / Da)			1	2	3	4	5	6	7		
(144.13)		eneperoxoic acid (C5CODBCO3H)									
		2-hydroxy-2-methyl-3,4- dioxo-pentanal (C6CO3MOH)									
		2-oxo-propionic acid 1- methyl-2-oxo-ethyl ester (C23O3MCHO)									
143.19	120	Unidentified	366*	**	406*	129	78	75	30*		
141.18	140	Unidentified	126	111	**	132	138	75	60		
139.18 (138.16)	400	3,5-dimethyl-phenyl- hydroperoxide (DMPHOOH)	309*	78	**	51	3	66	3		
137.19 (136.19)	220	2,4,6-trimethyl phenol (TM135BZOL)/(D)	81	75	96	54	**	15	15		
		(3,5-dimethyl-phenyl)- methanol (TMBOH)									
(136.15)		m-xyloquinone									
136.09	400	Unidentified organic nitrate	114	132	141	87	45	96	n/m		
135.18 (134.18)	1000	3,5-dimethyl benzaldehyde (TMBCHO)/(W)	63	78	93	57	30	39	18		
(134.09)		2-hydroxy-2-methyl-3-oxo- propaneperoxoic acid (CHOMOHCO3H)									
(134.09)		2-hydroxy-3-oxo- butaneperoxoic acid (CO2H3CO3H)									
(134.09)		malic acid									
129.17 (128.13)	500	2-methyl-4-oxo-pent-2-enoic acid (C5CODBCO2H)	84	93	168	66	3	72	33		
		3-acetyl-2-methyl-oxirane-2- carbaldehyde (EPXMALKT)									
127.17	300	Related to Bicyclic Signals	90	90	144	96	99	57	27		
125.15 (125.10)	1200	Bicyclic Fragment: $[C_6H_5O_3]^+$	99	102	69	45	3	33	3		
123.17	400	Unidentified	**	**	183*	**	**	**	**		
119.18 (118.09)	200	2-hydroperoxy-2-methyl- malonaldehyde (C3MDIALOOH)	90	75	**	123	33	69	3*		
		Succinic acid									

Chapter 6			An	thropog	genic S	Second	ary Or	ganic	Aerosol	
Mass	Peak Signal / ncps	Tentative Assignment Name (MCM designation) /(Figure 6 identifier)	Appearance Time / Minutes							
measured <i>m/z</i>			Experiment							
(Actual / Da)			1	2	3	4	5	6	7	
117.14 (116.12)	140	3-hydroxy-pentane-2,4-dione (C5CO243OH)	174	129	183	84	42	81	12	
115.13 (114.10)	250	pentane-2,3,4-trione (C5CO234)	153	108	183	111	18	3	33*	
113.13 (112.08)	7400	methyl maleic anhydride (MMALANHY)/(AF)	15	15	33	15	9	3	6	
(112.13)		2-methyl-4-oxo-2-pentenal (C5MDICARB)/(R)								
(112.13)		3,5-dimethyl-3(2H)-2- furanone/(AF)								
(112.13)		3,5-dimethyl-5(2H)-2- furanone (MXFUONE)/(S)								
111.12 (110.04)	6000	3 methyl-5-methylidene-5- (2H) furanone	72	60	105	66	15	21	39	
109.15 (109.10)	400	TM135BPNO3 Fragment: MH ⁺ [-NO ₃ .3(CH ₃)O]	84	75	51	60	3	54	3	
103.11 (102.09)	150	2-hydroxy-2-methyl- malonaldehyde (C3MDIALOH)	150	126	**	126	93	12	27	
101.13 (100.07)	400	2,3-dioxobutanal	126	90	129	84	60	12	15	
99.12	160	Unidentified	183	171	n/m	177*	366	99	30*	
97.13	1000	Unidentified	72	78	102	81	51	9	33	
87.10	1200	Related to Bicyclic Signals	117	75	123	90	42	12	24	
85.11 (85.13) (84.07)	500	<i>m/z</i> 113 Fragment: MH ⁺ [-CO] butenedial	84	63	81	51	63	33	27	
77.07 (76.05)	1400	hydroxy acetic acid	99	135	168	90	36	63	15	
75.09 (74.08)	400	hydroxyacetone	141	66	147	105	72	66	3	
(74.04)		oxo-acetic acid (HCOCO2H)								
73.07 (72.06)	1600	methyl glyoxal (MGLYOX)/(Q)	36	30	39	15	9	36	15	
61.07 (60.05)	6000	acetic acid (CH3CO2H)/(X)	36	72	60	90	12	18	3	
(60.05)		glycoaldehyde								
(88.06)		pyruvic acid fragment								

Chapter 6			An	thropo	genic S	Second	ary Or	ganic A	Aerosol	
Mass	Peak	Tentative Assignment		Ар	pearan	ce Time	e / Minu	tes		
<i>m/z</i> (Actual / Da)	ncns	Name (MCM designation) /(Figure 6 identifier)	Experiment							
	перз		1	2	3	4	5	6	7	
(90.08)		lactic acid fragment								
59.08 (58.08)	1200	acetone	n/m	n/m	174	51	72*	207	27	
57.10 (57.07 / 57.11)	1000	carbonyl/hydrocarbon Fragment: $[C_3H_5O^+] / [C_4H_9^+]$	225	141	n/m	147	114	183	51	
47.01 (46.03)	600	formic acid/(Y)	198	105	69	72	72	252	**	
46.01 (46.01)	5000	PAN Fragment/organic nitrate: [NO ₂ ⁺]	102	105	105	72	93	72	51	
45.06 (44.05)	3500	methyl glyoxal Fragment acetaldehyde (CH3OOH)/(AE)	63	42	93	48	99	45	12	
43.04 (43.04 / 43.09)	5000	carbonyl/hydrocarbon Fragment: $[C_2H_3O^+] / [C_3H_7^+]$	63	18	69	57	3	3	0	
33.05 (32.04)	5000	methanol (CH3OH)/(AA)	105	141	399*	106	132	153	90	
31.03 (30.03)	1000	formaldehyde (HCHO)/(AC)	264	159	345*	132*	243*	249	27	

n/m = Compound not measured during specific experiment

* = Weak signal, high potential for error in appearance time

** = Signal below detection limit on 10 minute time scale, appearance time not reported

6.4.7.3 Behaviour of the Gas Phase Organics under High NO_x Conditions

As a focus for discussion, the evolution of the entire measured VOC system of experiment 6 is presented in **Figure 11**. General features of note include the appearance of most species within the first 50 - 100 minutes of the experiment, including many high mass oxidation products. The high NO_x photooxidation system of TMB is also characterised by a peak in concentration of the heavier species around the mid-point of the experiment (~ 200 - 300 minutes). The lower molecular mass features demonstrate a continual rise in intensity up to the end of the experiment.



Figure 11: (a) Evolution of the gas phase organic species during experiment 6 (VOC/NOx \sim 2:1). (b) Signal intensity (z-axis) scaled to 2000 ncps to reveal lower concentration features

Looking more closely at the features recorded by CIR-TOF-MS (in **Table 4** and **Figure 11**), it is possible to follow the system evolution as outlined in **Figure 9**. Two of the earliest compounds to appear in the oxidation chain are the ring-retaining compounds, 2,4,6-trimethylphenol (D) and 3,5-dimethylbenzaldehyde (W). Both 2,4,6-trimethylphenol and 3,5-dimethylbenzaldehyde were measured in the chamber as protonated parent ions (*i.e. m/z* 137 and 135, respectively); their temporal profiles as measured under the high NO_x conditions of experiment 6 are shown in **Figure 12**. During experiment 6, 2,4,6-trimethylphenol and 3,5-dimethylbenzaldehyde were measured to rise relatively rapidly to peak concentrations of approximately 2.5 and 7 ppbV, respectively. Following its concentration peak 3,5-dimethylbenzaldehyde was observed to reach a concentration plateau, whereas 2,4,6-trimethylphenol underwent significant decay. The rapid decay of 2,4,6-trimethylphenol was most likely due to it being oxidised at a greater rate than it was produced in the early chamber atmosphere, however, eventually steady state appeared to become established in its chemistry, with concentrations levelling to a plateau after ~ 120 minutes.



Figure 12: Temporal evolution of 3,5-dimethylbenzaldehyde (D.M.B.) and 2,4,6-trimethylphenol (T.M.P.) during high NO_x experiment 6. The black vertical line indicates the start of the 'dark phase' and the grey vertical line indicates the NO injection time.

As described in Section 6.4.7.1, the majority of mass transit through the TMB oxidation system occurs *via* addition of OH to the aromatic ring, followed by production of the trimethyl peroxide bicyclic radical (E) and its peroxy radical counterpart (K). The various subsequent pathways shown in **Figure 9** can lead to an array of O₂-bridged aromatic compounds (L – P). Within this work the first firm evidence for the existence of these O₂-bridged species is reported, along with documentation of their *real-time* evolution, as measured by the CIR-TOF-MS. As summarised in **Table 4**, peaks consistent with the O₂-bridged nitrate (L), diol (O) and ketone (P) were recorded at m/z 232, 169 and 185, respectively. Two fragment ions of the nitrate were also measured (at m/z 214 and 109), as was a signal tentatively assigned to be the aromatic ring fragment of the O₂-bridged species (m/z 125). No ion corresponding to the protonated O₂-bridged peroxide (M) was measured, indeed this comes as no surprise as organic peroxides are not well ionised by proton transfer. Comparison of the measured temporal profiles of the O₂-bridged species with simulations using the chamber box model incorporating detailed TMB degradation chemistry taken from the MCMv3.1, is discussed later in Section 6.4.9.

The concentration-time profiles of the measured O_2 -bridged bicyclic species are shown in **Figure 13(a)**. Due to relatively high levels of NO early in the experiment, the O_2 -bridged nitrate (L) was the first of the triumvirate to appear in the chamber, at ~ 10 – 50 minutes. The O_2 -bridged nitrate is formed in relatively high yield when compared to the other aromatic systems (Bloss *et al.*, 2005b). As the chamber matrix evolved and levels of HO₂ and RO₂ began to increase, the O_2 -bridged diol and ketone (and presumably the peroxide (M): see Section 6.4.9) were produced, appearing roughly together at ~ 40 – 60 minutes.





The primary bicyclic nitrate remained in a state of production whilst NO was present in the chamber, up to a peak near 250 minutes, followed by decay as its rate of loss *via* oxidation (and/or loss to the aerosol, see Section 6.4.10) overtook its rate of production as the precursor TMB was consumed and as chamber $[NO_x]$ fell towards zero. The O₂-bridged diol and ketone followed a similar profile to the nitrate early in the experiment but continued on a steady rise in concentration as HO₂ and RO₂ became more prevalent within the chamber.

According to the mechanism outlined in **Figure 9**, the O₂-bridged ketone (P) and alkoxy radical (N) act as conduits for further mass transit through the oxidation system. Both compounds are liable to undergo ring cleavage to yield an array of lower molecular mass oxygenated and nitrated compounds, the first and most abundant of which are methyl glyoxal (Q) and 3,5-dimethyl-5(2H)-2-furanone (S), measured as protonated parent ions at m/z 73 and 113, respectively. A variety of oxygenated species, all of nominal mass 112, appear in the TMB oxidation chain and were measured collectively at m/z 113 (*i.e.* protonated) by CIR-TOF-MS. Along with 3,5-dimethyl-5(2H)-2-furanone, laboratory studies have identified these to be the furanones, 3,5-dimethyl-3(2H)-2-furanone (AF) and 3-methyl-furan-2,5-dione (methyl maleic anhydride) (AC), and the δ -dicarbonyl, 2-methyl-4-oxo-2-pentenal (R) (Smith *et al.*, 1999). Also observed here in the chamber matrix was a fourth furanone, 3-methy-5-methylidene-5(2H)-2-furanone, measured at m/z 111 (AE) (Smith *et al.*, 1999).

As can be seen from observation of **Figure 13(b)**, both methyl glyoxal and the m/z 113 oxygenates were amongst the first compounds to appear in the chamber (after ~ 3 – 30 minutes), being formed *via* a series of highly reactive radical intermediates during the early, NO_x dominated stages of the high NO_x experiment. The concentrations of methyl glyoxal, 3- methy-5-methylidene-5(2H)-2-furanone and the m/z 113 compounds increased rapidly from 'lights on', to peaks of ~ 110, 30 and 65 ppbV, at roughly 320, 450 and 170 minutes, respectively. Eventually the chemistry generating these oxidation products reached steady state, as indicated by the observed concentration plateaus. Throughout the experiment methyl glyoxal, 3 methyl-5-methylidiene-5(2H)-2-furanone and the m/z 113 species were amongst the most dominant features of the mass spectrum, being produced first *via* the alkoxy radical (N) and the bicyclic nitrate (L), and then subsequently through the HO₂ and RO₂ controlled pathways. At their concentration peaks the (mass percent) VOC yields (Y_{VOC}) for these compounds were estimated to be ~ 22, 8 and 40 %, respectively. Clearly then, these compounds alone account for a significant fraction of mass within the 1,3,5-TMB oxidation system.

As the oxidation process progressed a multitude of organic species with a variety of functional groups were formed within the chamber, many of which were detected by CIR-TOF-MS (see Table 4). Figure 13(c) gives the concentration-time profiles for three such compounds formed following ring cleavage, the multifunctional tertiary products 2-methyl-4oxo-pent-2-enoic acid (CO(CH₃)CH=C(CH₃)COOH) and 3-acetyl-2-methyl-oxirane-2carbaldehyde (CH₃C(O)CH(-O-)C(CH₃)CHO) (measured together at m/z 129) and hydroxy acetone (m/z 75). Collision energy studies have shown that 2-methyl-4-oxo-pent-2-enoic acid also undergoes a small amount of dehydration following proton transfer to yield a fragment of m/z 111. Also given in Figure 13(c) is the signal measured at m/z 43, a generic marker for carbonyls using the PTR-MS technique (see Chapter 3). All such later stage oxidation products displayed similar behaviour, a steady rise to plateau roughly coinciding with peak aerosol mass. Strong signals corresponding to nitrated VOCs (even m/z number and low mass excess) were also measured further down the oxidation chain; these included peroxy acetyl nitrate (PAN) (fragment ion at m/z 46 (Hansel and Wisthaler, 2000), see Figure 17(b) for temporal profile) and two unidentified compounds of m/z 96 and 136 (shown below in Figure 19). Signals corresponding to pyruvic acid (m/z 89) and formaldehyde (m/z 31), two potential monomer units for the TMB oligomer (Kalberer et al., 2004), were also measured in all experiments.

Further inspection of Table 4 shows that a number of other simple organic acids were observed in the gas phase, including hydroxy acetic acid (m/z 77), acetic acid (m/z 61) and formic acid (m/z 47). As shown in Figure 13(d) and Table 4, the various late stage acids appeared in the chamber $\sim 20 - 200$ minutes after lights on. Concentrations of hydroxy acetic acid rose steadily to a peak of around 30 ppbV at 400 minutes ($Y_{VOC} = 6$ %), followed by a steady decline due to gas phase oxidation, deposition and potential loss to the aerosol. Both formic and acetic acid levels continued to rise throughout experiment 6 as the system became more oxidised, with concentrations eventually reaching 100 - 120 ppbV (Y_{VOC} ≈ 11 and 16 %, respectively). It should be noted that during 'blank' experiments (no precursor VOC), small quantities of formic and acetic acid was observed in the gas phase following liberation from the illuminated chamber walls. After \sim 7 hours of blank experiment \sim 10 ppbV of both formic and acetic acid was measured, hence concentrations quoted here constitute an upper limit and should be considered with care. However, Fisseha and colleagues (Fisseha et al., 2004) recently recorded similar gas phase concentrations of formic acid during TMB photooxidation (~ 80 ppbV after 9 hours), along with significant levels within the aerosol (~ 15 μ g m⁻³ at peak aerosol concentration). They presented lower acetic acid concentrations

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than were measured here (\sim 30 ppbV), with differences most likely explained by potential contribution to mass channel 61 from other species in the CIR-TOF-MS measurements (including fragment ions derived from other organic acids).

6.4.7.4 Variation of the VOC/NO_x Ratio under High NO_x Conditions

When NO_x was initially introduced only in the form of NO (experiment 2), the distribution and variety of ions within the mass spectrum and their concentration-time profiles were generally very similar to those of other experiments with initial VOC/NO_x ~ 2:1. The main exception to this was a delay in the appearance times of most compounds, corresponding to the time required to liberate HONO and NO₂ from reactions on the chamber walls and hence for the radical chemistry to initiate. Also, the oxidation products reached higher peak concentrations due to the enhanced level of starting material, but ultimately achieved similar mass yields to the other experiments of VOC/NO_x ~ 2:1 (see **Table A6.2** in the Appendix). The behaviour of the VOC component of the chamber differed more significantly when the VOC/NO_x ratio was reversed to a value of ~ 1:2. The most obvious point of note was that despite generally exhibiting similar temporal behaviour to other high NO_x experiments, the oxidation products of the *reverse* system took significantly longer to appear and achieve peak concentrations.

6.4.7.5 Variation of the VOC/NO_x Ratio, Low NO_x Conditions

The low NO_x experiments conducted here (*i.e.* experiments 5 and 7, VOC/NO_x ~ 16:1) were significantly different to the high NO_x experiments not only in terms of the aerosol phase, but also in terms of the composition and temporal behaviour of the gas phase VOC matrix. Along with exhibiting significantly earlier nucleation events, due in part to the presence of the HONO radical source, experiments 5 and 7 were also characterised by the much earlier appearance of all gas phase VOC oxidation products when compared to other experiments, as can be seen in **Table 4**.

Figures 14 and **15** show that once present within the chamber, the TMB oxidation products exhibited significantly different temporal behaviour under low NO_x conditions when compared to other experiments. The majority of the primary oxidation products were observed to increase in concentration more gradually from 'lights on' to a concentration plateau, rather than a distinct peak. Consequently, the point of maximum concentration often occurred later than in other experiments, *e.g.* methyl glyoxal (*m*/*z* 73) and the *m*/*z* 113 compounds reached maxima around 50 – 70 minutes later than in experiment 6, achieving concentrations of ~ 50 and 20 ppbV, respectively. Correspondingly, the later stage oxidation

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products also presented different temporal profiles. As seen in **Figure 15(c)** and **(d)** the tertiary products presented more linear growth profiles early in the experiment, being produced more rapidly due to the presence of an OH source. The 'start-up' lag seen in other experiments, corresponding to the time required to establish the OH cycle was absent. During low NO_x experiments, the tertiary products were often characterised by linear profiles due to a roughly constant level of oxidant.



Figure 14: Temporal evolution of 3,5-dimethylbenzaldehyde (D.M.B.) and 2,4,6-trimethylphenol (T.M.P.) during low NO_x experiment 7. The black vertical line indicates the start of the 'dark phase' and the grey vertical line indicates the NO injection time.

Most VOC yields (determined for the calibrated compounds) during the low NO_x experiments were similar in magnitude to those of the high NO_x experiments of VOC/NO_x ~ 2:1, with some significant exceptions. The hydroxy acetic acid, acetic acid and formic acid yields obtained during low NO_x experiments were on average significantly larger than those of high NO_x experiments, *i.e.* 14, 33 and 49 % compared to 4, 15 and 13 %. Furthermore, the yields of the O₂-bridged compounds were also enhanced under low NO_x relative to high NO_x conditions; however, discussion of this is reserved for Section 6.4.10. Yields for methyl glyoxal and the *m*/*z* 113 compounds were slightly lower under low NO_x conditions, being ~ 20 and 30 %, respectively.





6.4.7.6 Elucidating the Gas Phase Oxidation Mechanisms

In order to elucidate the chemical mechanism underlying the TMB oxidation system, at the conclusion of certain experiments chamber lights were switched off and the total chamber ozone was titrated from the system with the addition of excess NO to the matrix. During experiments 6 and 7 the chamber lights were switched off at 460 and 550 minutes, respectively, with the addition of NO some 70 and 10 minutes later. Approximately 200 ppbV NO was introduced into the chamber during experiment 6 and approximately 100 ppbV NO was introduced during experiment 7. The effect of this 'dark phase' on the inorganic components of the matrix and the VOCs for experiments 6 and 7 can be seen in Figure 2(a) and Figures 12 - 15.

During the dark phase the photochemically driven pathways became 'switched off' as photolysis and OH production from both ozone and HONO ceased. Also, as the chamber ozone was titrated away, chemistry occurring *via* ozonolysis reactions became negligible. Consequently, the system chemistry was switched from a regime where reactions of RO₂ were controlled by OH and HO₂ to one in which the majority of RO₂ species were removed from the system following reaction with the injected NO. This resulted in a 'burst' in production of NO₂ and, to a minor extent, some nitrogenated and carbonyl compounds. The major fraction of the additional NO₂ measured during the dark phase clearly results from the NO + O₃ \rightarrow NO₂ + O₂ reaction. However, it is likely that NO₂ will also be liberated from the thermal decomposition of reservoir, PAN type compounds and initially from RO₂ + NO reactions. Manipulating the chemistry in this manner and observing the resultant effect on the VOC evolution provides insight into the chemistry involved.

The concentration-time profile of the peroxide bicyclic ketone, seen in **Figure 13(a)**, began to fall significantly when chamber lights were switched off, suggesting that its production must result from reactions involving RO_2 , HO_2 and OH as detailed in **Figure 9**. As the photolytic formation of radicals was 'switched off' under dark phase conditions, production of the bicyclic ketone was no longer possible and its chamber concentration began to decay due to a combination of: the instability of this species, its reaction with NO_3 and its partitioning to the aerosol phase and chamber walls. Conversely during the dark phase, the fall in concentration of the bicyclic nitrate was arrested before levelling off to a plateau as its major loss processes (*i.e.* photolysis and reaction with OH) were switched off.

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Following the addition of NO to the chamber a significant increase in the signal measured at m/z 113 was observed. This response is essentially a consequence of the parent O₂-bridged species decomposing through ring opening pathways to yield various (isobaric) oxygenated products. For example, following the photooxidation mechanism outlined in **Figure 9**, it is likely that the peroxide bicyclic ketone decays *via* several intermediate steps to 3,5-dimethyl-5(2H)-2-furanone, verifying the significant contribution made from further reaction of the bicyclic ketone to the signal measured at m/z 113.

The findings presented here highlight the importance of reaction routes involving both the bicyclic ketone and nitrate compounds during the early stages of the experiment in the production of other potentially crucial SOA forming oxidation products (see Section 6.4.10).

6.4.8 Principal Component Analysis

As noted by Baltensperger *et al.* (Baltensperger *et al.*, 2005) the VOCs observed in the oxidation of TMB can be separated into several distinct categories according to their temporal profiles. In order to better identify trends within the time series, a Principal Component Analysis (PCA, (Naes and Martens, 1988)) was carried out for each experiment. PCA is an exploratory data analysis technique that will summarise correlated time behaviour of certain masses into a set of principal components. Each principal component consists of a pair of vectors: the scores vector (depicting time related behaviour) and the loadings vector (representing how strongly this behaviour is represented on each of the masses). The PCA algorithm will first find the strongest collective time trend in the data and its associated mass spectrum, followed by the second strongest and so on. Consequently, it may be possible to represent key trends in the whole experiment with only a few principal components. Ultimately the PCA can be used to identify which compounds are related in the oxidation system.

Generally during each of the PC analyses the majority of the temporal variability within the VOC data was captured by the first three principal components (PC1 accounted for ~ 75 – 95 % of the variance, PC2 ~ 4 – 22 % and PC3 only ~ 0.6 – 1.5 %). As an example of the high NO_x data, the scores and loading plots obtained from a PCA conducted for experiment 6 are given in **Figure 16(a)**. The scores plots generated for PC1 for each high NO_x experiment exhibited roughly the same pattern, *i.e.* a sigmoidal rise to peak and plateau. The most significant masses comprising the corresponding loadings vector were m/z 43 (carbonyl marker), 46 (PAN marker), 61 (acetic acid), 73 (methyl glyoxal), 77 (hydroxy acetic acid), 87 (unidentified), 111 (3-methyl-5-methylidiene-5(2H)-2-furanone) and 185 (the O₂-bridged 237

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ketone). All of these masses (except m/z 185) constitute secondary or tertiary oxidation products of the TMB system (although methyl glyoxal also constitutes a primary product). The PAN and acetic acid signals were the greatest contributors towards the first principal component in all high NO_x experiments, suggesting a strong contribution to the chamber matrix from these compounds.



Figure 16: Principal component analysis conducted on VOC data for (a) experiment 6 (high NO_x, VOC/NO_x ~ 2:1) and (b) experiment 7 (low NO_x, VOC/NO_x ~ 17:1). Percentage variance captured: PC1 = 78.0%, PC2 = 19.7% and PC3 = 1.9% for experiment 6 and PC1 = 90.0%, PC2 = 8.0% and PC3 = 0.6% for experiment 7.

The scores generated for PC2 were characterised by a rapid rise to peak followed by a similarly steep decay towards steady state. The most significant corresponding loadings were m/z 45 (methyl glyoxal fragment), 73 (methyl glyoxal), 85 (m/z 113 fragment), 113 (isobaric furanone and δ -dicarbonyl ring opening products), 125 (bicyclic fragment), 135 (3,5-dimethyl
benzaldehyde), 109, 214 and 232 (bicyclic nitrate). These compounds constitute the primary oxidation products of the TMB oxidation system. The m/z 73 and 113 signals were the greatest contributors towards the second principal component in all high NO_x experiments, demonstrating the importance of these compounds early within the chamber atmosphere. PC3 accounts for very little of the variance within all experiments, only ~ 1 % and is composed mainly of three significant loadings, which correspond to masses 57, 61 and 113.

The PCA for low NO_x experiment 7 is shown in Figure 16(b). Comparison of the scores plots with those of experiment 6 (Figure 16(a)) demonstrates the dramatic differences in the temporal behavior of the oxidation products, with no evidence of an incubation period in the VOC chemistry, *i.e.* the primary, secondary and tertiary products of oxidation appear in the system early on in the experiment. PC1 for the low NO_x system is primarily composed of the same compounds as in the high NO_x system, but with a different distribution of abundances. Under low NO_x conditions m/z 45, 46, 73, and 111 all show significantly lower contributions to the overall secondary products, although m/z 61 remains the greatest contributor, suggesting a more dominant role for acetic acid in the absence of NO_x. In contrast to this, PC2 is composed of a slightly different set of masses with distinctly different abundances. Masses 45, 73, 97 (unidentified), 125, 135 and particularly 111 all give stronger contributions to the overall signal than in the high NO_x experiments. Furthermore, the second principal component also contains contributions from masses 101 (unidentified), 129 (organic acid), 139 (potential organic peroxide), 169 (O_2 -bridged diol) and 185, contrary to the high NO_x These findings suggest that although ultimately the same end stage oxidation system. products are reached, during the early stages of the low NO_x experiments (*i.e.* approximately around the time of nucleation), the system chemistry is somewhat different, generating an organic gas phase matrix that is more strongly dominated by the primary O₂-bridged bicyclics, methyl glyoxal and the m/z 113 compounds. This finding implicates therefore, that such species may play some role in the formation of aromatic SOA.

6.4.9 Model Simulation

The TMB chamber box model described in Section 6.3.5 was run using specific initialisation parameters in order to simulate (high NO_x) experiment 6 and (low NO_x) experiment 7 (Rickard, 2007). The box model simulated concentration profiles for a number of the most significant gas phase species are presented in **Figures 17** and **18**, along with corresponding experimental measurements.

6.4.9.1 Modelled 1,3,5-TMB and Inorganic Species

Figure 17(a) and Figure 18(a) present the modelled and measured profiles for TMB, NO, NO₂ and O₃. From first inspection of these figures it is clear that the model is able to simulate the oxidation of the precursor TMB, with some level success. The only minor discrepancy between modelled and measured TMB occurs late during each experiment, where after ~ 345 and 305 minutes for experiments 6 and 7, respectively, the model slightly over predicts measured TMB values (indicating an under prediction of the oxidising capacity of the system). For experiment 7, the ratio of modelled/measured TMB was at most ~ 1.7 after ~ 305 minutes, whereas for experiment 6, the over prediction in TMB concentration was minor (modelled/measured ratio at most ~ 1.1).

From Figures 17(a) and 18(a) it is also clear that the chamber box model was reasonably successful in the simulation of measured NO during both experiments. However, the modelled and measured NO₂ and O₃ concentration profiles appear only to be in agreement up to the point of peak NO₂ concentration, which is predicted well, e.g. for experiment 6 the modelled and measured peak NO₂ concentrations were ~ 200 and 190 ppbV, respectively, occurring in both cases at ~ 110 minutes. After the NO₂ peak the modelled and measured profiles diverge, with the model over predicting measurements throughout the remainder of the experiment. Ultimately, modelled NO₂ reaches minimal concentrations around 90 minutes later than measurements during experiment 6. At most the modelled/measured NO_2 ratio was ~ 2.3 during both experiments 6 and 7. The over prediction of modelled NO₂ was matched by a concomitant over prediction in modelled O₃. Again, there is good agreement between the simulation and measurements during the early stages of both high and low NO_x scenarios, but after the peak in NO₂ concentration, the O₃ profiles diverge. For experiments 6 and 7, the general behaviour of both simulated and measured O_3 profiles are similar, *i.e.* rise to peak followed by decay in experiment 6 and continual rise during experiment 7, however concentrations achieved, and the point of maximum concentration during experiment 6 are somewhat dissimilar. Under high NO_x conditions the modelled peak in O₃ concentration occurs some 50 minutes later than the measured equivalent, with a modelled/measured concentration ratio of ~ 1.2 .





1,3,5-TMB chemical reaction scheme extracted from MCMv3.1 (See legend for compound key)

Similar findings regarding the over prediction of simulated NO₂ and O₃ concentration were reported in a comparable study by Bloss *et al.* (Bloss *et al.*, 2005a; Bloss *et al.*, 2005b). Bloss *et al.* compared the measurements obtained from a series of simulation chamber experiments with the output of a box model similar to that employed here, which also incorporated oxidation mechanisms extracted from the MCM. It was found that for substituted aromatic compounds, the modelled NO₂ and O₃ concentrations were in excess of measured values, as was observed within the current study. The authors attributed the greater simulated O₃ concentrations directly to the larger simulated NO₂ concentrations, which they suggested, resulted from an under prediction in the rate of conversion of NO to NO₂. Bloss *et al.* linked the low NO conversion rate to an observed under prediction in the simulated rate of VOC oxidation (with respect to measurements), and hence a lower modelled (OH) oxidant level.

The discrepancies between modelled and measured NO₂ and O₃ in the current study are not as extreme as those reported by Bloss *et al.*, and as was described above, simulated and measured TMB and NO data are in reasonably good agreement here, under both high and low NO_x conditions. Also, as shown in **Figures 17(b)** and **18(b)**, during the initial stages of the experiments there is reasonably good agreement between the modelled and measured data for $HO_2 + RO_2$ and inferred OH (from the decay of TMB). Hence, following similar logic to that of Bloss *et al.*, it would seem that in the current study there exists an under prediction in modelled OH levels towards the latter half of the experiment.

As can be seen from comparison of **Figures 17** and **18** with **Figure 4**, the majority of the discrepancies observed between modelled and measured data occur after the nucleation event has taken place; indeed the magnitude of all discrepancies noted appear to increase with total aerosol volume. This finding seems to imply therefore, that SOA may constitute an additional heterogeneous OH radical source (Rickard, 2007).

In a recent study by Metzger *et al.* (Metzger *et al.*, 2008a), a modified version of the chamber box model (described in Section 6.3.5) was employed alongside similar chamber experiments (also conducted at the PSI facility), in order to evaluate the MCMv3.1 degradation scheme for TMB. Metzger *et al.* observed somewhat similar discrepancies between modelled and measured data to those noted here, as well as significantly higher measured HONO concentrations in comparison with the model. In order to account for the higher measured HONO concentrations, Metzger and colleagues included an additional light induced, heterogeneous NO₂ to HONO conversion reaction within the chamber specific auxiliary Chapter 6

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mechanism. The inclusion of this additional HONO formation pathway improved model performance for all experiments. Such a strong, light induced reaction was not included in the simulations of Bloss *et al.* (Bloss *et al.*, 2005a; Bloss *et al.*, 2005b)

6.4.9.2 Modelled Gas Phase Organic Oxidation Products

Figures 17 and **18(c)** and **(d)** give the modelled and CIR-TOF-MS measured profiles of several major 1,3,5-TMB oxidation products, *i.e.* 3,5-dimethylbenzaldehyde (9), 2,4,6-trimethylphenol (10), methyl glyoxal (11), the O₂-bridged ketone (12), the m/z 113 compounds (13) and the O₂-bridged nitrate (14); **Figures 17(b)** and **18(b)** also give the modelled and measured profiles for PAN. In most cases the modelled and measured profiles are in good agreement in terms of temporal behaviour and concentration magnitude. However, one particular discrepancy between simulated and measured profiles, observed at the start of both experiments 6 and 7, is the generally more rapid rise in the measured concentration of 3,5-dimethylbenzaldehyde, 2,4,6-trimethylphenol, and to a minor extent, the m/z 113 compounds, when compared to simulated values. This result implies a slight over prediction in the loss rate of these primary products within the model during the initial stages of the experiment.

A further difference between modelled and measured data is observed in the magnitude of the concentration plateau of 2,4,6-trimethylphenol and the m/z 113 compounds under high NO_x conditions. The measured m/z 113 compounds are observed to decay to a plateau at a slower rate than as predicted by the model; moreover the measured concentration plateau is roughly two fold greater than that of the simulation. One potential reason for this may be that the MCMv3.1 includes only three of the four compounds believed to occupy the m/z 113 channel; the formation of 3,5-dimethyl-3(2H)-2-furanone is not considered (Smith *et al.*, 1999). In order to ascertain the contribution of 3,5-dimethyl-3(2H)-2-furanone to the m/z 113 channel in this regard, further, speciated measured m/z 113 compounds in the latter half of experiment 7, suggesting that under low NO_x conditions there may be potential under prediction in the simulated loss of either methyl maleic anhydride, 2-methyl-4-oxo-2-pentenal or 3,5-dimethyl-5(2H)-2-furanone.

Figures 17(b) and (d) and Figures 18(b) and (d) show excellent agreement between the simulated and measured profiles for methyl glyoxal, PAN and the O_2 -bridged compounds under different experimental VOC/NO_x conditions. Unfortunately, as will be discussed in detail below, no reliable calibration factor has yet been derived for PAN or the O_2 -bridged

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compounds. Consequently, the PAN data have been given in signal units, *i.e.* ncps, and the O_2 -bridged compounds have been given in mixing ratio units following calibration using a surrogate scaling factor. Although the surrogate calibration factor for the O_2 -bridged compounds is not expected to give an accurate concentration, it provides a rough guide. As a result, it is not possible to comment on the magnitude of the measured concentration of the O_2 -bridged ketone and nitrate, however, the excellent correlation observed in their temporal profiles with respect to the simulated data, provides further evidence to support their respective identity assignments. The high level of correlation achieved between the simulated and measured organic oxidation products, proves that MCMv3.1 is doing a good job in simulating the photochemical degradation of TMB under the experimental conditions applied. The measured and modelled profiles of the O_2 -bridged nitrate do exhibit some differences however, after ~ 280 and 180 minutes, respectively during experiments 6 and 7; these findings will be discussed in the Section 6.4.10, along with further results from the chamber box model regarding organic hydroperoxide formation.

6.4.10 Identification of Compounds Contributing to SOA Formation and Growth Although in most chamber experiments a large fraction of SOA mass remains to be identified, recent studies into the composition of aerosol formed from aromatic compounds has highlighted the presence of a discrete set of organic species originating directly from gas phase oxidation of the precursor. Of these compounds previously identified within the aerosol, several were measured (or their analogous counterparts were measured) in the gas phase during the present study, including 3,5-dimethylbenzaldehyde (Hamilton *et al.*, 2003) from the ring retaining route, several of the isobaric m/z 113 compounds (Forstner *et al.*, 1997; Hamilton *et al.*, 2003) and methyl glyoxal (Kalberer *et al.*, 2004) from the ring opening route, along with the later stage decay products hydroxy acetone, glycoaldehyde (Cocker III *et al.*, 2001), formic acid and acetic acid (Fisseha *et al.*, 2004).

For the gas phase species to take part in the SOA *formation* process, first of all their presence in the chamber must coincide with or precede the onset of nucleation. By the time nucleation had occurred in the high NO_x experiments, the majority of the measured organic species had appeared within the chamber and hence (where possible) were available for partitioning. In contrast, a more select group of only thirteen spectral features were present in the mass spectra of both low NO_x experiments prior to nucleation, and hence available to partition to the aerosol. This result implies that the early stage aerosol in the low NO_x systems may be compositionally less diverse. Several of the 'early' compounds of the low NO_x system were observed within the first few minutes of experiment: these include the O₂-bridged nitrate (at m/z 232, 214 and 109), O₂-bridged diol (m/z 169), the fragment ion of the O₂-bridged compounds (m/z 125), methyl glyoxal (m/z 73) and the m/z 113 ring opening compounds. Other notable cases of early appearance include the O₂-bridged ketone, 3,5-dimethyl benzaldehyde, hydroxy acetic acid, acetic acid and the carbonyl marker (m/z 185, 135, 77, 61 and 43, respectively). As some VOCs are not easily ionised using the proton transfer reaction technique (*e.g.* organic peroxides) and as detection limits may have excluded some compounds from observation, it is not possible at present to conclusively assign the nucleating species using only measured data. However, with only the above listed compounds measured before nucleation in every experiment, it is possible that at least some of these will be of importance in the SOA formation process.

The appearance times of most of the oxidation products observed during low NO_x experiment 5 were slightly greater than in the corresponding low NO_x experiment 7, as was the time of the nucleation event. Although nucleation during experiment 7 was influenced by the presence of the inorganic seed particles, the slightly higher [OH] (resulting from minor inaccuracies in the HONO input magnitude between experiments) would have facilitated faster oxidation and therefore earlier SOA formation. A similar trend was also noted when the VOC/NO_x ratio was set to ~ 1:2. Here the appearance times of most of the TMB oxidation products were significantly delayed with respect to all other experiments. For example the m/z 113 compounds appeared ~ 30 minutes later, and several of the signals observed in mass channels representative of the primary bicyclic compounds (e.g. m/z 214 and 125) up to a full hour later than in experiment 6 (see Table 4 for further comparison). Subsequently many compounds reached their peak concentrations later than in other experiments, including methyl glyoxal, the m/z 113 oxygenates and the O₂-bridged nitrate, which reached their respective peaks 170, 80 and 80 minutes later than in experiment 6. This delay and subsequent shift in concentration peak coincided with the delay in nucleation described earlier, further implicating the importance of such compounds in aerosol formation and growth.

As noted above, in comparison with the high NO_x system, the low NO_x system was characterised by enhanced yields for certain gas phase species, including several organic acids. Hydroxy acetic acid, acetic acid and formic acid yields during the low NO_x experiments were on average ~ 3.5, 2.2 and 3.7 times larger than during the high NO_x experiments of VOC/NO_x ~ 2:1, and 1.5, 2.8 and 6.8 times larger than during high NO_x

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experiment 3 of VOC/NO_x ~ 1:2. As experiment 3 was conducted with the same initial TMB concentration as the two low NO_x experiments, concentration-dependent yield artefacts suggested by some authors can be ruled out (Ng *et al.*, 2007).

Considering that these organic acids were available in the gas phase matrix from early on in all experiments, it is possible that their enhanced gas phase yields were at least in some part responsible for the observed increase in aerosol yields obtained under low NO_x conditions, particularly in light of recent reports concerning the importance of organic acids in the composition of SOA. For example, Fisseha et al. (2004) have shown that around the point of maximum aerosol number density, organic acids comprised as much as 43 % of aerosol mass. As well as simply being detected in the aerosol phase, evidence has come to light implicating that such organic acids may become incorporated into polymer-like structures found within SOA (Gross *et al.*, 2006; Kalberer *et al.*, 2006). Other findings published recently by various authors indicate that an acidic environment is important (but not necessarily a prerequisite) for the formation of such polymeric species *via* various mechanistic pathways (Jang and Kamens, 2001; Czoschke et al., 2003; Limbeck et al., 2003; Gao et al., 2004; Tolocka et al., 2004; Northcross and Jang, 2007; Surratt et al., 2007; Verheggen et al., 2007). However, as noted above, in the current study no distinct difference in aerosol yield was observed between the homogeneous nucleation experiment (5) and the acid-seeded experiment (7). It would seem reasonable to assume, therefore, that if enough SO₂ was present to cause an acid seed effect and that the observed enhancement in aerosol yield is related to the enhancement in yields of the gaseous organic acids, then the levels of acids produced under low NO_x conditions were large enough to facilitate any acid-catalysed polymerisation without the need for the inorganic acid surface. Alternatively, the organic acids may contribute to SOA mass without involvement in additional acid-catalysed polymerisation (*i.e.* addition of the COOH functional group brings about a significant reduction in the vapour pressure of a compound, see Chapter 7).

With no calibration method or reliable kinetic information available for the primary bicyclic compounds, it is not possible at present to derive their absolute concentrations or yields. However, pseudo yields may be derived by applying the CIR-TOF-MS sensitivity for a structurally similar compound, and in this instance *m*-tolualdehyde was employed. Regardless of the absolute values obtained, a ratio of the yields for the low *versus* high NO_x experiments can be used to infer the importance of the primary bicyclic species in the SOA formation/growth process. Using data from experiments 6 and 7, the ratio (experiment 7:experiment 6) of pseudo yields obtained for the O₂-bridged nitrate was 1.36, suggesting a

small enhancement in the production of this compound under low NO_x conditions. The corresponding ratios for m/z 169 and 185 were 4.83 and 2.89, respectively, indicating much stronger production of the O₂-bridged diol and the O₂-bridged ketone in the absence of NO_x. Similar yield ratios were obtained for the measured O₂-bridged compounds when comparing high and low NO_x experiments with the same starting concentration of TMB (*i.e.* experiments 3 and 7, respectively), hence again any concentration-dependent yield artefacts can be ruled out.

As with the organic acids, the increased yield of the O_2 -bridged compounds could explain the enhanced SOA yield observed under low NO_x conditions, particularly when supported by evidence of their appearance in the chamber prior to nucleation in each experiment. Furthermore, modelling studies by Stroud *et al.* (Stroud *et al.*, 2004) and Johnson *et al.* (Johnson *et al.*, 2005) have shown that the analogous O_2 -bridged nitrate (as well as other multi-functional O_2 -bridged products) in the toluene system and the O_2 -bridged ketone (as well as other 5 and 6 membered ring compounds bearing nitrate and hydroperoxide functionalities) in the TMB system, are liable to undergo partitioning to the aerosol phase and make a significant contribution to simulated SOA mass.

Using the methodology applied by Ng *et al.* (Ng *et al.*, 2006) it is possible to obtain further information regarding which species contribute to SOA growth *via* close inspection of the VOC time series profiles. The concentration peaks of the O_2 -bridged nitrate, the unidentified organic nitrate at m/z 136 and the isobaric m/z 113 oxygenates roughly coincide with the nucleation event. Indeed, it was observed that a shift in the time at which these compounds achieved their respective concentration peaks, was matched by a corresponding shift in the time of nucleation. Subsequently, the period over which these species were 'lost' from the gas phase was coincident with the period over which the aerosol was observed to grow. The high level of correlation observed between VOC consumed (or 'reacted') after peak concentration and SOA mass 'produced' (up to the point of maximum mass) for the O_2 -bridged nitrate, the m/z 136 organic nitrate and the isobaric m/z 113 compounds is shown in **Figures 19 – 22**.



Figure 19: (a) Temporal evolution of the O₂-bridged nitrate (m/z 232) (solid blue line) during experiment 6 (high NO_x). Plot includes total amount of m/z 232 formed (dashed green line) and total amount lost (red circles). Also included is an overlaid profile of SOA mass (solid black line). (b) Correlation between m/z 232 mass lost and SOA mass formed (up to the point of peak mass) for experiment 6. Line fit coefficients quoted \pm one standard deviation.



Figure 20: (a) Temporal evolution of the unidentified nitrate of m/z 136 (solid blue line) during experiment 6 (high NO_x). Plot includes total amount of m/z 136 formed (dashed green line) and total amount lost (red circles). Also included is an overlaid profile of SOA mass (solid black line). (b) Correlation between m/z 136 mass lost and SOA mass formed (up to the point of peak mass) for experiment 6. Line fit coefficients quoted \pm one standard deviation.



Figure 21: (a) Temporal evolution of the m/z 113 compounds (solid blue line) during experiment 6 (high NO_x). Plot includes total amount of m/z 113 formed (dashed green line) and total amount lost (red circles). Also included is an overlaid profile of SOA mass (solid black line). (b) Correlation between m/z 113 mass lost and SOA mass formed (up to the point of peak mass) for experiment 6. Line fit coefficients quoted \pm one standard deviation.

The good correlation observed in **Figure 19** between gas phase VOC mass lost and SOA mass produced indicates that the O₂-bridged nitrate contributes to SOA growth, either by direct partitioning or *via* further its reaction generating condensable products. Through comparison of **Figure 19(b)** with **Figure 22(a)** it is clear that the relationship between the quantity of the O₂-bridged nitrate lost and SOA mass produced under high NO_x conditions (experiment 6) was similar to the relationship observed under low NO_x (experiment 7). A steeper line fit obtained for the low NO_x experiment suggests more rapid SOA growth with respect to expenditure of the O₂-bridged nitrate in the absence of NO_x (see **Figures 19** and **22** for line fit coefficients). The presence of a non-zero intercept on the ordinate axis (~ 16 and 19 µg m⁻³ for experiments 6 and 7, respectively) implies that some quantity of SOA mass had formed before any contribution to aerosol growth from the O₂-bridged nitrate.



Figure 22: Correlation between mass of VOC lost and mass of SOA formed (up to the point of peak mass), for (a) the O_2 -bridged nitrate, (b) the m/z 136 organic nitrate and (c) the m/z 113 compounds during experiment 7 (low NO_x). Correlation coefficients quoted \pm one standard deviation.

Correlation plots for loss for the m/z 136 organic nitrate and the m/z 113 oxygenates under low NO_x conditions were comparable in nature to those of the bicyclic nitrate (see **Figure 22**). Similarly therefore, under low NO_x conditions it appears that the nitrate of m/z 136 and one or more of the compounds measured at m/z 113 contributed to SOA growth once some quantity of aerosol mass had formed. As shown in **Figures 20** and **21** for high NO_x experiment 6, the quantities of m/z 136 and 113 lost from the gas phase exhibited yet higher correlation with the growth of SOA mass ($r^2 = 0.94$ and 0.97, respectively), providing further strong evidence that these species play an important role in TMB-SOA growth. However, as with the bicyclic nitrate the steepness of this correlation was greater under low NO_x conditions. Interestingly, for the m/z 136 and 113 compounds, under high NO_x conditions there exists a small negative intercept on the ordinate axis, suggesting that either no, or very little SOA mass had formed prior to loss of these compounds from the gas phase. This result suggests that as well as contributing to SOA growth, the nitrate of m/z 136 and the compounds of m/z 113 play some role in particle formation under high NO_x conditions.

Further evidence to suggest that the O_2 -bridged nitrate contributors to SOA growth comes from close inspection of results obtained from the chamber box model. From observation of the modelled and measured data presented in **Figures 17** and **18**, it can be seen that the simulated and measured profiles of the O_2 -bridged nitrate only diverge after nucleation has occurred (184 and 22 minutes for experiments 6 and 7, respectively). More specifically, after the nucleation event, the model begins to over predict the gas phase concentration of the bicylic nitrate. This 'missing' mass in the measured gas phase data may potentially result from partitioning of the O_2 -bridged nitrate to the aerosol phase, which is not considered within the model.

It would seem, from the evidence presented thus far, that the O_2 -bridged nitrate and m/z 113 compounds contribute towards SOA growth, along with compounds such as the unidentified m/z 136 organic nitrate, the O_2 -bridged diol and the lower molecular mass organic acids. However, from the data obtained from the low NO_x experiments, it appears that the presence of certain other semi-volatile organic species may be required to initiate nucleation.

As was discussed in Sections 6.4.3 - 6.4.5 there exists evidence from this work and from that of previous studies, that organic hydroperoxides may play a significant role in SOA formation and growth (Johnson *et al.*, 2005). Considering the mechanism outlined in **Figure 9**, the most dominant organic hydroperoxy-1,3,5-trimethyl-6,7-dioxabicyclo[3.2.1]oct-3-en-8-ol, compound (M) in **Figure 9**, TM135BPOOH in the MCM), formed from reaction of the parent O₂-bridged peroxy radical (K) with HO₂. No direct measurements of the bicyclic peroxide were made within this study (organic peroxides are not easily ionised by proton transfer); however its temporal profile as simulated by the chamber box model (described in Sections 6.3.5 and 6.4.9 (Rickard, 2008)) is shown in **Figure 23** below, for both high and low NO_x conditions (experiment 6 and 7). Also given in **Figure 23** are the CPC SOA number density data and modelled profiles for two further significant organic peroxides observed to form within the chamber simulations; 3-hydroperoxy-4-hydroxy-3,5-dimethyldihydrofuran-2(3H)-one

(MXYFUOOH in the MCM) and 4-hydroperoxy-2,4,dimethyl-5-oxotetrahydrofuran-3-ylnitrate (NMXYFUOOH in the MCM). Both MXYFUOOH and NMXYFUOOH (structures (i) and (ii), respectively, in **Figure 24**) are produced during the oxidation of 1,3,5-TMB from the ring opening product 3,5-dimethyl-5(2H)-2-furanone (m/z 113).



Figure 23: Simulated profiles for (1) the O_2 -bridged peroxide (TM135BPOOH), (2) MXYFUOOH and (3) NMXYFUOOH under (a) high NO_x (experiment 6) and (b) low NO_x (experiment 7) conditions. Also given is the measured SOA particle number density (N.D.) temporal profile. Far left axis for (a) gives MXYFUOOH concentration and for (b) gives MXYFUOOH and NMXYFUOOH concentration.



Figure 24: Potential SOA forming organic hydroperoxides formed during 1,3,5-TMB oxidation

The data presented in Figures 23(a) and (b) provide crucial information for the identification of nucleating species in the 1,3,5-TMB system, *i.e.* under both high and low NO_x conditions the onset of nucleation coincides with the (simulated) formation and appearance of the low volatility O₂-bridged primary peroxide. The modelled profiles of the O₂-bridged peroxide suggest that it would have been formed in significant concentrations within the gas phase. with maximum values of 16 and 6 ppbV simulated for experiments 6 and 7, respectively (*i.e.* $Y_{VOC} = 7.0$ % for experiment 6 and 11.9 % for experiment 7). Also, from Figure 23(a) it appears that in the high NO_x system both MXYFUOOH ($Y_{VOC} 0.2 = \%$) and NMXYFUOOH $(Y_{VOC} 4.9 = \%)$ also appear just prior to nucleation. These findings combined with peroxy radical measurements and results obtained from the partitioning theory of equation (E6.4) (Figure 5 and Figure 7), provide strong evidence that primary and secondary peroxides play a role in SOA formation during the oxidation of 1,3,5-TMB, and potentially during the oxidation of various other aromatic compounds. As nucleation occurred, under both high and low NO_x conditions, only once the O₂-bridged primary peroxide had appeared in the chamber model, it seems that this compound may be particularly important in initiating nucleation. Furthermore, the three organic peroxides TM135BPOOH, MXYFUOOH and NMXYFUOOH were significant contributors to the simulated aerosol mass in the study of Johnson et al. (Johnson et al., 2005).

One additional compound which may contribute to new particle formation is the O_2 -bridged ketone. The bicyclic ketone was present in the gas phase before nucleation in almost all experiments and has a (modelled and measured) temporal profile that grows in line with SOA mass. Furthermore, the higher gas phase yield for the bicyclic ketone under low NO_x conditions is matched by an ultimately higher aerosol yield. This suggestion also supports the modelling studies of Johnson *et al.*, who propose significant partitioning of the O_2 -bridged ketone to the aerosol phase in their gas-aerosol coupled box model (Johnson *et al.*, 2005).

It is possible to gain further insight into the potential of a gaseous compound to contribute towards SOA mass by estimating its vapour pressure and aerosol partitioning coefficient. Following the methodology employed by Jenkin (Jenkin, 2004) and Johnson *et al.* (Johnson *et al.*, 2004), the (sub-cooled) liquid vapour pressure (p^{o}_{L}) of a compound may be determined using the Clausius-Clapeyron equation:

$$\ln \frac{p_{L}^{o}}{760} = \frac{-\Delta S_{vap}(T_{b})}{R} \left[1.8 \left(\frac{T_{b}}{T} - 1 \right) - 0.8 \left(\ln \frac{T_{b}}{T} \right) \right]$$
(E6.5)

where, T_b = the boiling point of the compound under inspection (K), $\Delta S_{vap}(T_b)$ = the entropy change of vaporisation at the specified value of T_b , T = experiment temperature (K) and R = the ideal gas constant (8.314 J mol⁻¹ K⁻¹). Once a value has been determined for the vapour pressure of a compound, the Pankow equation (Pankow, 1994; Jenkin, 2004) may be used to calculate a corresponding aerosol partitioning coefficient (K_p):

$$K_{p} = \frac{7.501 \times 10^{-9} RT}{MW_{om} \zeta p_{L}^{o}}$$
(E6.6)

where, MW_{om} = the mean molecular weight of material resident within the aerosol phase (g mol⁻¹) and ζ = the aerosol phase activity coefficient of the condensing compound. In order to add further validity to the theory that the primary bicyclic compounds observed/investigated within this work do indeed contribute towards the formation and growth of SOA during the oxidation of aromatic compounds, equations (E6.5) and (E6.6) have been used to determine their respective p_L^o and K_p values, the results are presented in **Table 5**.

MCM Designation	Structure	Boiling Point (<i>T_b</i>) / K	Vapour Pressure (p ^o _L) / Torr	$K_p * / m^3 \mu g^{-1}$
TM135BPNO3		788.12	6.93 × 10 ⁻⁸	2.05
TM135BP2OH	НОООООН	661.08	5.16 × 10 ⁻⁵	2.75 × 10 ⁻³
ТМ135ОВРОН	HOOO	641.39	1.40×10^{-4}	1.01 × 10 ⁻³
TM135BPOOH	HO O H	683.50	1.64 × 10 ⁻⁵	8.67 × 10 ⁻³

Table 5: Boiling point, vapour pressure and partitioning coefficient for each of the primary bicyclic compounds formed during the gas phase oxidation of 1,3,5-TMB

* Calculated with $MW_{om} = 130 \text{ g mol}^{-1}$

For the determination of p_{L}^{o} and K_{p} in this instance, the boiling point of each compound was estimated using the *ChemDraw Ultra* (V7.0) software package (see (Johnson *et al.*, 2004) for methodology and further details), $\Delta S_{vap}(T_{b})$ for each compound was set to an average value of 10.5R, and average values of 130 g mol⁻¹ and 1 have been assumed for MW_{om} and ζ , respectively (see (Jenkin, 2004) for further details). It should be noted that following the method of Johnson *et al.* (2004), the nitrate group structure was estimated as R–O–N(=O)=O.

As can be seen from inspection of **Table 5**, each of the bicyclic compounds have vapour pressures of ~ 10^{-4} Torr or less, with the O₂-bridged nitrate and peroxide having the lowest vapour pressures (and highest corresponding partitioning coefficients) of the quartet. If the p°_{L} values of **Table 5** are compared to those of compounds known to partition readily to the aerosol phase, for example pinic acid, formed from the oxidation of α -pinene ($p^{\circ}_{L} = 4.7 \times 10^{-4}$ Torr, (Jenkin, 2004)), it is clear that the O₂-bridged bicyclic compounds are indeed highly likely to partition readily to the condensed phase and hence contribute to the formation and growth of TMB-SOA.

6.5 Conclusions

The work presented here constitutes the most comprehensive set of gas phase measurements made to date describing the unexplored composition and evolution of the organic oxidation products of an anthropogenic SOA precursor. VOC measurements made by CIR-TOF-MS include gas phase oxidation products with the highest mass observed in aerosol simulation experiments so far. Furthermore, the high spectral resolution available in TOF-MS has helped in the identification of these high mass compounds as certain primary bicyclic oxidation products (measurements of which have not previously been reported within the literature), which crucially give support to our current understanding of aromatic hydrocarbon oxidation. Moreover, compound appearance times, temporal behaviour and enhanced yields under low NO_x conditions (that correlate with enhanced SOA yields) imply a role for the oxygen-bridged species and certain organic acids in the growth of TMB-SOA.

From the analysis conducted here on data obtained from experiments of various VOC/NO_x ratios, it has been possible to highlight a potential role for various other (multi-functional) gas phase organics in SOA growth, which appear at various stages in the oxidation chain. These include, 3,5-dimethylbenzaldehyde, nitrogenated compounds, furanone and dicarbonyl type species as well as simple low molecular weight organic acids. Along with methyl glyoxal, the O₂-bridged ketone and the m/z 113 isobaric furanone and δ -dicarbonyl ring opening products act as 'mass conduits' through which a significant portion of mass transit occurs. Such strong

markers could be used during gas phase measurements to 'fingerprint' SOA formation episodes in the real atmosphere.

Good correlation has been achieved between measured and simulated gas phase species, using a chamber box model incorporating the detailed 1,3,5-TMB oxidation scheme extracted form the MCMv3.1. The model/measurement comparison made here provides important findings which help support current understanding of the gas phase oxidation mechanisms of aromatic compounds. Moreover, the data obtained from the box model simulations provide crucial information, which has helped to illuminate the role that several primary and secondary organic hydroperoxides hold in the initiation of the SOA nucleation process. Owing to the excellent correlations obtained between simulated and measured data, the model results presented here may be employed with some level of confidence.

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Chapter 7

Gas Phase Precursors to Biogenic Secondary Organic Aerosol: Detailed Observations of Isoprene and α-Pinene Oxidation

7.1 Summary

The final body of work presented within this thesis constitutes a continuation of that given in Chapter 6. Here, however, focus is shifted to the investigation of the oxidation mechanisms of, and secondary organic aerosol (SOA) formation from two biogenic precursors, isoprene and α -pinene. During the eleven photooxidation and ozonolysis experiments studied, a wide array of gaseous organic oxidation products were measured, with high temporal and spectral resolution, including various multifunctional carbonyl compounds, carboxylic acids and organic nitrates. A number of potential SOA forming organic oxidation products were identified and highlighted.

7.2 Introduction

Biogenic Volatile Organic Compounds (BVOCs) are ubiquitous in the global troposphere, being emitted primarily from terrestrial plant life (Kanakidou *et al.*, 2005). It is estimated that the total annual emission rate of all (non-methane) BVOCs is roughly ten times that of all anthropogenic volatile organic compounds, being around $491 - 1150 \text{ Tg C Yr}^{-1}$ (Guenther *et al.*, 1995). With the exception of methane, the most dominant species of BVOC, in terms of emission strength, reactivity and their impact upon the atmosphere, are terpenes (Reinnig *et al.*, 2008). Terpenoids are a subdivision of BVOCs, which are composed primarily of hemiterpenes (C₅), monoterpenes (C₁₀), sesquiterpenes (C₁₅) and diterpenes (C₂₀) (Atkinson and Arey, 2003; Kanakidou *et al.*, 2005). By far the most abundant species of terpenes, and indeed non-methane hydrocarbons within the atmosphere, are the hemiterpene, isoprene (2-methyl-1,3-butadiene, *i.e.* CH₂=C(CH₃)CH=CH₂), and the monoterpene, α -pinene, which have emission rates of ~ 500 and ~ 25 Tg C Yr⁻¹, respectively (Guenther *et al.*, 1995; Seinfeld

and Pankow, 2003). The concentrations of isoprene and α -pinene are generally highest over forested areas (Kroll *et al.*, 2005; Librando and Tringali, 2005), but both compounds are often detected in urban and remote air masses (Calvert *et al.*, 2000; Kanakidou *et al.*, 2005).

Isoprene and α -pinene are highly reactive within the troposphere, being able to react with the three primary oxidants, OH, O₃ and NO₃, at appreciable rates (*e.g.* (Calvert *et al.*, 2000; Koch *et al.*, 2000; Fantechi *et al.*, 2002; Capouet *et al.*, 2004; Kroll *et al.*, 2006)) such that their atmospheric lifetimes are of the order 1 – 2 and 0.5 – 3 hours, respectively (Guenther *et al.*, 1995; Capouet *et al.*, 2004). Because of their large emission rates and high reactivities, isoprene and α -pinene have a strong impact upon the chemistry of the troposphere on the local, regional and global scales (Jaoui and Kamens, 2001). More specifically both compounds have high photochemical ozone creation potentials (POCP: 114 and 63 for isoprene and α -pinene, respectively¹ (Derwent *et al.*, 2007)), and complex and extensive oxidation pathways (*e.g.* (Calvert *et al.*, 2000; Capouet *et al.*, 2004; Jenkin, 2004; Surratt *et al.*, 2006)). Consequently, both compounds are able to perturb the oxidising capacity of the troposphere (Librando and Tringali, 2005). Further to this, the atmospheric oxidation of both isoprene and α -pinene is known to lead to the production of secondary organic aerosol (SOA) (*e.g.* (Baltensperger U. *et al.*, 2005; Kanakidou *et al.*, 2005; Kroll and Seinfeld, 2008) and references therein).

The first recognised observations of SOA generated from BVOC activity were made in 1960 by Went (Went, 1960), who reported on the 'blue haze' produced over forested areas. Following these preliminary observations much attention has been given to biogenic SOA, which has since been estimated to account for a significant fraction of total global SOA. Modelling studies suggest the annual global production rate of biogenic SOA is of the order 16.4 Tg Yr⁻¹, of which isoprene oxidation alone accounts for ~ 6.2 Tg Yr⁻¹ (Henze and Seinfeld, 2006).

Because of its relatively large emission rate and its propensity to form relatively heavy, polar and multifunctional oxidation products, α -pinene was chosen as the focus for many early investigations into SOA formed through biogenic activity (Jenkin, 2004; Kanakidou *et al.*, 2005). Various laboratory (Koch *et al.*, 2000), field (Kalberer *et al.*, 2006), modelling (Jaoui and Kamens, 2001; Johnson *et al.*, 2006) and chamber studies (Larsen *et al.*, 2001) have been conducted over the last two decades in order to investigate the formation mechanisms and

¹ POCP values given relative to ethene, which is conventionally defined to have a value of 100.

chemical composition of a-pinene SOA, with varying levels of success. Findings from simulation chamber studies have demonstrated that α -pinene is able to produce SOA in significant yields (Y_{SOA}) that vary according to a number of different experimental parameters, including the oxidant type (Jenkin, 2004), NO_x level (*i.e.* $Y_{SOA} \propto 1/[NO_x]$) (Koch et al., 2000; Presto et al., 2005), seed presence and type (Y_{SOA} \propto seed acidity) (Koch et al., 2000; Gao *et al.*, 2004), temperature (Y_{SOA} \propto 1/T) and humidity (Y_{SOA} \propto 1/RH) (Czoschke and Jang, 2006). Typically, SOA yields obtained from the oxidation of α -pinene range from ~ 10 – 70 % (Lee et al., 2006a; Lee et al., 2006b; Northcross and Jang, 2007), with larger values generally obtained from α-pinene ozonolysis (Jenkin, 2004; Lee et al., 2006a). Despite much investigation, the molecular composition of α -pinene-SOA is still not well known, with only ~ 40 % of material in the condensed phase generally identified in compositional studies (Larsen et al., 2001; Reinnig et al., 2008). However, of the identified mass the largest fraction is generally found to be composed of carboxylic acids, including pinic, pinonic, norpinic and norpinonic acid (Koch et al., 2000; Jaoui and Kamens, 2001; Kamens and Jaoui, 2001; Larsen et al., 2001). Such species have very low vapour pressures and hence are able to condense to the aerosol phase relatively easily (Pinho *et al.*, 2007). Indeed of these species the dicarboxylic variant, pinic acid, is believed to be highly capable of initiating homogeneous nucleation in the absence of preformed particulate matter (Jenkin et al., 2000; Koch et al., 2000).

Having a low molecular weight and relatively volatile first generation oxidation products, isoprene was long thought not to contribute towards atmospheric SOA (Kroll et al., 2005), a fact seemingly confirmed by initial simulation chamber experiments (Pandis et al., 1991). However, the SOA forming potential of isoprene has recently received much renewed examination on account of several important findings. The first of these came from laboratory experiments which showed that simple volatile carbonyl compounds could contribute towards SOA growth via newly proposed acid-catalysed heterogeneous reactions on the aerosol surface (Jang and Kamens, 2001; Czoschke et al., 2003; Limbeck et al., 2003; Matsunaga et al., 2003; Matsunaga et al., 2005). Soon after these findings were published, reports were made detailing the observation of a number of isoprene oxidation products in ambient SOA during a field study in the Amazonian rain forest (Claevs et al., 2004). Specifically, these compounds comprised two isomeric 2-methyl-tetrols, which possess very low vapour pressures and high hygroscopicity (Claeys et al., 2004) and hence have considerable affinity for the condensed phase. Several subsequent studies have been able to confirm the presence of 2-methyl-tetrols in isoprene SOA, during both chamber studies (Edney et al., 2005; Boge et al., 2006; Surratt et al., 2006) and field studies (Claeys et al.,

2004; Ion *et al.*, 2005). Findings suggest that the 2-methy-tetrols could contribute up to ~ 2 Tg Yr⁻¹ towards global SOA mass (Claeys *et al.*, 2004). Compositional studies of isoprene SOA have also highlighted the presence of compounds such as 2-methyl glyceric acid (Edney *et al.*, 2005; Surratt *et al.*, 2006), methyl glyoxal, glycoaldehyde and hydroxy acetone within isoprene SOA (Matsunaga *et al.*, 2005).

Recently, several simulation chamber studies have been conducted to investigate various aspects of SOA formation from isoprene. Results have shown that SOA is formed with yields which are dependent on factors such as NO_x level (Kroll *et al.*, 2006; Surratt *et al.*, 2006), seed presence/type (Edney *et al.*, 2005) and temperature (Kroll *et al.*, 2005), in the same manner as α -pinene. Typical isoprene SOA yields range from < 1 – 5 % (Kroll *et al.*, 2005; Dommen *et al.*, 2006). Despite having a relatively low SOA creation potential, its considerable source strength makes isoprene highly significant in the production of secondary organic aerosol on the global scale.

Despite much investigation, the formation mechanisms and chemical composition of biogenic SOA are still not well characterised (Librando and Tringali, 2005); indeed under certain conditions as much as 80 – 90 % of SOA mass is unidentified (Limbeck et al., 2003; Kalberer et al., 2006). However, it has recently been determined that acid-catalysed heterogeneous chemistry plays a significant role in SOA growth, through the production of high molecular weight oligomeric compounds. Oligomers with molecular weights between 250 and 1000 amu have been detected in both α -pinene (Tolocka *et al.*, 2004) and isoprene (Dommen *et al.*, 2006) SOA, and are believed to account for as much as 22 - 34 % of total SOA mass (Kalberer et al., 2006; Surratt et al., 2006). Various studies have shown that biogenic SOA yield increases dramatically with increased seed acidity (Jang et al., 2003; Gao et al., 2004; Edney et al., 2005; Czoschke and Jang, 2006; Kleindienst et al., 2006; Surratt et al., 2007), although it has been determined that the presence of an acid surface is not a prerequisite for oligomer formation (Jang et al., 2005; Dommen et al., 2006; Kalberer et al., 2006; Surratt et al., 2007). The various recently proposed oligomer formation mechanisms, by which heavy, low volatility organic compounds are produced in the condensed phase, can now be used to explain the reactive uptake of relatively high volatility compounds from the gas phase into the aerosol (Kroll and Seinfeld, 2008).

Despite recent advances made in determining the composition of biogenic SOA, there still exists a significant lack of information regarding the composition and evolution of the organic gas phase matrix during aerosol formation, and most importantly the mechanisms by which gas phase species ultimately produce SOA (Kroll *et al.*, 2005; Librando and Tringali, 2005). In the many studies conducted on biogenic SOA, very few organic species generally constitute the target for gas phase analysis; indeed often only the major first generation product(s) and simple end stage species such as acetone and formaldehyde are routinely measured (*e.g.* (Librando and Tringali, 2005; Surratt *et al.*, 2006)). Consequently, the many organic species generated during the complex gas phase oxidation of BVOCs such as isoprene and α -pinene are neglected and remain unidentified (*e.g.* (Lee *et al.*, 2006a; Lee *et al.*, 2006b)).

The work presented here aims to address these issues, with focus on isoprene and α -pinene. The study of isoprene and α -pinene SOA formation is vital, as in combination the two species contribute significantly to global SOA loading. Within this study the gas phase oxidation products of isoprene and α -pinene were monitored in detail and with good temporal resolution during SOA formation, using the newly developed Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS). Generally, during VOC oxidation/SOA formation experiments only a limited number of gas phase organics are targeted. However, using CIR-TOF-MS all mass channels are captured in chorus, hence a highly detailed picture of the organic matrix may be constructed. Eleven separate experiments were conducted as part of this study, at the Paul Scherrer Institut (PSI) atmospheric simulation chamber. Included were nine high NO_x photooxidation experiments (conducted with VOC/NO_x ratios constrained to values of 1:1 and 2:1), one (isoprene) low NO_x photooxidation experiment and two (isoprene) ozonolysis experiments. The current work presents detailed observations which help support understanding of the atmospheric oxidation mechanisms of isoprene and α -pinene, as well as highlighting potential organic oxidation products which may contribute to biogenic SOA formation and growth.

7.3 Experimental

The experiments under investigation within this chapter were conducted alongside those described in Chapter 6, in which the oxidation mechanisms and SOA forming potential of the anthropogenic VOC 1,3,5-trimethylbenzene (TMB) were explored. Besides the alternative use of either isoprene or α -pinene as the starting material, all other experimental details regarding the chamber and instrumentation were as described in Chapter 6, hence only certain experiment specific details are provided here. The specific starting conditions of all experiment are given below in **Tables 1** and **2**. The eleven experiments described within this

Table 1: employe	: Summary of t d for VOC mor	he major gas p iitoring	hase parameters	for isoprene	experiments 1 -	7 along with Cl	IR-TOF-MS co	nditions	
Exp. No.	Initial [VOC] / ppbV	Initial [NO] / ppbV	Initial [NO ₂] / ppbV	VOC/NO _x Ratio	Relative Humidity / %	Exp. Duration / mins.	Estimated [OH] ¹ / pptV	CIR-MS Conditions ² (E/N) / Td	
-	1716	416	420	2.1	49	556	0.117 (0.197)	140 / 190	
2	836	264	295	1.5	55	554	0.097 (0.242)	110/190	
3	293	55	58	2.6	60	617	0.050 (0.091)	90 / 150	
4	477	141	144	1.7	57	626	0.072 (0.132)	90 / 190	
5	461	$\sim 10 \text{ ppbV}$	V HONO ³	~ 46.1	53	1360	0.033 (0.055)	90 / 190	
6^4	1800	1777 pj	pbV O ₃	n/a	51	458	0.070 (0.278)	140 / 190	
7 5	1130	300 & 34(0 ppbV O ₃	n/a	0	140		90 / 190	
			¹ Ex ² Co ⁵ Oz	perimental av rerage reactor intinuous HOI conolysis expe conolysis expe	erage OH conc E/N / ECC E/N NO input, cham sriment conduct sriment conduct	entration (peak ber average HO ed in main chan ed in auxiliary t	OH concentration NO maintained aber ag	on) $ $ at $\sim 10 \text{ ppbV}$	
I able 2. empoye	for VOC mon	ne major gas p itoring	nase parameters	tor α -pinene	experiments & -	11 along with	UIK-10F-MIS c	onditions	-
Exp. No.	Initial [VOC] / ppbV	Initial [NO] / ppbV	Initial [NO ₂] / ppbV	VOC/NO _x Ratio	Relative Humidity / %	Exp. Duration / mins.	Estimated [OH] ¹ / pptV	CIR-MS Conditions (<i>E</i> /N) / Td	¹ Experimental average [OH] (peak [OH]) ² [o_nineal ([1, 3, 5-
8	124	31	41	1.7	49	482	0.199 (0.305)	140 / 190	TMB])
6	208	48	60	1.9	52	1489	0.184 (0.369)	120 / 190	${}^{3}[\alpha-\text{pinene}]/[\text{NO}_{x}]$ ([α -pinene + 1.3.5-
10	$191 (60)^2$	57	76	$1.4(1.9)^3$	51	516	0.222 (0.367)	120 / 190	TMB]/[NO _x])
11	205	115	110	0.9	0	350	0.265 (0.533)	120 / 190	

Chapter 7 **Biogenic SOA Formation** work have been labelled 1 - 11, of which the isoprene experiments are numbers 1 - 7 and the α -pinene experiments are numbers 8 - 11.

The main deviation from those experimental conditions already described in Chapter 6, came during the isoprene ozonolysis experiments (experiments 6 and 7). Of the two ozonolysis experiments conducted, the first (experiment 6) took place in the main chamber and the second (experiment 7) took place in a small 'auxiliary' bag, $\sim 1.5 \text{ m}^3$ in volume, constructed from DuPont Teflon fluorocarbon film. For both ozonolysis experiments a single injection of ozone (~ 1800 and 300 ppbV, respectively) was made prior to injection of the VOC. During experiment 7 a second injection of ozone (340 ppbV) was made once ozone levels had fallen towards zero. Both experiments were conducted in the absence of light and an OH scavenger.

Besides the ozonolysis experiments, a further change to experimental protocol was made during α -pinene experiment 11, which was conducted in the absence of humidity and with an initial CO mixing ratio of approximately 5 ppmV. It should also be noted that to assist measurements of the aerosol phase (Gross *et al.*, 2006), for experiment 10, a small quantity of 1,3,5-TMB (60 ppbV) was injected into the chamber along with the α -pinene prior to the start of the experiment. On account of the low concentration employed, the presence of TMB and its oxidation products are not expected to adversely perturb measurements made of the α -pinene degradation system in this instance.

As was described in Chapter 6, it is not practical to calibrate the CIR-TOF-MS for the entire host of oxidation products formed from such complex molecules as isoprene and α -pinene. As such, for those measured compounds where no calibration factor was available, that of a structurally and kinetically similar surrogate was employed. Specific calibration details for the current study can be found in **Table A7.1** of Section A7 of the Appendix.

7.4 **Results and Discussion**

7.4.1 The Inorganic Species and the SOA Precursor

During the present study eleven different experiments were conducted, the majority of which comprised photooxidation studies conducted under 'high NO_x' conditions (*i.e.* $[NO_x] > 70$ ppbV). For the high NO_x photooxidation experiments, *i.e.* isoprene experiments 1 - 4 and α -pinene experiments 8 - 11, the initial precursor VOC concentrations ranged from $\sim 120 - 1700$ ppbV, to give similar starting VOC/NO_x ratios of $\sim 1 - 2.5$. In order to explore the effect of NO_x and ozone-alkene reactions on VOC evolution and SOA formation, a single isoprene photooxidation experiment (experiment 5) was carried out under low NO_x conditions (*i.e.* $[NO_x] < 17$ ppbV) and two isoprene ozonolysis studies (experiments 6 and 7) were conducted in the absence of NO_x (see **Tables 1** and **2**).

The temporal profiles presented in **Figure 1** show how the concentrations of NO, NO₂ and O₃ varied with time during the isoprene and α -pinene experiments conducted within the main PSI chamber^b. For all photooxidation experiments (1 – 5 and 8 – 11) the start (zero) time is taken as the point at which chamber lights were switched on and hence the photochemistry initiated. For the ozonolysis experiments (6 and 7) the start time is taken as the point at which the precursor VOC was injected into the chamber. On average the duration of each experiment was of the order of 8 – 10 hours, with the exception of experiments 5 and 9, which were run for almost 24 hours in order to explore the behaviour of the system over a longer time period. **Figures 2(a)** and **3(a)**, respectively, display the isoprene and α -pinene concentration profiles recorded by CIR-TOF-MS during all main chamber experiments. **Figures 2(b)** and **3(b)** give the concomitant profiles of the major primary oxidation products in each case, *i.e.* methacrolein and methyl vinyl ketone (MVK) (measured together at *m/z* 71) in the case of isoprene and pinonaldehyde in the case of α -pinene.



Figure 1: Temporal evolution of the major inorganic gas phase components of the isoprene (left panel) and α -pinene (right panel) oxidation systems: (a) and (b) NO, (c) and (d) NO₂ and (e) and (f) O₃. For (e), the right axis gives [O₃] for experiments 3, 4 and 5. Note the [NO_x] increase and [O₃] decrease in the 'dark phase' conducted at the conclusion of experiments 3, 4 and 5 (see text and Chapter 6 for details).

^b NO, NO₂ and O₃ measurements supplied courtesy, and with permission of Axel Metzger (PSI, Ch.)

The basic underlying chemistry of the photooxidation experiments discussed here is similar to that of the 1,3,5-TMB systems described in Section 6.4 of Chapter 6. Indeed the observations presented in **Figures 1** – **3** for the inorganic species and VOC precursors are broadly in line with corresponding observations made during the 1,3,5-TMB study. As such only experiment specific points are highlighted here.



Figure 2: Temporal evolution of (a) isoprene and (b) the sum of primary oxidation products methacrolein and methyl vinyl ketone, during experiments 1 - 6. For experiments 1, 2 and 6 the concentrations are given on the left ordinate axis and for experiments 3, 4 and 5 the concentrations are given on the right ordinate axis.



Figure 3: Temporal evolution of (a) α -pinene and (b) primary oxidation product pinonaldehyde, during experiments 8 - 11

The temporal profiles of NO, NO₂ and O₃ shown in **Figure 1** were similar between experiments and were largely independent of whether the organic precursor was isoprene or α -pinene. As expected peak NO₂ and O₃ concentrations were proportional to the level of

starting material employed. Full details regarding peak NO₂ and O₃ concentrations are given in **Table 3**. As shown in **Figures 2** and **3**, the temporal profiles of isoprene and α -pinene were also generally similar between experiments, being characterised by a short initial plateau followed by non-linear decay. By the conclusion of each photooxidation experiment more than 95 % of the precursor had been consumed. The quantity of precursor reacted in each experiment is listed in **Table 3**. Owing to the introduction of high levels of oxidant into the chamber at the onset of the ozonolysis experiments, the isoprene oxidation profiles observed were significantly different to those of the photooxidation systems, *i.e.* for experiments 6 and 7 (not shown) a roughly exponential decay was observed with no initial concentration plateau.

Exp. No.	VOC Consumed	Max. [O ₃] Time	Max. [O ₃] / ppbV	Max. [NO ₂] Time	Max. [NO ₂] / ppbV
	/ %	/ mins.		/ mins.	
1	97.11	168	454.2	85	760.1
2	99.01	304	391.5	135	486.2
3	97.68	386	153.0	127	93.0
4	98.90	347	259.3	139	232.2
5	98.02	784	103.0	-	-
6	87.69	-	-	-	-
7	59.57	-	-	-	-
8	96.63	444	88.2	64	61.8
9	98.13	166	98.6	53	85.8
10	96.57	176	117.0	55	115.8
11	95.71	431	183.1	118	167.8

 Table 3: Quantity of organic precursor consumed and peak inorganic concentrations

For the current experiments a plot of ln[VOC] *versus* time does not give a straight line, unlike the ln[1,3,5-TMB] profiles of Chapter 6. Indeed such plots for isoprene and α -pinene exhibit a significant change in slope with time, which correlates with the accumulation of ozone shown in **Figure 1**. This result is to be expected as both isoprene and α -pinene will react with ozone as well as with the primary chamber oxidant, OH, where as 1,3,5-TMB will only react with OH under the chamber conditions employed (Calvert *et al.*, 2000). Also, unlike 1,3,5-TMB, both isoprene and α -pinene will react at a reasonable rate with the NO₃ radical (Calvert *et al.*, 2000), which as suggested by the chamber box model of Chapter 6, may be formed within the chamber under high NO_x conditions. As no direct measurements are available to elucidate the actual concentrations of NO₃ under the current experimental conditions, it is difficult to comment further upon the possible existence of this highly photolabile radical under the chamber lights. Consequently, if the loss of isoprene and α -pinene is assumed to result only from reaction with either OH or O₃, and if the process is treated as pseudo first order (assuming sufficiently high oxidant levels such that reaction of the precursor VOC is rapid), a simple expression may be derived to define the rate of loss of the VOC:

$$-\frac{d[VOC]}{dt} = [VOC](k_{OH}[OH] + k_{O3}[O_3])$$
(E7.1)
$$\ln[VOC] = -(k_{OH}[OH] + k_{O3}[O_3])t$$
(E7.2)

Using published rate constants (http://www.iupac-kinetic.ch.cam.ac.uk; Calvert *et al.*, 2000, see Section 7.4.2), equation (E7.2) may be employed along with VOC and O₃ measurements to infer a time-dependent estimate of [OH]. The OH concentration was estimated in this manner for each experiment over consecutive 20 minute intervals, as exemplified in **Figure 4** and **Figure 5** below. It should be noted however, that if the NO₃ radical did form within the chamber during the current experiments, those OH concentrations presented here would constitute an upper limit value.



Figure 4: Temporal evolution of OH during isoprene photooxidation experiment 4. Also shown is the fractional loss of isoprene *via* reaction with OH (broken line) and with ozone (solid line), given in percentage terms. OH concentrations were inferred from CIR-TOF-MS isoprene measurements.



Figure 5: Temporal evolution of OH during α -pinene photooxidation experiment 8. Also shown is the fractional loss of α -pinene *via* reaction with OH (broken line) and with ozone (solid line), given in percentage terms. OH concentrations were inferred from CIR-TOF-MS α -pinene measurements.

The results presented in **Figures 4** and **5** show the variation in [OH] during isoprene and α pinene experiments 4 and 8, respectively, which constitute typical examples of the high NO_x photooxidation systems. During the high NO_x experiments, the inferred OH levels reached maxima of ~ 0.09 – 0.24 pptV in the case of isoprene photooxidation, and 0.31 – 0.53 pptV in the case of α -pinene photooxidation. The maximum concentration reached in each instance was proportional to the level of starting materials employed. Average and peak OH concentrations (reported in **Tables 1** and **2**) were greatest during α -pinene photooxidation experiments, an unsurprising result considering the more complex oxidation pathway possessed by monoterpenes. For both precursors and in all experiments, the trend in OH was approximately parallel to that of O₃, with OH and O₃ peak values reached at roughly the same time. In each experiment, the level of OH was observed to decrease as the precursor VOC concentration approached zero.

Figures 4 and **5** also show the contributions made to precursor oxidation by reaction with either OH or O₃ during the typical high NO_x experiments (assuming [NO₃] to be minimal). For the isoprene system, oxidation took place predominantly by reaction with OH, but the contribution made by ozonolysis increased with [O₃] throughout the experiment, *i.e.* by ~ 500 minutes the isoprene-O₃ reaction accounted for ~ 25 - 33 % of precursor oxidation. The loss of α -pinene *via* ozonolysis was generally greater throughout each experiment than was the case with isoprene. This result can be attributed to the higher VOC + O₃ rate constant possessed by α -pinene and the faster accumulation of O₃ that results from the monoterpene chemistry. In general after only ~ 20 minutes of oxidation, ozonolysis accounted for ~ 15 - 21 % of α -pinene loss. By the end of each experiment the α -pinene-O₃ reaction typically accounted for ~ 45 % of precursor oxidation.

As was detailed in Chapter 6, it is only possible to make reliable peroxy radical measurements under low NO_x conditions using the PERCA technique, and hence the only results reported here concerning HO₂ and RO₂ levels are those obtained from isoprene experiment 6 (see **Figure 6**). During experiment 6 the concentration of peroxy radicals within the chamber rose rapidly from lights on due to their high rate of production, which early within the experiment was in excess of their rate of loss. Ultimately, due to a balance being achieved in the rate of production and loss, a plateau was reached in HO₂ + RO₂ concentration (which was coincident with that of chamber ozone) at ~ 115 – 120 (+/- 49) pptV by ~ 415 minutes.



Figure 6: Temporal evolution of the sum of hydro and organic peroxy radicals (*i.e.* Σ (HO₂+RO₂)) recorded by the PERCA (coloured markers) during low NO_x experiment 5 (VOC/NO_x ratio ~ 46.1:1), and [OH] inferred from CIR-TOF-MS measurements of isoprene (black line with markers).

7.4.2 The Aerosol Phase

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Figure 7 and **Tables 4** and **5** summarise the major aerosol phase parameters measured by the SMPS and CPC during all main chamber experiments of the present study^c. The parameters measured include the total aerosol number density (ND), geometric mean particle diameter (GMD) and total aerosol volume (employed to give aerosol mass concentration, see below).

No seed was employed in the simulation chamber during the current experiments, and hence aerosol formation would have occurred *via* homogeneous nucleation in all instances (Seinfeld and Pankow, 2003; Holmes, 2007). Following their formation, chamber particles evolved in a similar manner across all experiments, as described in Section 6.4.3 of Chapter 6. The particles formed from α -pinene oxidation grew to possess larger maximum geometric diameters than those formed from isoprene, *i.e.* ~ 370 – 510 nm compared to 60 – 270 nm. As can be seen from observations of **Tables 1** and **4**, the maximum particle diameter achieved was proportional to the initial VOC concentration for both species of precursor. Following the same method as was employed in Section 6.4.3 of Chapter 6, the particle volume concentration measured by SMPS was used to calculate an SOA mass profile for each main chamber experiment. Assuming densities of 1.4 and 1.3 g cm⁻³ for isoprene and α -pinene SOA, respectively (Baltensperger U. *et al.*, 2005; Dommen *et al.*, 2006), the total aerosol mass achieved during isoprene oxidation ranged from 0.5 – 153 µg m⁻³ and for α -pinene oxidation, 116 – 225 µg m⁻³. As no wall loss corrections have been applied to the aerosol phase data, it should be noted that these values constitute lower limits to the SOA mass.

^c Aerosol phase measurements supplied courtesy, and with permission of Axel Metzger (PSI, Ch.)



Figure 7: Temporal evolution of aerosol parameters during the isoprene (left panel) and α -pinene (right panel) oxidation systems: (a) and (b) number density (ND), (c) and (d) geometric mean diameter (GMD) and (e) and (f) mass concentration For Figure (a), right axis gives ND for Experiment 6 and for Figure (e), right axis gives mass for Experiments 3 and 5. For legend, see Figure 1. ND taken from CPC measurements, GMD and mass (*i.e.* volume total) taken from SMPS measurements.

Following the methods of Odum et al. (Odum et al., 1996) described in Section 6.4.3 of Chapter 6, a 'relative' SOA yield was determined for each main chamber experiment. As shown in **Table 4**, the SOA yields obtained from the oxidation of α -pinene were substantially greater than those obtained from the oxidation of isoprene. In general the yields obtained were proportional to the initial VOC concentration employed and quantity of VOC reacted. These results are entirely consistent with a number of previous studies (e.g. (Kroll et al., 2005)). It is interesting to note that the highest yield achieved was for α -pinene experiment 11 (Y = 50.63 %), which included an initial input of 5 ppmV CO. Introduction of CO into the chamber facilitated an increase in the fractional conversion of OH to HO₂ and hence NO to NO_2 . Perturbation of the chemistry in this manner ultimately led to the increased O₃ production observed in Figure 1(f). It has recently been proposed that α -pinene ozonolysis constitutes a significant SOA formation route, as the resultant major primary oxidation products generated comprise a range of low volatility carboxylic acids which readily partition to the aerosol phase (Jenkin, 2004). The correlation between enhanced ozone concentration and enhanced SOA yield obtained during experiment 11 would seem to be consistent with this theory.

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Chapter 7 7.4.2.1 Isoprene SOA

Following methods employed by Ng *et al.* (Ng *et al.*, 2007), the SOA mass formed during each main chamber experiment was plotted against the amount of precursor reacted (Δ VOC) in order to generate a series of time-dependent growth curves (shown in **Figure 8** and **Figure 9** for isoprene and α -pinene respectively). As SOA mass was not wall loss corrected, all curves were terminated at the point of maximum mass.

Figure 8(a) gives the time-dependent growth curves for the higher concentration isoprene experiments (*i.e.* experiments 1, 2 and 6) and Figure 8(b) gives the corresponding plots for the lower concentration experiments (*i.e.* experiments 3, 4 and 5). From inspection of Figure 7 and Figures 8(a) and (b), it can be seen that with the sole exception of the ozonolysis study, all experiments exhibit an initial 'incubation period' after lights on, during which no SOA was measured despite oxidation of the precursor VOC. As shown in Figure 8 and Table 5 the amount of precursor reacted by the point of nucleation during isoprene photooxidation ranged from ~ 160 to 300 ppbV.



Figure 8: SOA time-dependent growth curves for isoprene oxidation experiments 1-6

The time-dependent growth curves obtained from isoprene photooxidation are similar across all experiments, *i.e.* following incubation and nucleation, the curves exhibit non-linear mass growth with respect to isoprene expenditure, such that SOA mass increases even as the precursor concentration falls towards zero. Similar time-dependent growth curves were also obtained from isoprene photooxidation conducted by Ng and co-workers (Ng *et al.*, 2006),

who were further able to show that SOA growth proceeds for some time after all initial isoprene had been reacted. As stated by Ng *et al.*, this behaviour suggests that the nucleating species of isoprene SOA are most likely formed from reaction of the primary oxidation products, *i.e.* it is likely that both double bonds of the isoprene precursor must be oxidised to produce nucleating compounds of sufficiently low volatility (Ng *et al.*, 2007). Indeed several studies have shown that oxidation of methacrolein (a primary photo-oxidant and ozonolysis product of isoprene) produces SOA in substantial yields (Surratt *et al.*, 2006).

The length of the incubation period, and therefore the time of the nucleation event (N_T, using CPC data as defined in Chapter 6) varied markedly between each isoprene experiment, and appeared to be related to the magnitude of the initial precursor concentration employed and the oxidative capacity of the system (see **Tables 1**, **3** and **5**). The earliest nucleation event observed (at ~ 64 minutes) occurred during experiment 1 when the initial isoprene concentration was ~ 1.7 ppmV, and peak O₃ and OH concentrations were 454 ppbV and 0.2 pptV, respectively. As the initial precursor concentration (and subsequent oxidant level) was decreased below this value, the length of the incubation period increased, *i.e.* for ~ 830, 480 and 290 ppbV initial isoprene, N_T ≈ 113, 234 and 290 minutes, respectively.

It has recently been shown for several different precursors that under high NO_x conditions the length of the incubation period is related to ambient levels of NO, with SOA formation generally not occurring until NO concentrations have fallen towards zero (Johnson *et al.*, 2005; Kroll *et al.*, 2005). This was found to be the case during experiments 3 and 4 of the present study, where [NO] at nucleation was ~ 1 ppbV (see **Table 5**). Other studies have also shown that for some SOA precursors, low NO_x or NO_x-free conditions allow rapid SOA formation with little or even no incubation time at all (Ng *et al.*, 2007). The results obtained under the NO_x free conditions of ozonolysis experiment 6 are in line with such findings, during which the incubation period was minimal (see **Figure 7** and **Figure 8(a)**) with particles measured by the SMPS after only 3 minutes of experiment (mass concentration ~ 20 μ g m⁻³). As was discussed in Chapter 6, similar findings were also noted during all 1,3,5-TMB experiments, which can most likely be attributed to SOA formation being initiated by low volatility organic hydroperoxides, which form in the gas phase in the absence of NO following reactions between HO₂ and RO₂ radicals (Johnson *et al.*, 2005; Surratt *et al.*, 2006).

In contrast to results obtained from experiments 3 and 4, during experiments 1 and 2, where starting concentrations were greatest, the levels of NO at nucleation were far from negligible, being \sim 93 and 67 ppbV, respectively. At NO concentrations of this magnitude, the fraction

of HO₂ and RO₂ radicals forming peroxides would be insignificant (< 1 %, assuming similar HO₂ and RO₂ profiles to those obtained from the modelling of 1,3,5-TMB oxidation under high NO_x conditions, see Chapter 6), which suggests that some other SOA formation mechanism must dominate under high concentration chamber conditions. The nucleating species under such conditions are likely to be the more oxidised, multifunctional and highly polar species that tend to form towards the later stages of the isoprene oxidation chain, which would be generated more rapidly in an early chamber atmosphere of such high OH and O₃ concentrations (*i.e.* experiments 1 and 2 generated the largest peak radicals and O₃ concentrations and in the shortest time, see **Tables 1, 2** and **3**). The formation of oxidation products from the precursor VOC and their role in SOA production and growth will be discussed further in Section 7.4.3.

Finally it should be noted that under the low NO_x conditions of isoprene photooxidation experiment 5, the onset of nucleation was substantially later than was observed in all high NO_x experiments, *i.e.* $N_T \approx 290$ minutes. No obvious anomalies explain this unlikely result, except possible inaccuracies in the input of the HONO radical source. Indeed the slow oxidation rate of the precursor and delayed appearance of reaction products (see **Figure 3** and Section 7.4.3) would suggest a lower oxidant level than was observed in other experiments.

7.4.2.2 α-Pinene SOA

As shown in **Figures 7** and **9**, α -pinene experiments 8 – 10 were characterised by an initial incubation period prior to nucleation, the length of which was similar across all three experiments. Nucleation occurred substantially earlier during the photooxidation of α -pinene compared to that of isoprene, with N_T ranging from ~ 32 to 47 minutes.



Figure 9: SOA time-dependent growth curves for α -pinene oxidation experiments 8 - 11
During all α -pinene experiments the concentration of NO at nucleation was > 10 ppbV, meaning only a very small fraction of RO₂ species would have undergone reaction *via* the HO₂ + RO₂ channel (< 0.3 % assuming similar HO₂ and RO₂ profiles to those obtained from the modelling of 1,3,5-TMB oxidation under high NO_x conditions, see Chapter 6), with the vast majority being converted to their alkoxy radical (RO) equivalent *via* the NO + RO₂ route. As was the case with the high concentration isoprene experiments, this result would seem to suggest a potential role for species other than organic hydroperoxides in chamber SOA formation from α -pinene. Indeed, this finding would appear to be in line with those of recent studies, which highlight the presence of various types of (primary) acids in significant quantities within α -pinene-SOA (Larsen *et al.*, 2001; Jenkin, 2004).

The time-dependent growth curves for the α -pinene experiments (given in **Figure 9**) all show generally similar behaviour, *i.e.* a short incubation zone followed by nucleation and linear mass growth with respect to the quantity of precursor reacted. With the exception of experiment 11 (chamber CO ~ 5 ppmV), SOA formation occurred within a narrow band of reacted precursor, *i.e.* 18 – 24 ppbV. Again as aerosol wall losses have not been considered, it is not possible to comment on the possibility of continued SOA growth once the precursor had been fully consumed. It should be noted that under similar NO_x conditions, Ng *et al.* also obtained linear growth curves up until the point of VOC expiration, subsequently followed by a vertical 'tail' indicating that further SOA growth does indeed occur after complete oxidation of α -pinene (Ng *et al.*, 2007). This finding would suggest that the further oxidation of primary products is important in α -pinene SOA growth (Ng *et al.*, 2006).

7.4.3 The Atmospheric Chemistry of Isoprene and α -Pinene

Before discussion is made of the CIR-TOF-MS VOC measurements, a brief review is given describing the primary oxidation mechanisms of both isoprene and α -pinene. The review presented here has been constructed through an amalgamation of previous system descriptions (Tuazon and Atkinson, 1989; Tuazon and Atkinson, 1990a; Aschmann and Atkinson, 1994; Benkelberg *et al.*, 2000; Calvert *et al.*, 2000; Jenkin *et al.*, 2000; Jaoui and Kamens, 2001; Kamens and Jaoui, 2001; Larsen *et al.*, 2001; Fantechi *et al.*, 2002; Atkinson and Arey, 2003; Capouet *et al.*, 2004; Jenkin, 2004; Surratt *et al.*, 2006; Ma *et al.*, 2007; Pinho *et al.*, 2007; Johnson and Marston, 2008), the MCMv3.1 isoprene and α -pinene subset mechanisms (extracted from MCMv3.1: http://mcm.leeds.ac.uk/MCM) and measurements made by CIR-TOF-MS during this study. The simplified mechanisms described are shown schematically in

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Figures 10 – **14**. In the following descriptions all significant products and intermediates have been given an identification letter, which corresponds only to the figure under discussion.

7.4.3.1 OH Initiated Oxidation of Isoprene

The atmospheric oxidation of **isoprene** proceeds primarily *via* reaction with the hydroxyl radical ($k_{OH} = 2.7 \times 10^{-11} e^{390/7}$ cm³ molecule⁻¹ s⁻¹, http://www.iupac-kinetic.ch.cam.ac.uk). The OH radical will react with isoprene by addition to one of the two C=C double bonds available in the C5 base structure (**Figure 10**). Due to there being four possible locations for addition to occur, four different radical adducts may initially be produced. As two of the radicals are allylic in nature, they may undergo isomerisation to generate a further two different species of isoprene OH-radical adduct (Calvert *et al.*, 2000; Wayne, 2002). Consequently, in total six isobaric, yet structurally different OH-radical adducts may be formed from the reaction of OH with isoprene. Once formed, each radical adduct will readily undergo reaction with O₂. Reaction of the initial four OH-radical adducts with O₂ will lead to the production of four different **C5** β-hydroxyperoxy radicals (for simplicity only two are shown in Figure 10; B₁ and B₂, following addition at the C1 and C4 positions), whereas the isomerisation products will react with O₂ to give the equivalent **C5** δ-hydroxyperoxy radicals (B₃ and B₄) (Calvert *et al.*, 2000).

In the presence of NO_x, the four C5 β -hydroxyperoxy radicals are able to undergo reaction with NO to produce a C5 β -hydroxynitrate compound (*e.g.* C₁ and C₂), or a C5 β hydroxyalkoxy radical (D₁ and D₂) (http://mcm.leeds.ac.uk/MCM, v3.1). The δ hydroxyperoxy radicals will react with NO to produce a C5 δ -hydroxynitrate (C₃ and C₄) or a C5 δ -hydroxyalkoxy radical (D₃ and D₄), which will undergo isomerisation to give the equivalent δ -hydroxy aldehyde (M₁ and M₂) (Calvert *et al.*, 2000). As shown in Figure 10 the hydroxyalkoxy radicals may also form following reaction of their parent hydroxyperoxy radicals with other RO₂ species.

As shown in **Figure 10**, **\beta-hydroxyalkoxy radicals** (D₁) and (D₂), formed by OH addition to the C1 and C4 carbons of the isoprene structure, will ultimately proceed by unimolecular decomposition to give **MVK** (E) and **methacrolein** (F), with yields (Y_{VOC}) of roughly 0.32 – 0.44 and 0.22 – 0.28, respectively (Tuazon and Atkinson, 1990b; Calvert *et al.*, 2000; Sprengnether *et al.*, 2002). OH addition to the C2 and C3 positions of the isoprene molecule will also result in the production of MVK and methacrolein, although for simplicity, these routes have not been shown. Hydroxyalkoxy radicals (D₁) and (D₂) may also yield the **C4**and **C5-hydroxy carbonyls** (I₁) and (I₂).



Figure 10: Mechanistic summary of the hydroxyl radical initiated oxidation of isoprene (adapted from (http://mcm.leeds.ac.uk/MCM, v3.1) and references given above)

Under low NO_x conditions the primary C5-hydroxyperoxy radicals may react with HO₂ to form an equivalent **C5-hydroxy hydroperoxide** (G₁ – G₃). Following their formation the C5-peroxides will eventually yield various C4- and C5-hydroxy carbonyl compounds (I – M) *via* photolysis or reaction with OH. Other oxidation products formed in the photooxidation of isoprene include **3-methyl furan** (N) (Y_{VOC} = 0.02 - 0.05) (Tuazon and Atkinson, 1990b; Paulson and Seinfeld, 1992; Jenkin *et al.*, 1998; Benkelberg *et al.*, 2000; Sprengnether *et al.*, 2002), various **C5-dihydroxy** and **trihydroxy carbonyls** (O), (P) and **C5-diols** (H) (Benkelberg *et al.*, 2000; Zhao *et al.*, 2004; Surratt *et al.*, 2006; http://mcm.leeds.ac.uk/MCM, v3.1). Further oxidation of all products described here will ultimately lead to the generation of a range of different types of lower molecular weight compounds, including **methyl glyoxal** (Q), **glyoxal** (R), **glycoaldehyde** (S), **hydroxy acetone** (T), **acetic acid** (U), **acetaldehyde**, **methanol** and **formaldehyde** (V).

7.4.3.2 O₃ Initiated Oxidation of Isoprene

Under atmospheric conditions **isoprene** will also react with O₃, albeit at a substantially slower rate than with OH ($k_{O3-isop} = 1.03 \times 10^{-14} e^{-1995/T} cm^3$ molecule⁻¹ s⁻¹, http://www.iupackinetic.ch.cam.ac.uk). Ozonolysis is initiated by a concerted cycloaddition of a molecule of ozone across one of the C=C double bonds of the isoprene molecule, producing a highly unstable **primary ozonide** (B₁ and B₂ in **Figure 11**) containing a central ring like C–O₃–C structure, as shown in **Figure 11** (Johnson and Marston, 2008). The unstable primary ozonide is very short lived and will readily break down *via* cleavage of an O–O bond and the previously unsaturated C–C bond. Depending on the position of O₃ addition, decomposition of the primary ozonide will produce **methacrolein** (C) or **MVK** (H), as well as **formaldehyde** (F) (Y_{HCHO} = 0.52 – 0.90, (Calvert *et al.*, 2000)) and various **Criegee intermediates** (D, E, I). Unlike the photooxidation of isoprene, the ozonolysis of isoprene generates methacrolein in a greater yield than MVK, *i.e.* 0.23 – 0.67 compared to 0.10 – 0.26, respectively (Calvert *et al.*, 2000).



Figure 11: Mechanistic summary of isoprene ozonolysis (adapted from (Aschmann and Atkinson, 1994; Calvert *et al.*, 2000; http://mcm.leeds.ac.uk/MCM, v3.1)

The ozonolysis of isoprene is also known to constitute a source of radicals, including OH (Johnson and Marston, 2008). Formed primarily from rearrangement of Criegee intermediate (I) (Calvert *et al.*, 2000), OH is believed to form from isoprene with yields of the order 0.25 (Johnson and Marston, 2008). Should the Criegee intermediates (E) and (I) undergo stabilisation, they may proceed *via* reaction with water to form an equivalent thermally unstable peroxide, which will decompose to give **methacrolein** and **hydrogen peroxide** or **methacrylic acid** and **water**, in the case of intermediate (E), and **MVK** and **hydrogen peroxide** in he case of intermediate (I) (Calvert *et al.*, 2000). Criegee intermediate (D) will either undergo stabilisation followed by reaction with water to give HOCH₂OOH, or will undergo decomposition to give CO, CO_2 , H_2 , H_2O and the H^{*} radical (Aschmann and Atkinson, 1994; Calvert *et al.*, 2000).

7.4.3.3 OH Initiated Oxidation of Methacrolein and Methyl Vinyl Ketone

The primary atmospheric oxidation pathways of **methacrolein** and **MVK** are initiated by reaction with the hydroxyl radical ($k_{OH+methac} = 1.7 \times 10^{-11} e^{175/T}$, $k_{OH+MVK} = 2.6 \times 10^{-12} e^{610/T}$ cm³ molecule⁻¹ s⁻¹, (Calvert *et al.*, 2000) http://www.iupac-kinetic.ch.cam.ac.uk), as shown in **Figures 12(a)** and (**b**). Both methacrolein and MVK may also undergo reaction with O₃ and NO₃ and are also liable to undergo photolysis.

In the case of **methacrolein** (compound (A) in **Figure 12**), reaction may occur either by OH addition to the C=C double bond (branching ratio = 55 %) or by abstraction of the aldehydic hydrogen atom (45 %) (Orlando *et al.*, 1999). The addition of OH at the C1 terminal unsaturated carbon atom, will ultimately result primarily in the production of **hydroxy acetone** (B) ($Y_{VOC} = 0.47$), whereas OH addition at the C2 unsaturated carbon atom will result in the production of **methyl glyoxal** (C) ($Y_{VOC} = 0.08$) (Tuazon and Atkinson, 1990a; Orlando *et al.*, 1999). Abstraction of the aldehydic hydrogen will lead to the production of a range of compounds, including **methacrylic acid** (L), **acetic acid** (F), **peracetic acid** (G), **methanol** (H), **peroxyacetyl nitrate** (**PAN**) (I) and **methacryloylperoxynitrate** (**MPAN**) (E) ($Y_{VOC} = 0.04 - 0.30$) (Tuazon and Atkinson, 1990a; http://mcm.leeds.ac.uk/MCM, v3.1). Both reaction routes are also known to generate **formaldehyde** (D) ($Y_{VOC} \approx 0.30$) (Tuazon and Atkinson, 1990a). As will be described in the following discussion, oxidation of the aldehydic functional group of methacrolein and the subsequent production of acid compounds is likely to be important in SOA formation (Surratt *et al.*, 2006).





Figure 12: Mechanistic summary of the hydroxyl radical initiated oxidation of **(a)** methacrolein and **(b)** MVK (adapted from (Tuazon and Atkinson, 1989; Tuazon and Atkinson, 1990a; Orlando *et al.*, 1999; http://mcm.leeds.ac.uk/MCM, v3.1))

Unlike methacrolein, oxidation of **MVK** (J) by OH occurs solely by radical addition, the major products of which lead to formation of **methyl glyoxal** (C) and **glycoaldehyde** (K) with a combined yield of 0.89 (Tuazon and Atkinson, 1989). **Methyl glyoxal** is known to form following OH addition to the C2 unsaturated carbon atom, whereas **glycoaldehyde** will form following OH addition to the C1 terminal unsaturated carbon atom (Tuazon and Atkinson, 1989). **Formaldehyde** (D) ($Y_{VOC} = 0.54$) and **PAN** (I) have also been measured during OH initiated oxidation of MVK (Tuazon and Atkinson, 1989). Following methodology employed in the MCM, other possible products of MVK oxidation include certain **C4 hydroxy** and **dihydroxy carbonyls** and **peroxides** (http://mcm.leeds.ac.uk/MCM, v3.1).

7.4.3.4 OH Initiated Oxidation of α-Pinene

As with isoprene, the primary atmospheric oxidation route of α -pinene involves initial reaction with OH ($k_{\text{OH-}\alpha pin} = 1.21 \times 10^{-11} e^{444/T} \text{ cm}^3$ molecule⁻¹ s⁻¹ (Calvert *et al.*, 2000)). Reaction of OH with α -pinene may proceed by either hydrogen abstraction from the central ring, or by OH addition to the endocyclic C=C double bond (Calvert *et al.*, 2000), as shown in **Figure 13**.



Figure 13: Mechanistic summary of the atmospheric oxidation of α -pinene by OH and O₃ (adapted from references given above and (http://mcm.leeds.ac.uk/MCM, v3.1))

By far the most dominant reaction pathway is that of OH addition, with a branching ratio of ~ 88 % (Capouet *et al.*, 2004). It is reported that OH addition occurs roughly equally between the C1 (44 %) and C2 (44 %) carbon position (Capouet *et al.*, 2004), to produce two isomeric OH radical adducts. Both adducts will react readily with O₂ to generate their **hydroxyperoxy radical** equivalents, (B₁) and (B₂) in **Figure 13** (Pinho *et al.*, 2007). After reaction with O₂, the C2-OH adduct is also believed undergo isomerisation to produce the hydroxyperoxy radical (J), which following various reactions with NO, RO₂ and O₂ will lead to the formation of **acetone** (N) (Y_{VOC} = 0.05 – 0.15) and a range of cyclic compounds (L and O₁ – O₄) (http://mcm.leeds.ac.uk/MCM; Capouet *et al.*, 2004; Jenkin, 2004; Pinho *et al.*, 2007). Reaction of α -pinene with OH *via* hydrogen extraction is expected to be a minor route (branching ration ≤ 12 % (Capouet *et al.*, 2004)), resulting in the production of various carbonyl compounds *via* an alkoxy radical (*e.g.* P in **Figure 13**).

The two primary hydoxyperoxy radicals (B₁) and (B₂) will most likely react with NO or RO₂ (depending on prevailing NO_x levels) to produce β -hydroxyalkoxy radicals (G₁) and (G₂), which are liable to undergo C-C scission before reaction with O₂ to yield the primary oxidation product, **pinonaldehyde** (Y_{VOC} = 0.06 – 0.87) (Yu *et al.*, 2008). It has recently become established that the β -hydroxyalkoxy radicals (G₁) and (G₂) may also react further following scission with NO or RO₂ to form **pinonic acid** (Y_{VOC} = 0.44) (Larsen *et al.*, 2001).

In the presence of NO_x the hydroxy peroxy radicals (B₁) and (B₂) may also undergo addition of NO to produce the isomeric **hydroxy nitrates** (C₁) and (C₂). Under NO_x free or NO_x limited conditions, the hydroxy peroxy radicals (B₁) and (B₂) may also react with HO₂ or RO₂ to form **pinanediol** (D), **oxypinone** (E) or **hydroxy peroxides** (F₁) and (F₂) (Jaoui and Kamens, 2001; Jenkin, 2004).

7.4.3.5 O₃ Initiated Oxidation of α-Pinene

a-pinene reacts at an appreciable rate with O₃ under atmospheric conditions ($k_{O3-\alpha pin} = 1.01 \times 10^{-15} \text{ e}^{-732/\text{T}} \text{ cm}^3$ molecule⁻¹ s⁻¹, (Calvert *et al.*, 2000)), such that despite its chemistry being controlled primarily by reaction with OH, under certain scenarios the contribution made by ozonolysis can be significant, indeed more so than is the case with isoprene (Went, 1960; Calvert *et al.*, 2000).

The ozonolysis of α -pinene begins with the addition of a molecule of ozone across the endocyclic C=C double bond, to produce a highly energetic primary ozonide (compound (Q) in **Figure 13**). The ozonide will rapidly decompose to yield one of two different excited

Criegee intermediates, (R_1) or (R_2) , with branching ratios of 60 and 40 %, respectively (Calvert et al., 2000; Jenkin, 2004; http://mcm.leeds.ac.uk/MCM, v3.1). The Criegee intermediates are highly energetic and are liable to undergo decomposition to yield OH and various smaller carbonyl compounds. Should however, the Criegee intermediate undergo stabilisation by a third body collision, it may have a sufficient lifetime so as to be able to undergo bimolecular reactions (e.g. with H₂O and NO) or rearrange to give a number of key stable products (Johnson and Marston, 2008). It is believed that stabilisation accounts for \sim 13 % of initial Criegee intermediates (Hatakeyama et al., 1989; Calvert et al., 2000). In the case of intermediate (R_1) , stabilisation will result in the production of **pinonaldehyde** (H) $(Y_{VOC} = 0.06 - 0.53)$ and pinonic acid (I) $(Y_{VOC} \sim 0.016)$ (Jenkin, 2004). The corresponding stabilisation of Criegee intermediate (R_2) will also give pinonaldehyde as well as hydroxypinonaldehyde (AA) and peroxy radical (U). Peroxy radical (U) will react via a number of intermediary steps to ultimately yield a range of products including 10hydroxypinonic acid (W), pinalic-3-acid (X), pinic acid (Y), (Calvert et al., 2000; Koch et al., 2000; Jenkin, 2004) and various other multifunctional carbonyls (including acetone and formaldehyde), alcohols, acids and peroxides (Yu *et al.*, 2008; http://mcm.leeds.ac.uk/MCM, v3.1). As with the ozonolysis of isoprene, the ozonolysis of α -pinene is known to lead to the production of OH; measured OH yields from α -pinene are reported to be of the order 0.76 – 0.85 (Calvert et al., 2000).

7.4.3.6 OH Initiated Oxidation of Pinonaldehyde

The major primary product of α -pinene oxidation, **pinonaldehyde** (compound (A) in **Figure 14**), will react under atmospheric conditions to produce a host of different compounds with a range of functionalities. Pinonaldehyde will react primarily with the hydroxyl radical and by hydrogen abstraction ($k_{OH-pinon} = 4 - 9 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) (Noziere *et al.*, 1999; Fantechi *et al.*, 2002; Atkinson and Arey, 2003; Capouet *et al.*, 2004). Hydrogen abstraction may occur at six different sites on the pinonaldehyde molecule to produce six different radicals, each of which will react further by addition of O₂ to form an equivalent peroxy radical (Fantechi *et al.*, 2002). Hydrogen abstraction occurs mainly from the aldehydic functional group (branching ratio 59 % (Fantechi *et al.*, 2002)), the radical product of which will proceed by reactions with O₂ and RO₂ or HO₂ to form **pinonic acid** (B) (http://mcm.leeds.ac.uk/MCM), and with NO to produce **norpinonaldehyde** (C) (Y_{VOC} = 0.166) and **4-hydroxynorpinonaldehyde** (D) (Y_{VOC} = 0.229 – 0.382). Hydrogen abstraction from the C2 and C3 positions (branching ratios 23 and 8.5 %, respectively) will also lead to the production of **norpinonaldehyde** as well as **acetone** (E) (Y_{VOC} = 0.099). Hydrogen

in ring scission and the production of acetone, formaldehyde and a number of different **multifunctional hydroxycarbonyl** compounds ($Y_{VOC} = 0.166$). **Nitrates** have also been measured at various stages of pinonaldehyde oxidation with $Y_{VOC} = 0.303$ (all yields and branching ratios taken from Fantechi *et al.* (Fantechi *et al.*, 2002)). Reaction by hydrogen abstraction at other sites is minimal, but leads to the production of a range of other multifunctional hydroxy carbonyl compounds. Pinonaldehyde is also likely to undergo photolysis at tropospheric wavelengths (*j*(pinonaldehyde) = $0.3 - 0.9 \times 10^{-5} \text{ s}^{-1}$) to give radical products which ultimately lead to the production of various compounds including norpinonaldehyde (http://mcm.leeds.ac.uk/MCM; Capouet *et al.*, 2004).



Figure 14: Major oxidation products of pinonaldehyde following oxidation by OH

7.4.4 Measurements of the Gas Phase Organic Compounds

The precursor VOCs and their oxidation products were monitored during each experiment by CIR-TOF-MS. The CIR-TOF-MS data were collected and analysed according to the methods described in Chapter 6. Figure 15 presented below gives an overview of the measurements made during two typical experiments investigating the isoprene and α -pinene oxidation systems (experiments 4 and 9, respectively). Both figures constitute a construct of all mass spectra recorded to show the evolution of the gas phase organic compounds during isoprene and α -pinene photooxidation.

During a typical photooxidation experiment (depending on the drift cell conditions employed) around $30 - 70^d$ and 30 - 40 peaks were recorded in the mass spectra of isoprene and α -

^d Variability due to different CIR-TOF-MS reactor and ECC settings between certain experiments (see **Table 1**). 284

pinene, respectively, between m/z 0 and 300. Of those peaks measured approximately $15 - 50^{d}$, in the case of isoprene and approximately 10 - 13, in the case of α -pinene, possessed a mass greater than that of the precursor (*i.e.* m/z 69 and 137, respectively). As was described in Chapter 6, the E/N value of the exit/collision cell was periodically increased in order to help identify and exclude potential molecular ion-water clusters (*i.e.* MH⁺.(H₂O)_n).



Figure 15: Evolution of the gas phase organic compounds during (a) isoprene experiment (4) and (b) α -pinene experiment (9).

The sections that follow will describe the identification of each major spectral feature and their behaviour under oxidation and during SOA formation will be examined. The findings made will subsequently be employed to evaluate and elucidate the current oxidation pathways described in the literature and employed in the MCM, and to help identify potential gas phase SOA precursors in the isoprene and α -pinene oxidation systems.

7.4.4.1 The Oxidation Products of Isoprene and SOA Formation

The major spectral features common to all isoprene experiments are listed in **Table A7.2** of Section A7 of the Appendix. Where possible, each spectral feature has been given a tentative compound assignment. All compound assignments have been made using a combination of information, namely experimentally derived spectral fingerprint, accurate mass measurement, appearance time, temporal profile, and data available from published literature and the Master Chemical Mechanism (MCMv3.1). **Table A7.2** also lists in detail the signals, concentrations

and (mass percent) yields obtained for each identified compound and the accurate mass of each spectral feature over all experiments. The complex information provided by Table A7.2 is summarised in Table 6, which provides details regarding observed nominal masses, compound assignments and yield range over all experiments.

The temporal profiles for most of the compounds identified in Table 6 are given in Figure 16, using data obtained from experiment 4 (a typical example of the high NO_x oxidation system). The profiles for methacrolein and MVK for all experiments were shown earlier in Figure 2(b).

Table 6: Isoprene oxidation products measured by CIR-TOF-MS and their respective (mass percent) yield range over all experiments. Identification letter given in brackets refers to Figure 10. See Table A7.2 of the Appendix for full details including accurate mass measurements.

m/z	Tentative Assignment	Yields / %
117, 99	4-hydroxy-2-methyl-but-2-enoic acid (O)	1.2 - 2.4
103	C5-alkenediols (H) / C4-hydroxydialdehydes / MPAN	0.6 - 0.8
101	C5-hydroxycarbonyls (I2,, J, K, M1,, M2)	1.8 - 13.4
87	C4-hydroxycarbonyls (I_1) / methacrylic acid	2.8 - 4.9
85	C5-carbonyls	1.6 - 4.0
83	3-methyl furan (N)	0.7 - 7.0
75	hydroxy acetone (T)	0.9 - 10.0
71, 55	methacrolein (F) / methyl vinyl ketone (E)	45.9-65.9
73, 45	methyl glyoxal (Q)	5.8 - 9.8
61	glycoaldehyde (S) / acetic acid (U)	0.3 - 8.1
59	propanal / glyoxal (R)	1.9 - 8.3
57	acrolein	1.3 – 5.1
47	formic acid ¹	1
46	organic nitrate marker ^{1,F}	1
45	acetaldehyde	1.3 - 5.0
43	acylium ion ^F	4.6 - 18.7
33	methanol	0.4 - 2.7
31	formaldehyde ¹ (V)	1

¹ Compound not calibrated

^F Denotes a fragment ion.



Figure 16: Temporal evolution of a selection of VOC products derived from the oxidation of isoprene during experiment 4. Figures (b), (c) and (d) (solid lines), concentration given in ppbV, Figures (a), (e) and (f) (lines and markers), concentration given in ncps (*i.e.* uncalibrated signal). Compounds: (1) m/z 113, (2) 4-hydroxy-2-methyl-but-2-enoic acid, (3) m/z 103, (4) 3-methyl furan, (5) C4-hydroxycarbonyls, (6) C5-hydroxycarbonyls, (7) methyl glyoxal, (8) m/z 61, (9) hydroxy acetone, (10) acetone, (11) m/z 45, (12) acrolein, (13) acylium ion, (14) organic nitrate marker- NO₂⁺, (15) formaldehyde.

Early stage organic compounds

The first products to appear during each experiment were methacrolein and MVK, observed within minutes of oxidation being initiated. Methacrolein and MVK (measured together at m/z 71), were formed in yields that agree well with reports made in the literature, *i.e.* $Y_{VOC} = 45.9 - 65.9$ % over the range of conditions employed. Beside m/z 71, a number of other ions appeared equally early during each experiment: these included m/z 83, 87 and 101, as exemplified in **Figure 16(b)** for experiment 4 and m/z 85 in **Figure 17(c)**. The ions of m/z 83, 85 and 101 are tentatively assigned as 3-methyl furan, the sum of C5-carbonyls and the sum of C5-hydroxy carbonyls, respectively. The peak at m/z 87 is tentatively assigned to be a

combination of the sum of C4-hydroxy carbonyls and methacrylic acid. These compounds were measured with yields in the range 0.7 - 13.4 % (see **Table 6**). It should be noted that as surrogate calibration factors were applied here (see Appendix **Table A7.1**), this yield range constitutes only a rough guide. It should also be noted that compounds containing alcoholic functional groups are liable to fragment following proton transfer to form a product of $m/z = MH^+$ -18 (amu). With this in mind, CIR-TOF-MS reactor energy modulation was carried out during certain experiments in order to promote and dampen collision-induced dissociation, and thus aid identification of potential fragment ions. The findings obtained suggest that relatively little overlap occurred for these mass channels, with the exception of the spectral feature assigned to be 3-methyl furan, which may contain some contribution from the C5-hydroxy carbonyls of m/z 101.

Owing to the symmetry of OH-initiated isoprene oxidation, several different compounds are produced with the same chemical composition but different structures (see Figure 10). Because of their isobaric nature and similar functional group content, speciation is not possible in all cases when proton transfer is used as the ionisation method. Consequently, a number of compounds are reported together here as an oxidation product group. These groups, some of which were introduced above, are listed in Table 7 with example compounds and structures.

Parent <i>m/z</i>	Oxidation Product Group	Example Compound
103	C5-alkenediols (or C4-hydroxydialdehydes)	но
_		2-methyl-but-2-ene-1,4-diol
101	C5-hydroxycarbonyls	OH 4-hydroxy-3-methyl-but-2-enal
87	C4-hydroxycarbonyls	HO 1-hydroxy-but-3-en-2-one
85	C5-carbonyls	2-methyl-but-3-enal

Table 7: Identity and structure of the major isobaric oxidation products of isoprene

As was described in Section 7.4.2 and as can be seen from observation of **Figures 10** and **11**, methacrolein and MVK are primary products, presumably as are the C5-carbonyls, while the C4- and C5-hydroxy carbonyl compounds can be formed *via* both primary and secondary routes. 3-methyl furan is possibly derived from the isomerisation and dehydration of the hydroxyalkoxy radicals that also form the C5-hydroxy carbonyls (Benkelberg *et al.*, 2000; Surratt *et al.*, 2006), and methacrylic acid is formed from further oxidation of methacrolein. Following their formation, each of these compounds exhibit similar temporal concentration profiles, with steep, roughly linear production to a distinct peak followed by sharp loss. It is interesting to note that for the profiles of m/z 71 (methacrolein and MVK) and 85 (C5-carbonyls), the point of peak concentration roughly coincides with the nucleation event and the 'loss period' of these species from the gas phase occurs as the aerosol begins to grow. Following the methods employed in Chapter 6 (*e.g.* (Ng *et al.*, 2006)), this relationship was examined further by plotting the mass of m/z 71 and 85 consumed (or 'lost') after their concentration peak *versus* the SOA mass 'produced' (up to the point of maximum mass), the results are shown in **Figure 17**.



Figure 17: (a) and (c) temporal evolution of m/z 71 and 85, respectively (solid blue line) during experiment 4. Plots also display total VOC formed (dashed green line) and total VOC lost (red circles). Also included is SOA mass (solid black line). (b) and (d) show the correlation between m/z 71 and 85 mass consumed and SOA mass formed (up to peak mass). Line fit coefficients quoted \pm one standard deviation.

The strong correlation between the mass of m/z 71 lost and the mass of SOA produced shown in **Figure 17(b)**, indicates that methacrolein and/or MVK contribute to SOA growth, either by direct partitioning or *via* further reaction generating condensable products. Due to their relatively high volatility, it is unlikely that either methacrolein or MVK partition directly to the aerosol phase and indeed, neither compound has been observed in the many compositional studies conducted on isoprene SOA (e.g. (Healy et al., 2008)). It would seem then from the observations made here and from the time-dependent growth curves (see Section 7.4.2.1), that it is the (multifunctional) oxidation products of methacrolein and/or MVK that partition to the aerosol phase and hence contribute to SOA growth. This theory was first suggested by Kroll et al. and Ng et al. who presented similar findings to those reported here (Kroll et al., 2005; Ng et al., 2006) and later strengthened by Surratt et al. who also showed that there is no role for direct reactive uptake of methacrolein to the aerosol (Surratt et al., 2006). Further to this, Surratt showed that mass transit from isoprene to the aerosol occurs primarily via methacrolein; it was shown that methacrolein generates SOA in yields similar to isoprene, whereas MVK produces no aerosol. This finding has been attributed to the generation of low volatility acidic products which form from the further oxidation of the aldehydic functionality possessed by methacrolein. Such (acidic) products, including methacrylic acid, are known to exist within the condensed phase (Surratt et al., 2006).

The presence of a non-zero intercept on the ordinate axis of Figure 17(b) (~ $3.2 \ \mu g \ m^{-3}$), indicates that a small amount of SOA mass had formed in the current experiments prior to net loss of m/z 71. This finding may imply that although the products of methacrolein contribute to SOA they are not necessarily the nucleating species. However, it is clear from Figure 16 that the reaction products of methacrolein begin to appear during the growth period of the m/z 71 trace. Hence it may be possible that these species are sufficiently involatile that they rapidly reach the required vapour saturation concentration, and that homogeneous nucleation occurs before the net oxidative loss of methacrolein. This issue requires further investigation.

As shown in **Figure 17(d)**, a similarly significant correlation exists between the loss of m/z 85 and the production of SOA mass, suggesting that C5-carbonyl species also contribute to isoprene SOA. As was the case with methacrolein and MVK, an intercept on the ordinate axis of **Figure 17(d)** (~ 4.6 µg m⁻³) suggests that some quantity of SOA mass had formed prior to significant contribution from these compounds. Owing to their relatively high volatilities, C5-carbonyl species are not observed within the condensed phase (Healy *et al.*, 2008); hence it is more likely that their oxidation products contributed towards SOA growth here. Various recent studies have highlighted the importance of carbonyl species to SOA

composition, due primarily to their ability to undergo heterogeneous accretion reactions within the aerosol phase to produce large, oligomer type molecules (Kroll and Seinfeld, 2008)

It may be possible that the decrease in concentration of m/z 83 (3-methyl furan), 87 (C4-hydroxy carbonyls/methacrylic acid), 101 (C5-hydroxy carbonyls) and 103 (C5-alkenediols/C4-hydroxy dialdehydes, see discussion below) observed in **Figure 16** may also be due to mass transfer to the aerosol. However as the concentration peaks of these features occurred later than those of m/z 71 and 85, their respective 'loss phases' fall into the period where wall interactions perturb the aerosol mass data. Consequently, no correlation can be drawn with the data available. However from various recent reports made within the literature, it would appear that each of these compounds are likely candidates to contribute to isoprene SOA. For example:

- (i) 3-methyl furan has been reported to generate SOA under photooxidation (Surratt *et al.*, 2006).
- (ii) Under high NO_x conditions methacrylic acid is believed to undergo heterogeneous chemistry within the aerosol phase to give 2-methylglyceric acid, a primary monomer unit of the observed isoprene-SOA oligomer (Claeys *et al.*, 2004; Wang *et al.*, 2004; Edney *et al.*, 2005; Surratt *et al.*, 2006).
- (iii) Various multifunctional hydroxy carbonyl compounds have been observed within the condensed phase (*e.g.* (Healy *et al.*, 2008)), where they are liable to undergo heterogeneous chemistry. For example, Surratt *et al.* (2006) report the presence of a C4-hydroxy dialdehyde (2-methyl-but-3-ene-1,2-diol) within isoprene-SOA in hemiacetal oligomeric form (Surratt *et al.*, 2006; Kroll and Seinfeld, 2008).

Besides those species discussed above, also observed early in the chamber atmosphere was formaldehyde (m/z 31), which is produced at various stages of isoprene photooxidation (see **Figure 10**). As shown in **Figure 16(f)**, the level of formaldehyde increased up to roughly 300 minutes, after which a concentration plateau was reached as steady state became established in its chemistry.

Figure 16(e) displays the temporal profiles of the acylium ion/carbonyl marker (m/z 43) and the NO₂⁺ ion/organic nitrate marker (m/z 46). The m/z 43 signal exhibited a reasonably strong correlation with those signals corresponding to primary products (*e.g.* m/z 71, 85, 87 and 101), appearing within minutes after the chamber lights were switched on and peaking at ~ 410 minutes. The rate of production of the m/z 46 signal was much slower than that of m/z 43, suggesting a smaller contribution from organic nitrates to the early chamber matrix.

However, after ~ 410 minutes the rate of organic nitrate production began to increase until a concentration plateau was reached towards the end of the experiment, by which time, during experiment 4 for example, the m/z 46 signal accounted for ~ 6.5 % of the total ion signal recorded by the CIR-TOF-MS. Although, at the point of nucleation during experiment 6, the contribution made by organic nitrates to the total ion signal was only ~ 2 %.

Second and third generation oxidation products

As the chamber matrix evolved, various other organic species were observed in the CIR-TOF-MS mass spectra (**Figure 15**). Hydroxy acetone (m/z 75), methyl glyoxal (m/z 73) and glycoaldehyde and acetic acid (both m/z 61) (*i.e.* the oxidation products of methacrolein and MVK) formed soon after the primary species, as did acetone (m/z 59), acrolein (m/z 57) and acetaldehyde (m/z 45). As shown in **Figure 16**, the temporal behaviour of each of these compounds was characterised by a steady rise in concentration throughout the experiment. There is some evidence for plateau behaviour in the traces of methyl glyoxal, acetone and acrolein, presumably as a steady state became established in their chemistry. Of these compounds, hydroxy acetone, methyl glyoxal and glycoaldehyde were observed within the aerosol phase during a similar study conducted at the PSI chamber, with yields of 1.3, 1.4 and 1.0 %, respectively (Healy *et al.*, 2008). Various other recent studies have also highlighted the presence of these compounds within the aerosol under both simulated (Surratt *et al.*, 2006) and ambient (Matsunaga *et al.*, 2003; Matsunaga *et al.*, 2005) conditions.

Late stage, 'heavy', organic compounds

After approximately 100 minutes of oxidation, a number of 'large' molecular weight compounds (*i.e.* m/z > 100) were observed to appear within the gas phase, the most abundant of which appeared in the m/z 103, 113, 115 and 117 channels. From nominal mass alone, the peak at m/z 103 may potentially be comprised of three different products, *i.e.* (i) C5alkenediols (potential 2-methyltetrol precursors proposed by Boge *et al.* (Boge *et al.*, 2006)), (ii) C4-hydroxydialdehydes (oligomer monomer unit observed in isoprene-SOA by Surratt *et al.* (Surratt *et al.*, 2006)), or (iii) MPAN (an oxidation product of methacrolein under high NO_x conditions). From close inspection of the accurate mass data and concentration/time profiles, it would seem most likely that the m/z 103 peak is primarily composed of the former of these three. Specifically, as can be see in **Figure 16(a)**, the observed m/z 103 signal increased in magnitude significantly as the system NO levels decreased (c.f. **Figure 1**), and furthermore, it appeared within minutes of oxidation being initiated under low NO_x conditions (not shown). This behaviour is indicative of RO₂ chemistry, which is central to the formation of the C5-alkenediol (as proposed by Boge (Boge *et al.*, 2006) and Surratt (Surratt *et al.*, 2006)). Also, during experiments 3 and 4, a 'dark phase' was introduced as described in Chapter 6, during which the m/z 103 trace levelled off to a plateau. If the peak contained a significant contribution from MPAN, it is likely that a signal drop would have been observed, as PAN type compounds are thermally unstable and hence are liable to undergo unimolecular decomposition.

It is difficult to rule out completely at least some degree of contribution from C4hydroxydialdehyde compounds to m/z 103, and therefore further work is required to facilitate a more confident assignment. As both the C5-alkenediol and C4-hydroxydialdehyde compounds lead to the formation of known isoprene-SOA oligomer molecules (Surratt *et al.*, 2006), their speciation and detailed measurement could prove crucial to elucidating the link between gas and aerosol phase composition in the isoprene-SOA system.

The temporal profiles of the m/z 113, 115 and 117 ions were very similar in behaviour, *i.e.* after late appearance, a steady rate of production up to the onset of plateau (*e.g.* see Figure 16(a)). The ions m/z 113 and 115 remain to be identified, however that of m/z 117 is tentatively assigned to be 4-hydroxy-2-methyl-but-2-enoic acid (and isomers thereof) (compound (O) in Figure 10).

Beyond m/z 117, ~ 23 – 29 ions of various signal intensities were observed in the CIR-TOF-MS mass spectra, the most dominant of which included m/z: 127, 143, 146, 148, 157, 160, 162 and 249, with peak signals of around 30 – 120 ncps. As yet these masses remain to be identified; however it is interesting to note the presence of several even mass ions within the group. Despite being of low signal intensity, the even mass ions exhibit a temporal profile similar to that of the organic nitrate marker at m/z 46 (NO₂⁺), which along with their even nature and high molecular weight would seem to suggest that they may belong to the organic nitrate product group (being parent or fragments ions thereof).

For the results of the principle component analysis (PCA) conducted on the CIR-TOF-MS VOC measurements of the isoprene photooxidation system, the reader is referred to Section A7 and **Figures A7.1** and **A7.2** of the Appendix.

7.4.4.2 The Ozonolysis of Isoprene and SOA Formation

Significant differences were observed in the evolution of the gas phase organics between ozonolysis and standard photooxidation conditions, as is exemplified for isoprene and methacrolein and MVK in **Figure 2**, and for a selection of other key products in **Figure 18**.

The different behaviour of the precursor and its oxidation products during experiments 6 and 7 can be attributed to the large initial oxidant levels employed generating a highly reactive system. As can be seen in **Figure 18**, the rate of production of compounds such as glycoaldehyde and the C4-hydroxy carbonyls/methacrylic acid was rapid during the early stages of the experiment, however as ozone was consumed the rate of production of such compounds was observed to decrease (c.f. **Figure 1**).



Figure 18: Temporal evolution of m/z 61 (glycoaldehyde/acetic acid), 73 (methyl glyoxal), 87 (C4-hydroxy carbonyls and methacrylic acid) and 85 (C5-carbonyls) during isoprene ozonolysis experiment 6.

Figure 19 given below, shows the gas phase composition as measured by CIR-TOF-MS (a) over the whole experiment and (b) at nucleation, for isoprene photooxidation experiment 1 (red bars) and ozonolysis experiment 6 (blue bars). When the gas phase organic components of the ozonolysis and photooxidation systems are compared, we see that the conditions of the former produce an organic gas phase matrix that is less compositionally diverse; primarily no ion of m/z > 103 was observed during ozonolysis and the signals obtained in most mass channels were lower. However despite this fact, SOA formation occurred extremely early during experiment 6 (N_T = ~ 3 minutes) and particle growth was more rapid than under any other conditions (see **Figure 7**). In addition, despite the presence of fewer different gas phase organic compounds, the aerosol yield obtained during ozonolysis experiment 6 was similar to that of photooxidation experiment 1 (*i.e.* Y_{SOA} = 2.43 *versus* 3.04, respectively), which was conducted with a similar initial VOC level.



Figure 19: (a) the sum of all mass spectra recorded during experiments 1 (red bars) and 6 (blue bars) and (b) CIR-TOF-MS mass spectra recorded at nucleation during experiments 1 and 6. Note, m/z 71 off scale in both figures.

From close inspection of Figure 19 we see that at nucleation, for those compounds common between experiments, concentrations were in the main lower under ozonolysis conditions than in the photooxidation system. The significant exceptions to this were m/z 71 (methacrolein 85 and MVK). 73 (methyl glyoxal), (C5-carbonyls) and 87 (C4-hydroxy carbonyls/methacrylic acid), the signals for which were larger at nucleation during ozonolysis. Not only this, but the ultimate yields obtained for methyl glyoxal, the C5-carbonyls and C4hydroxy carbonyls/methacrylic acid were also slightly greater during ozonolysis than photooxidation (see **Table A7.2** of Section A7 of the Appendix). Furthermore, methacrolein and methacrylic acid are known to be significant primary oxidation products of isoprene ozonolysis (Section 7.4.3.2), hence considering earlier findings (Section 7.4.2.1) and the rapidity observed in SOA growth during experiment 6, it seems likely that such compounds (formed quickly during initiation of the experiment), are indeed important contributors to SOA.

With relatively few other compounds observed at significant levels at the point of nucleation during experiment 6 and in light of the subsequent rapid aerosol growth, it seems likely that the C5-carbonyls and C4-hydroxy carbonyls (examples in **Table 7**) may have played some role in the formation and growth of isoprene SOA, along with methacrolein and methacrylic acid. This result is in line with earlier findings regarding the potential contribution of these species to SOA.

7.4.4.3 The Oxidation Products of α-Pinene and SOA Formation

The major spectral features common to all α -pinene experiments are listed in **Table A7.3** of Section A7 of the Appendix. Again where possible, each spectral feature has tentatively been

given a compound assignment, as described in Section 7.4.3. The information provided by **Table A7.3** is summarised in **Table 8**, which provides details regarding observed nominal masses, compound assignments and (mass percent) yield range over all experiments.

m/z	Tentative Assignment	Yield /%
185, 167, 139, 125	pinonic acid ¹ (I)	1
183, 165	4-oxopinonaldehyde	0.6 - 1.5
169, 151, 107, 99, 71	pinonaldehyde (H)	15.4 - 25.1
157, 139	trioxoheptanal /	3.8 - 8.2
	hydroxymethyl-dimethyl cyclobutyl- ethanone	
155	norpinaldehyde	0.5 - 1.0
153, 109	$\alpha\text{-pinene}$ oxide / $C_{10}H_{16}O$ ketone / norpinonic	4.3 - 6.8
	acid / pinanediol (D)	
141	hydroxy-dioxoheptanal isomers ^F /	2.8 - 5.7
	trimethyl-cyclohex-2-en-1-ol	
115	3,4-dioxopentanal / 3-oxo pentanal	0.6 - 1.0
101, 83	dioxobutanal	0.9 - 1.6
87	2-oxomalonaldehyde	0.4 - 1.4
85	hydroxy-butane-2,3-dione ^F	1.0 - 1.2
73, 45	methyl glyoxal / propanedial	2.1 - 10.3
61	acetic acid	3.4 - 19.9
59	acetone	5.5 - 9.3
47	formic acid	12.1 - 23.9
46	organic nitrate marker ^{1,F}	1
45	acetaldehyde / methyl glyoxal ^F	1.2 - 3.1
43	carbonyls- acylium ion ^F	2.8 - 7.9
33	methanol	0.9 - 2.2
31	formaldehyde ¹	1

Table 8: α -pinene oxidation products measured by CIR-TOF-MS and respective (mass percent) yield range over all experiments. Identification letter given in brackets refers to **Figure 13**. See **Table A7.3** of the Appendix for full details including accurate mass measurements.

 $\frac{1}{E}$ Compound not calibrated

^F Denotes a fragment ion.

The temporal profiles for most of the compounds identified in **Table 8** are given in **Figure 20**, using data obtained from experiments 8 and 9. The profiles for pinonaldehyde for all experiments were shown earlier in **Figure 3**.

Early stage organic compounds

The first oxidation product of α -pinene to appear during each experiment, observed within minutes of oxidation being initiated, was pinonaldehyde. No calibration standard was available for quantification in this instance; hence a structurally similar surrogate was employed instead (see **Table A7.1** of the Appendix). Despite this, the yields obtained here for pinonaldehyde (*i.e.* Y_{VOC} = 15.4 – 25.1 %) are in reasonable agreement with reports made within the literature (Calvert *et al.*, 2000; Atkinson and Arey, 2003; Yu *et al.*, 2008).



Figure 20: Temporal evolution of a selection of VOC products derived from the oxidation of α -pinene during experiments 8 and 9. Figures (b), (c), (d) and (e), concentration in ppbV, Figures (a) and (f), concentration in ncps (*i.e.* uncalibrated signal). Lines and markers = experiment 8 and solid lines = experiment 9. Compounds: (1) pinonic acid, (2) norpinaldehyde, (3) 4-oxopinonaldehyde, (4) α -pinene oxide / C₁₀H₁₆O ketone / norpinonic acid / pinanediol, (5) trioxoheptanal, (6) dioxobutanal, (7) 2-oxomalonaldehyde, (8) hydroxy-butane-2,3-dione, (9) acetone, (10) methyl glyoxal, (11) *m/z* 45, (12) formic acid, (13) acetic acid (14) acylium ion, (15) organic nitrate marker- NO₂⁺.

As described in Sections 7.4.3.4 and 7.4.3.5, pinonaldehyde is the major primary reaction product generated during the photooxidation and ozonolysis of α -pinene, and it essentially

constitutes a conduit via which a significant amount of mass transit occurs through the As can be seen through comparison of Figure 3(b) and Figure 7(f), the system. concentration of pinonaldehyde increased from 'lights on' to a peak (~ 200 minutes), which roughly coincided with the point of maximum aerosol mass. There exists no distinct correlation here between the subsequent 'loss' of pinonaldehyde from the gas phase and SOA mass produced, as was the case for methacrolein and MVK in the isoprene system. This behaviour may seem to suggest that pinonaldehyde and oxidation products thereof do not play a significant role in SOA formation. However, it should be noted that pinonaldehyde may have contributed towards SOA formation/growth before the observed net concentration loss. Furthermore, pinonaldehyde has previously been observed as a minor component of α -pinene SOA (Jaoui and Kamens, 2001; Larsen et al., 2001; Chen and Griffin, 2005). Moreover, it was proposed by Tolokca *et al.* that pinonaldehyde (amongst other α -pinene gas phase oxidation products) may undergo heterogeneous chemistry within the aerosol phase (specifically aldol condensation and/or gemdiol formation) to form oligomeric compounds (Tolocka et al., 2004). Oligomeristion may, however, require some level of acid catalyst (Gao *et al.*, 2004). As shown in **Figure 3**, as the concentrations of the precursor approached complete expiration, a fall in pinonaldehyde concentration was initiated.

During all experiments, pinonic acid was observed to appear within the early chamber atmosphere simultaneously with pinonaldehyde, as exemplified for experiment 9 in **Figure 20** (c.f. **Figure 3(b)**) As described in Section 7.4.3.4, it is expected that pinonic acid constitutes a secondary product of α -pinene, formed following the further oxidation of pinonaldehyde. However, recent advances in mechanism development have suggested that pinonic acid is also likely to form as a primary product of α -pinene, following attack by both OH (Larsen *et al.*, 2001) and O₃ (Jenkin *et al.*, 2000) (see **Figure 13**). The temporal profiles presented here, would seem to support this theory with the coincident appearance of pinonaldehyde and pinonic acid in all experiments.

Recent studies have shown that oxidation products which contain carboxylic acid functionalities comprise the largest fraction of α -pinene SOA mass (Kanakidou *et al.*, 2005); indeed pinonic acid alone has been observed to be a significant contributor (*e.g.* (Jenkin *et al.*, 2000; Jaoui and Kamens, 2001; Larsen *et al.*, 2001; Chen and Griffin, 2005; Johnson *et al.*, 2005)). Consequently, in light of the short incubation period observed in each of the α -pinene experiments investigated here and as no correlation can be drawn between the quantity of (gas phase) pinonaldehyde consumed and SOA mass gained, it would seem further likely that such carboxylic acid species may indeed be formed from α -pinene as primary oxidation products.

That is not to say that primary formation is the sole route to the production of gas phase acids from α -pinene and indeed the data presented here suggests otherwise. Specifically, during each experiment as the α -pinene signal decayed, the concentration of pinonic acid was observed to reach a plateau, or in the case of the longer duration experiment 9, to decay at a slower rate than that of pinonaldehyde. This behaviour, as exemplified for experiment 10 in **Figure 21**, suggests the initiation of secondary formation routes for pinonic acid, *i.e.* as α pinene is no long available to remove OH from the system, reaction of OH with pinonaldehyde becomes more likely, resulting in the production of various products including pinonic acid (*e.g.* (Larsen *et al.*, 2001)).



Figure 21: Variation of pinonic acid with pinonaldehyde during experiment 10

From **Figure 20** it can be seen that as levels of pinonaldehyde and pinonic acid began to rise, other compounds were observed to appear within the chamber including norpinonaldehyde, a major oxidation product of both species. The chamber concentration of norpinonaldehyde was observed to increase during all experiments following expiration of α -pinene and during decay of pinonaldehyde and pinonic acid, confirming formation only occurs *via* secondary routes. Norpinonaldehyde is only expected to be a significant contributor to α -pinene SOA following further oxidation to products such as norpinonic acid (Chen and Griffin, 2005).

Also observed early on within the gas phase of the chamber were two strong and highly correlated signals at m/z 153 and 109, which have been previously attributed to α -pinene oxide (Yu *et al.*, 2008). α -pinene oxide has been observed in various α -pinene oxidation studies and several different mechanisms have been proposed to explain its formation route. According to Alvarado *et al.* (Alvarado *et al.*, 1988) α -pinene oxide is formed with yields of approximately 77 % following reaction of α -pinene with ground state atomic oxygen (*i.e.*)

 $O(^{3}P)$) and approximately 2 % following reaction with ozone. It has also been proposed, by Jaoui and Kamens, that α -pinene oxide may form following RO₂ chemistry involving the parent α -pinene molecule (Jaoui and Kamens, 2001). However, it should be noted that the fraction of a-pinene reacting with RO₂ would be somewhat small compared to the fraction reacting with OH or O_3 , and in the presence of NO_x , reactions of RO_2 with NO are the more likely fate. As the concentrations of NO were still relatively high (being in the range 5 - 49ppbV over experiments 8 - 10), and as the concentrations of O₃ were relatively low at the time of appearance of these masses, and as the signals of m/z 153 and 109 were relatively strong during all experiments (see Table A7.3), it is likely that these mass channels contain contributions from other compounds. Likely candidates include the dehydrated PTR products (*i.e.* MH⁺(-H₂O)) of pinanediol and norpinonic acid or an α -pinene ketone (C₁₀H₁₆O). As the formation pathway to pinanediol also involves RO₂ chemistry, as the temporal profile of $\Sigma(m/z \ 109 + 153)$ does not show any correlation with norpinonaldehyde (the precursor to norpinonic acid) and as the C₁₀H₁₆O ketone is believed to form with relatively low yield (Alvarado et al., 1988), it is likely that some other, as yet unidentified, contribution exists in this case. Owing to their early appearance and temporal profile, it is likely that the ions of m/z109 and 153 belong to a primary oxidation product of α -pinene.

Ozonolysis products

As each experiment evolved and as the chamber $[O_3]$ began to rise, α -pinene ozonolysis products were observed within the gas phase. Measured at m/z 183 and 165, 4oxopinonaldehyde was formed between ~ 45 and 155 minutes as O₃ concentrations rose to values of ~ 20 - 60 ppbV (Figure 20(a)). At this point of the experiment, ozonolysis accounted for 26 - 34 % of the fate of α -pinene. 4-oxopinonaldehyde constitutes a primary ozonolysis product, formed from proxy radical (U) (of Figure 13). Using a surrogate calibration factor (see Table A7.1), yields of 4-oxopinonaldehyde ranged from 0.6 - 1.52 % over all experiments. Unfortunately major ozonolysis products such as pinic acid and hydroxy pinonic acid were not exclusively observed in the current study. This result is most likely due to a combination of wall loss of these compounds on route to the CIR-TOF-MS and their fragmentation during ionisation, however further characterisation work is required for confirmation.

(4-membered) ring cleavage products

Following their production, compounds such as pinonaldehyde and pinonic acid are liable to undergo further oxidation, which may ultimately lead to cleavage of the 4-membered ring. Ring cleavage at this stage will result in the production of a wide range of multifunctional aliphatic compounds (http://www.mcm.leeds.ac.uk/MCM) that may be sufficiently nonvolatile such that transfer to the particle phase may transpire. A number of spectral features were observed during the current study that are here tentatively assigned to be ring opening products. These compounds include trioxoheptanal (MH⁺ at m/z 157 and MH⁺(-H₂O) at m/z139), dioxobutanal (MH⁺ at m/z 101 and MH⁺(-H₂O) at m/z 83), 2-oxomalonaldehyde (MH⁺ at m/z 87), hydroxy-butanedione (MH⁺(-H₂O) at m/z 85) and 3,4-dioxo-pentanal and/or 3-oxopentanedial (MH⁺ at m/z 115). Following their production between roughly 50 and 100 minutes, each of these compounds exhibited similar temporal behaviour, as exemplified for experiment 10 in **Figure 20(c)** (data for m/z 115 not shown).

Various other second and third generation products were observed across all α -pinene experiments, including acetone (*m/z* 59), methyl glyoxal and propanedial (*m/z* 73), acetic acid (*m/z* 61) and formic acid (*m/z* 47). A peak was also observed at *m/z* 45 which is tentatively assigned to be acetaldehyde. However, it should be noted that methyl glyoxal undergoes fragmentation following proton transfer ionisation to give a fragment ion which is isobaric with protonated acetaldehyde. Each of these compounds can be formed *via* a variety of different routes, but both acetone and acetic acid may also be formed as primary species (Capouet *et al.*, 2004; Jenkin, 2004; Pinho *et al.*, 2007; Yu *et al.*, 2008). The measured (mass percent) yields for acetone, methyl glyoxal/propanedial, acetic acid, formic acid and acetaldehyde during the current study were 5.5 – 9.3, 2.1 – 10.3, 3.4 – 19.9, 12.1 – 23.9 and 1.2 – 3.1 %, respectively.

Carbonyls and organic nitrates

Finally, **Figure 20(f)** gives the concentration/time profiles of the acyium ion (m/z 43) and the NO₂⁺ ion (m/z 46), which for the PTR technique constitute generic markers for carbonyl and organic nitrate species, respectively (see Chapter 3, (de Gouw *et al.*, 2003; Wyche *et al.*, 2005; Blake *et al.*, 2006)). It is interesting to note the high signal obtained in the m/z 46 mass channel, indicating significant contribution from organic nitrates to gas phase composition (*e.g.* ~ 9 % of the total signal at the conclusion of experiment 9). Several recent studies have found organic nitrates to be significant contributors to SOA mass generated from α -pinene photooxidation in the presence of NO_x. However, the contribution made by such species to the condensed phase of the α -pinene system is most likely dependent on the VOC/NO_x ratio (Koch *et al.*, 2000; Kamens and Jaoui, 2001; Presto *et al.*, 2005).

The measured signals of both the carbonyl and nitrate markers continued to increase up to the conclusion of each experiment, including experiment 9, which was run for almost 24 hours.

By ~ 500 minutes most VOC signals had decayed towards zero, or had reached a plateau as the chemistry of the respective compounds reached a steady state within the chamber atmosphere. The only signals measured to increase significantly at this time beside m/z 43 and 46, were those of acetic acid, formic acid, acetaldehyde and methanol (see **Figure 20**). It is expected that these four species would continue to rise in concentration towards the end of the experiment, as they constitute the end stage products of VOC oxidation, and also a small fraction of the acid species may be liberated from the chamber walls. Minor signal increases (< 100 ncps) similar to these were also observed in mass channels 129 and 113 (unidentified organics). However of these compounds, only acetic acid is known to contribute to the m/z 43 channel and none of these species are expected to contribute towards m/z 46. With this in mind it may be possible that post nucleation, a small portion of the m/z 43 and 46 signals originated from matter revolatilised from the aerosol.

7.5 Conclusions

The work presented here constitutes the first comprehensive set of on-line observations of the gas phase oxidation products of isoprene and α -pinene during SOA formation. *Real-time* measurements were made of a host of different compounds using CIR-TOF-MS. The high resolution available in TOF-MS has aided the identification of a number of different compounds. The analysis of spectral profiles suggests that methacrolein (and possibly MVK) and C5-carbonyls contribute to SOA growth during isoprene oxidation, most likely following further oxidation to form condensable products. The temporal behaviour of a number of other spectral features suggests that 3-methyl furan, C4-hydroxycarbonyls/methacrylic acid and C5hydroxy carbonyls may also contribute towards SOA growth. Ozonolysis of isoprene (conducted in the absence of NO_x) gave rapid SOA growth and a less compositionally diverse organic gas phase matrix. During ozonolysis, strong VOC signals at the point of nucleation imply further a role for C5-carbonyls and C4-hydroxy carbonyls and/or methacrylic acid in isoprene SOA formation/growth. A diverse range of multifunctional products were observed during α -pinene oxidation, including 4-member ring retaining and ring opening oxidation products. Strong signals were observed for pinonaldehyde and pinonic acid, the temporal behaviour of which suggests that the latter is formed via both primary and secondary mechanisms. Relatively short incubation times and higher SOA yields in the presence of heightened $[O_3]$ were noted, suggesting a role for primary acids in α -pinene SOA formation and growth.

Conclusions

The work presented within this thesis collectively describes the development, characterisation and application of a novel technique for the monitoring of volatile organic compounds (VOCs) within ambient air and during detailed laboratory experiments. This final chapter presents an overview of some of the key findings made during this work and provides a performance assessment of the CIR-TOF-MS technique. The review presented here aims to confirm the CIR-TOF-MS as an effective analytical tool for the detailed monitoring and measurement of atmospheric VOCs

8.1 Qualitative Performance

In Chapter 3, it was shown that the radioactive ion source of the CIR-TOF-MS is able to generate a number of different CI reagent ions, namely H₃O⁺, NH₄⁺, NO⁺ and O₂⁺⁺. Each species of reagent ion was generated 'cleanly' without the need for pre-selective filtering. In order to provide a foundation for future work, the ion-molecule chemistry of the four reagent ions was characterised for the analysis of a range of atmospherically significant VOCs. Several species of VOC were investigated, including aliphatic and aromatic hydrocarbons, aldehydes, ketones, alcohols, carboxylic acids, esters and nitriles. The various CI spectral fingerprints of each compound were obtained and species specific markers were identified. The findings presented within Chapter 3 indicate that the hydronium ion is the most universally successful CI reagent species of those employed here, particularly for the monitoring of complex matrices such as the atmosphere. In general the reaction of a VOC with H₃O⁺ occurs via proton transfer, resulting in the production of a simple mass spectrum with a dominant product ion, often of the form MH^+ or $M(-H_2O)^+$. It was shown, however, that the application of a second CI reagent ion may be useful for the separation of isobaric species/ions found in the proton transfer reaction mass spectrum. Under laboratory conditions the speciation of a number of isobaric aldehyde and ketone pairs was successfully performed. Chapter 3 provided sound verification of the ability of the CIR-TOF-MS to successfully ionise and detect the type and variety of VOCs commonly observed within the atmosphere.

8.2 Quantitative Performance

The performance of the CIR-TOF-MS during an OVOC measurement intercomparison was described within **Chapter 4**. Utilising an atmospheric simulation chamber, the exercise involved the measurement of fourteen different atmospherically significant OVOCs at various ambient level concentrations, *i.e.* $\sim 10.0 - 0.6$ ppbV. The CIR-TOF-MS was able to measure thirteen of the test compounds (utilising hydronium as the CI reagent) with a high level of accuracy and precision (*i.e.* 4 - 13 % and 3 - 15 %, respectively). Although signal averaging was required to achieve sub-ppbV detection, *real-time* measurements were possible for most species at mixing ratios of the order 10 ppbV. The combined analysis presented in Chapter 4 demonstrated that the CIR-TOF-MS has the required sensitivity, selectivity, detection capability and rapidity of response for the measurement of atmospheric VOCs, *i.e.* overall Chapter 4 provides validation of the technique for quantitative measurement. Finally, it is worthy of note that the performance of the CIR-TOF-MS, assessed in a recent article by the impartial intercomparison referee, was summarised thus:

"Overall performance of the instrument was good and this experiment demonstrated the viability for its use for the measurement of atmospherically relevant VOCs in the future".

8.3 Detailed Characterisation

Having proven the CIR-TOF-MS capable of ionising and detecting a host of atmospherically relevant VOCs, in both quantitative and qualitative terms, attention was given to a range of detailed instrument characterisation experiments, which would be required for the application of the technique to future scientific exploration. Having proved the most useful and universal CI reagent thus far, instrument characterisation was conducted primarily using hydronium. The results from these experiments were presented in Chapter 5. As part of this work various instrument sensitivity values for a range of VOCs were determined, and species specific trends in sensitivity were identified for variations in analyte humidity and reactor energy, *i.e.* the two most important factors which may perturb detection capability. It was found that instrument sensitivity varies from ~ 10 ncps ppbV⁻¹ for hydrocarbon compounds, to ~ 200 ncps $ppbV^{-1}$ for OVOCs, and that sensitivity decreases for most compounds with increasing reactor energy. Owing to their high polarity and high proton affinity, the instrument sensitivity to most OVOCs was found to be unaffected by sample humidity, whereas sensitivity to most hydrocarbons was shown to decrease with increasing humidity. Such crucial findings may be employed to optimise instrument settings for the measurement of specific analytes. The linearity of response was verified and compound specific detection

limits were determined, proving the CIR-TOF-MS able to monitor VOCs in *real-time* down to mixing ratios of ~ 5 ppbV, with sub-ppbV detection possible with signal averaging to the order of 10 minutes.

8.4 Atmospheric Monitoring

As part of the Leicester Air Monitoring Project, the CIR-TOF-MS was applied to the measurement of atmospheric VOCs in a typical modern urban environment. This work comprised the first major application of CIR-TOF-MS to the monitoring of VOCs outside of controlled laboratory conditions, offering a thorough test of the instrument's true ability. The findings from this field study, presented in the latter half of Chapter 5, confirm findings from all earlier tests, *i.e.* that the CIR-TOF-MS technique is capable of detecting and monitoring a variety of VOCs within ambient air. During LAMP a number of typical urban pollutants, such as acetaldehyde, acetone, methanol, and various aromatic compounds were measured at mixing ratios of the order 1 - 10 ppbV. VOCs were monitored with good temporal resolution, which was sufficient to detect local 'plume' spikes imposed upon diurnally varying profiles.

8.5 Elucidation of VOC Oxidation and SOA Formation Mechanisms

In combination, the work presented within **Chapters 6** and 7 comprised the application of the CIR-TOF-MS to the investigation of a complex system, with defined goals of elucidating the atmospheric oxidation mechanisms of, and secondary organic aerosol (SOA) formation pathways from several environmentally important VOCs, namely 1,3,5-trimethylbenzene (1,3,5-TMB), isoprene and α -pinene. The CIR-TOF-MS excelled by providing the most detailed and comprehensive gas phase measurements made thus far of the precursor VOCs and their oxidation products. Measurements made included a number of previously proposed yet unobserved primary bicyclic oxidation products of 1,3,5-TMB.

Within Chapters 6 and 7, the VOC data recorded by CIR-TOF-MS were employed with various other gas and aerosol phase measurements, and results from a box model simulation (employing data extracted from the Master Chemical Mechanism), to infer a role for a number of organic oxidation products in SOA formation and growth. More specifically, it was found that in the oxidation of the anthropogenic precursor, 1,3,5-TMB, potential SOA contributors include 3,5-dimethylbenzaldehyde, oxygen-bridged primary bicyclic compounds, furanone and δ -dicarbonyl ring opening products, nitrogenated compounds and various lower molecular weight carboxylic acids. In the case of the biogenic precursors, potential SOA

contributors include methacrolein, C5-carbonyls, C4-hydroxy carbonyls and/or methacrylic acid for isoprene and primary acid species for α -pinene.

8.6 Overall Performance of the CIR-TOF-MS and Future Developments

The work presented within this thesis has demonstrated that the CIR-TOF-MS is a valid and effective tool for the monitoring and measurement of atmospheric VOCs. The good temporal resolution and high sensitivity of the chemical ionisation reaction technique, combined with the high mass resolution, multi channel and non-mass discriminatory capability of time-of-flight mass spectrometry, allows even the most complex and transient systems to be measured with a high degree of detail. The CIR-TOF-MS has been comprehensively characterised, such that now instrument parameters can be tuned to optimise detection capability according to the target analyte and sample matrix conditions. Chapters 6 and 7 exemplify the capability of the CIR-TOF-MS and the type of scientific exploration to which it may now be applied. Measurements made provide support to our current understanding of the atmospheric oxidation mechanisms of VOCs and highlight potential secondary organic aerosol forming species.

Despite the high level of success achieve during these early years of CIR-TOF-MS development, a number of important issues have been raised within this thesis that need still to be addressed and various tasks are yet to be performed. These include:

- 1) Application of other CI reagents, e.g. NH_4^+ , NO^+ and O_2^{++} , to the monitoring of complex systems such as the atmosphere. How do these reagent ions perform and what benefits do they offer?
- 2) Quantitative and qualitative examinations of difficult to measure, yet atmospherically significant, VOCs. Certain important VOCs such as organic peroxides, glyoxal and formaldehyde have proven difficult to measure using proton transfer ionisation. Why is this and what can be done to facilitate better measurement?
- 3) *Detection of inorganic trace species.* Can CIR-TOF-MS be applied to the measurement of inorganic pollutants such as NO and NO₂ and other important trace species such as CFCs and HCFCs?
- 4) *Requirement for sub-ppbV detection on time scales of one-minute or less.* What hardware improvements can be made to the equipment in order to enhance detection capability, and what technology can be utilised for the development of successor instrumentation?

5) Further exploration of VOC oxidation and SOA formation mechanisms. Despite the progress made within the scientific community towards advancement in the understanding of the oxidation mechanisms and SOA forming capability of VOCs such as 1,3,5-TMB, isoprene and α -pinene, much work remains to be done, for instance further investigation into the discrepancies between modelled and measured data is required. Direct measurements of organic peroxides within the gas phase and a direct comparison between detailed gas and aerosol phase composition with high time resolution are currently lacking. Also, how well do we understand the degradation systems of other atmospherically important VOCs? How can a greater level of certainty be conferred to the identity of SOA forming species using CIR-TOF-MS gas phase measurements?

A number of projects are currently ongoing to address some of these issues, including the in house development of hardware in order to provide improved instrument performance. A number of these developments are outlined in brief in the following sections.

8.6.1 Hardware and Instrumentation Development

8.6.1.1 The ²⁴¹Am Radioactive Ion Source

Recently initial investigations have been made into the improvement of current ion source hardware; more specifically a second ²⁴¹Am radioactive foil has been incorporated into the high pressure ion source that was utilised within this work. Results show an increase in the measured hydronium yield from ~ 7000 counts s⁻¹ to ~ 15000 – 18000 counts s⁻¹. Also, compound sensitivity was observed to be higher for a number of test compounds, for example:

Analyte VOC	Sensitivity (1 × ²⁴¹ Am Source) / ncps ppbV ⁻¹	Sensitivity (2 × ²⁴¹ Am Source) / ncps ppbV ⁻¹
formic acid	32.9	47.5
acetic acid	64.6	95.6
isoprene	18.3	18.0

Table 1: Instrument sensitivity to a number of VOCs using 1 and $2 \times {}^{241}$ Am radioactive foils. E/N = 80 / 174 Td (reactor cell / ECC)

8.6.1.2 Source Drift Acceleration

The inclusion of a tuneable (*i.e.* energy variable), source drift region is likely to improve instrument sensitivity by facilitating the conversion of hydronium-water cluster ions to their base hydronium form before the reagent pool enters the reactor. A similar system is 307

employed in commercially available PTR-MS systems to positive effect. Initial work upon such modifications for the CIR-TOF-MS suggests hydronium yield enhancement and sensitivity improvements are likely.

8.6.1.3 Alternative Ion Sources: the Hollow Cathode Discharge Ion Source

Investigations have also recently begun into the use of a new hollow cathode discharge (HCD) ion source in place of the ²⁴¹Am radioactive variant. Initial results show that hydronium yields of ~ 40,000 counts s⁻¹ are possible with the HCD source. Furthermore it is likely that compound sensitivities will be improved.

8.6.2 New Mass Spectrometric Hardware: Hadamard Transform Time-of-Flight Mass Spectrometry (HT-TOF-MS)

As was highlighted within Chapter 2, perhaps the greatest drawback associated with time-offlight technology is its inherently low duty cycle. At best only ~ 5 % of ions generated within a typical ion source reach the detector and undergo analysis. If the duty cycle, and hence the fraction of the ion pool analysed, could be increased, then substantial improvements in overall instrument detection capability could be realised. Duty cycle improvement in TOF-MS may be facilitated through the application of the so-called *Hadamard Transform* (HT) technique, recently pioneered by Zare and co-workers (Brock *et al.*, 2000). The *modus operandi* of the HT technique is the modulation of the continuous ion beam according to a pre-determined pseudo random binary sequence, such that multiple, overlapping ion packs are passed into the flight chamber of the TOF-MS for analysis, as opposed to just one. Consequently, the detector records a superposition of many, overlapping time-of-flight mass spectra. The meaningful TOF mass spectrum may be retrieved by matrix multiplication involving the recorded data and the inverse of the modulation matrix.

An '*in-line gating*' system is employed to achieve the required fast multiplexing of the ion beam in a linear acceleration style TOF-MS. The 'gate' itself comprises two pairs of alternatively leaved wires in a mesh style grid, to which equal but opposite potentials are applied. Under control of the predetermined pseudo random binary sequence, voltage is applied to and removed from the gate in order to facilitate divergence and transmission of the ion beam (giving non-detection and detection events, respectively). As there are an equal number of transmission and deflection events, instrument duty cycle is improved to 50 %, and hence a ten-fold increase in sensitivity is gained over standard orthogonal acceleration TOF-MS. Also, as a consequence of the Hadamard matrix transformation of the TOF data,

instrument signal-to-noise ratio, and hence detection limit, is also improved significantly.

A HT system of this type is currently under development at the University of Leicester to form the 'next generation' CIR-TOF-MS system, termed HT-CIR-TOF-MS. A diagram of the HT-CIR-TOF-MS instrument, depicting the previously described 'gating' system, is shown in **Figure 1**. A diagrammatical representation of the basic principles behind the HT technique is also given.



Figure 1: The University of Leicester Hadamard Transform CIR-TOF-MS. (a) Ion transmission mode, (b) ion deflection mode. (c) Diagrammatical representation of basic principles behind the HT technique (Whyte personal communication).

The HT-CIR-TOF-MS should ultimately provide pptV level detection sensitivity in all mass channels on the second timescale.

8.7 Final Remarks

This thesis has demonstrated the successful development of the first chemical ionisation reaction time-of-flight mass spectrometer for the fast monitoring of atmospheric VOCs. The CIR-TOF-MS technique is highly versatile, providing ppbV detection sensitivities on time scales of the order minutes. The potential benefits of employing the CIR-TOF-MS are considerable, with the sample matrix being probed in more depth and detail than has been possible previously.

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Chapter 1

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Chapter 8

Brock, A., N. Rodriguez and R. Zare (2000). "Characterization of a Hadamard transform time-of-flight mass spectrometer." Review of Scientific Instruments **71**(3): 1306-1318

Appendix A6

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Figure A1.1: Atmospheric oxidation mechanisms leading to the formation of aldehydes and ketones (note, B represents a third body)



Figure A1.2: Atmospheric oxidation of a generic alkene *via* OH radical addition (note, B represents a third body)



Figure A1.3: Atmospheric oxidation of a generic alkene via reaction with ozone (taken from Monks, 2005)



Figure A1.4: Atmospheric oxidation of toluene via OH radical addition



Figure A1.5: Atmospheric oxidation of toluene via hydrogen abstraction from the aromatic ring



Figure A1.6: Atmospheric oxidation of toluene via hydrogen abstraction from the pendent alkyl group



Figure A1.7: Various heterogeneous reactions resulting in oligomer/polymer formation within SOA (Kroll and Seinfeld, 2008)


Figure A2.1: Schematic of the Kore MS-200 time-of-flight mass spectrometer

Compound	Purity / %	Source
acetaldehyde	99	Sigma Aldrich
acetic acid	≥99	Sigma Aldrich
acetone	> 95	Sigma Aldrich
acetonitrile	> 95	Sigma Aldrich
alphapinene	>99.0	Fluka
benzene	> 95	Sigma Aldrich
benzaldehyde	99.5	Sigma Aldrich
butanol	≥99	Sigma Aldrich
butan-2-one	99+	Sigma Aldrich
but-1-ene	1ppmv/N ₂	BOC Spec. Gases
cis-2-butene-1,4-diol	95	Sigma Aldrich
ethanol (anhydrous)	> 98	Sigma Aldrich
ethyl Acetate	> 95	Fisher Scientific
formic acid	≥99	Sigma Aldrich
hexanal	98	Sigma Aldrich
hexan-2-one	99+	Sigma Aldrich
hexan-3-one	98	Sigma Aldrich
hydroxyacetone	>90	Fluka
isoprene	99	Sigma Aldrich
lactic acid	≥99	Sigma Aldrich
methacrolein	95	Sigma Aldrich
methacrylic acid	99	Sigma Aldrich
methanol	95	Sigma Aldrich
methyl acetate	99	Sigma Aldrich
methyl benzoate	> 95	Sigma Aldrich
2-methyl-3-buten-2-ol	98	Sigma Aldrich
methyl vinyl ketone	95	Sigma Aldrich

Table A3.1: Source and purity of sample compounds.

Compound	Purity / %	Source
pentene		Sigma Aldrich
propan-1-ol	99.7	Sigma Aldrich
pyruvic acid	95	Sigma Aldrich
toluene	> 95	Fisher Scientific
1,3,5-trimethyl benzene	≥99	Sigma Aldrich
2,4,6-trimethylphenol	≥99	Sigma Aldrich

General notes for Tables A3.2 – A3.10:

- 1. Most abundant product ion (i.e. the base peak of the mass spectrum), given in bold.
- 2. All experiments carried out at a reactor E/N ratio of 151 Td unless starred (*). * denotes experiment conducted at a reactor E/N ratio of 120 Td.
- 3. N/I = not identified

Experiment specific notes provided under each table.

Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
1-butene (56)	CH ₂ CHCH ₂ CH ₃	MH^+	57	25
		$M(-CH_3)^+$	41	30
		$M(-CH_2CH)^+$	29	45
isoprene (68)*	CH ₂ C(CH ₃)CHCH ₂	\mathbf{MH}^+	69	46
		$M(-H)^+$	67	2
		N/I	43	1
		$M(-CH_2CH)^+$	41	39
		$M(-CH_3.CH_2)^+$	39	7
1-pentene (70)	CH ₂ CHCH ₂ CH ₂ CH ₃	MH^+	71	20
		$M(-CH_2CH)^+$	43	46
		$M(-CH_2CH_3)^+$	41	22
		$M(-C_2H_7)^+$	39	2
		$M(-CH_2CH_2CH_3)^+$	27	2
benzene (78)	C_6H_6	\mathbf{MH}^{+}	79	100
toluene (92)	CH ₃ C ₆ H ₆	\mathbf{MH}^{+}	93	100
α -pinene (136)*	$C_{10}H_{16}$	MH^+	137	36
	10 10	N/I	95	2
		$M(-C_4H_7)^+$	81	57
		N/I	67	1
acetonitrile (41)	CH ₃ CN	\mathbf{MH}^{+}	42	100

Table A3.2: Product ion distribution for reaction of H_3O^+ with a range of atmospherically significant non-oxygenated VOCs

Molecule	Formula	Product Ion	m/z	Relative
(molecular weight)				Abundance
acetaldehyde (44)	CH ₃ CHO	\mathbf{MH}^{+}	45	62
		$M(-H)^+$	43	26
		N/I	41	8
		N/I	39	1
propanal (58)	CH ₃ CH ₂ CHO	\mathbf{MH}^+	59	80
		$M(-CH_3)^+$	43	1
		$\mathrm{MH}^{+}(\mathrm{-H_2O})$	41	5
		N/I	31	12
methacrolein (70)	CH ₂ C(CH ₃)CHO	\mathbf{MH}^+	71	87
		$M(-C_2H_3)^+/MH^+(-CO)$	43	9
		$M(-CHO)^+$	41	4
butanal (72)	CH ₂ CH ₂ CH ₂ CHO	MH^+	73	3
o uuuluu (/=)	011,011201120110	$M(-H)^+$	71	1
		$MH^+(-H_2O)$	55	86
		$M(-H)^{+}(-H_{2}O)$	53	1
		$M(-CH_3CH_2)^+$	43 ¹	2
		$M(-CHO.H_2)^+$	41	1
		$M(-CHO.2H_2)^+$	39	2
hexanal (100)	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CHO	$M(-H)^{+}.H_{2}O$	117	2
		\mathbf{MH}^{+}	101	1
		$\mathrm{MH}^{+}(\mathrm{-H}_{2}\mathrm{O})$	83	49
		$M(-CH_3CH_2CH_2)^+$	57 ¹	2
		$M(-C_{3}H_{9})^{+}$	55	37
		$M(-CH_3(CH_2)_3)^+$	43 ¹	2
		$M(-CH_2CH_2CHO.H_2)^+$	41	2
		$M(-CH_2CH_2CHO.H_2)^+$	39	1
		$\mathrm{M(-CH_3(CH_2)_4)^+}$	29 ¹	1
benzaldehde (106)	C ₆ H ₆ CHO	\mathbf{MH}^+	107	91
		MH ⁺ (-CO)	79	3
		N/I	57	1

Table A3.3: Product ion distribution for reaction of H_3O^+ with a range of atmospherically significant aldehydes

Table A3.4: Product ion distribution for reaction of H_3O^+ with a range of atmospherically significant alcohols

Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
methanol (32)	CH ₃ OH	\mathbf{MH}^+	33	97
		$M(-OH)^+$	15	1
ethanol (46)	CH ₃ CH ₂ OH	\mathbf{MH}^+	47	79
		$\mathrm{MH}^{+}(-\mathrm{H}_{2}\mathrm{O})$	29	14
		M(-OH.H ₂)	27	5
1-propanol (60)	CH ₃ CH ₂ CH ₂ OH	$\mathrm{MH}^{+}(\mathrm{-H}_{2}\mathrm{O})$	43	40

¹ Potential contribution from equivalent alkyl ion (see Chapter 3 for details)

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Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
		$MH^{+}(-H_{2}O.H_{2})$	41	51
		$M(-OH.2H_2)^+$	39	6
		$M (-CHO.H_2)^+$	27	3
1-butanol (74)	CH ₃ CH ₂ CH ₂ CH ₂ OH	$\mathrm{MH}^{+}(-\mathrm{H}_{2}\mathrm{O})$	57	78
		$M(-CH_3.H_2O)^+$	41	14
		$M(-OH.CH_2.2H_2)^+$	39	1
		$M(-CH_2CH_2OH)^+$	29	3
		$M(-CH_2CH_2OH.H_2)^+$	27	1
hydroxy acetone (74)*	CH ₃ COCH ₂ OH	\mathbf{MH}^+	75	95
		$\mathrm{MH}^{+}(\mathrm{-H}_{2}\mathrm{O})$	57	1
MBO (86)	CH_CHC(CH_)(CH_)OH	MH^+	87	16
MDO (00)	engene(eng)(eng)on	MH ⁺ (-H ₂ O)	69	60
		$M(-OH C_2H_4)^+$	41	18
		$M(-(CH_3)(CH_3)OH)^+$	39	1
cis-2-butene-1,4-diol*	OHCH2CHCHCH2OH	MH^+	89	1
(88)		N/I	85	1
		MH ⁺ (-O)	73	1
		$MH^{+}(-H_{2}O)$	71	25
		N/I	69	23
		MH ⁺ (-CH ₂ CH ₂ OH.H ₂)	43	27
		N/I	42	11
		MH ⁺ (-OH.OH.CH ₂)	41	5
1,3,5-trimethylphenol	C ₆ H ₆ (CH ₃) ₃ OH	\mathbf{MH}^+	137	80
(130)*		$M(-H)^+$	135	1
		N/A	85	1
		N/A	43	4
		N/A	42	9

Table A3.5: Product ion distribution for reaction of H_3O^+ with a range of atmospherically significant organic acids

Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
formic acid (46)*	НСООН	\mathbf{MH}^+	47	100
acetic acid (60)*	CH ₃ COOH	MH+	61	79
	-	$MH^{+}(-H_{2}O)$	43	17
		$M(-H)^{+}$	59	1
pyruvic acid (88)*	CH ₃ COCOOH	MH+	89	2
15	5	N/I	61	1
		$M(-COOH)^+$	43	96
lactic acid (90)*	CH ₃ CH(OH)COOH	N/I	105	2
		N/I	99	5
		N/I	79	9
		N/I	77	2
		$MH^{+}(-H_{2}O)$	73	1
		N/I	63	1

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Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
		N/I	61	43
		N/I	51	1
		$M(-COOH)^+$	45	9
		$M(-COOH.H_2)^+$	43	18
methacrylic acid (86)*	CH₂CCH₃COOH	$M(H_2)^+$	88	13
		MH^+	87	6
		N/I	81	1
		$MH^{+}(-H_{2}O)$	69	44
		M(-COOH) ⁺	41	26

Table A3.6: Product ion distribution for reaction of H_3O^+ with a range of atmospherically significant ketones

Molecule (molecular weight)	Formula	Product Ion	m/z,	Relative Abundance
acetone (58)	CH ₃ COCH ₃	\mathbf{MH}^{+}	59	100
MVK (70)	CH ₂ CHCOCH ₃	$\begin{array}{c} \mathbf{MH}^{+} \\ \mathbf{MH}^{+}(\textbf{-}\mathbf{C}_{2}\mathbf{H}_{4}) \end{array}$	71 43	95 5
butan-2-one (72)	CH ₃ COCH ₂ CH ₃	\mathbf{MH}^+	73	100
hexan-2-one (100)	CH ₃ COCH ₂ CH ₂ CH ₂ CH ₃	$\begin{array}{c} \mathbf{MH}^{+} \\ \mathrm{MH}^{+}(-\mathrm{H}_{2}\mathrm{O}) \\ \mathrm{MH}^{+}(-\mathrm{C}_{3}\mathrm{H}_{7}) \\ \mathrm{M}(-\mathrm{C}_{3}\mathrm{H}_{9})^{+} \\ \mathrm{N}/\mathrm{I} \\ \mathrm{MH}^{+}(-\mathrm{C}_{4}\mathrm{H}_{9}) \end{array}$	101 83 57 55 45 43	88 2 1 1 3 1
hexan-3-one (100)	CH ₃ CH ₂ COCH ₂ CH ₂ CH ₃	$\begin{array}{c} \mathbf{MH}^{+} \\ \mathrm{MH}^{+}(-\mathrm{H}_{2}\mathrm{O}) \\ \mathrm{N/I} \\ \mathrm{M}(-\mathrm{C}_{3}\mathrm{H}_{9})^{+} \\ \mathrm{N/I} \end{array}$	101 83 61 55 45	91 1 1 1 1

Table A3.7: Product ion distribution for reaction of H ₃ C	⁺ with a range o	f atmospherically	v significant esters
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Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
methyl acetate (74)	CH ₃ OCOCH ₃	MH ⁺ M(-CH ₃ O)+	75 43	88 10
ethyl acetate (88)	CH ₂ CHCOCH ₃	$\begin{array}{c} \mathbf{MH}^{+}\\ \mathbf{M}^{+}(\textbf{-CH}_{2}\mathbf{CH})\\ \mathbf{M}^{+}(\textbf{-CH}_{3}\mathbf{OC})\end{array}$	89 61 43	5 74 21
methyl benzoate (136)	CH ₃ OCOC ₆ H ₆	\mathbf{MH}^+	137 105	88 12

Table A.3.8: Product ion distribution for reaction of NH_4^+ with a range of atmospherically significant VOCs

Appendix				Chapter 3
Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
Aldehydes				
acetaldehyde (44)	CH ₃ CHO	None Observed	-	-
methacrolein (70)	CH ₂ C(CH ₃)CHO	$M.NH_4^+$	88	91
		111.11114.11113	105	7
hexanal (100)	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CHO	$M.NH_4^+$	118	100
Ketones				
acetone (58)	CH ₃ COCH ₃	$M.NH_4^+$	76	91
		$M.NH_4.NH_3$ ⁺	93	9
MVK (70)	CH ₂ CHCOCH ₃	M.NH4 ⁺	88	95
		$M.NH_4.NH_3$ ⁺	105	5
Alcohols				
ethanol (46)	CH ₃ CH ₂ OH	None Observed	-	-
Esters				
ethyl acetate (88)	CH ₂ CHCOCH ₃	$M.NH_4^+$	106	95
		$M.NH_4.NH_3^+$	123	5
methyl benzoate (136)	CH ₃ OCOC ₆ H ₆	M.NH4 ⁺	154	90
		$M.NH_4.NH_3$ ⁺	171	10
Non-oxygenated				
1-butene (56)	CH ₂ CHCH ₂ CH ₃	None Observed	-	-
benzene (78)	C_6H_6	None Observed	-	-
toluene (92)	CH ₃ C ₆ H ₆	None Observed	-	-
acetonitrile (41)	CH ₃ CN	M.NH4 ⁺	59	95
		$M.NH_4.NH_3^+$	76	5

Table A.3.9: Product ion distribution for reaction of NO⁺ with a range of atmospherically significant VOCs

Molecule / molecular weight	Formula	Product Ion	m/z	Relative Abundance
Aldehydes				
acetaldehyde (44)	CH ₃ CHO	$M(-H)^+$	43	77
		N/I	41	18
		N/I	39	2
		$M(-OH)^+$	27	3

Appendix				Chapter 3
Molecule / molecular weight	Formula	Product Ion	m/z	Relative Abundance
propanal (58)	СНаСНаСНО	MH^+	50^{2}	30
propulai (50)	engenzento	M ⁺	58	4
		$M(-H)^+$	50 57	5
		$M(-CH_2)^+$	43	1
		$M(-CH_{2}H_{2})^{+}$	41	3
		N/I	31	7
		$M(-CH_3CH_2)^+$	29^{3}	10
		$M(-CHO.H_2)^+$	27	39
butanal (72)	CH ₂ CH ₂ CH ₂ CHO	MH^+	73	2
		$M(-H)^+$	71	2
		$MH^{+}(-H_{2}O)$	55	26
		$M(-CHO)^+$	43^4	20
		$M(-CHOH_{0})^{+}$	41	28
		$M(-CHO 2H_2)^+$	39	4
		$M_{(CH_2CH_2CH_2)}^+$	29	1
		$M(-CH_2CHO.H_2)^+$	27	7
methacrolein (70)	CH ₂ C(CH ₃)CHO	$M(-H)^+$	69	5
	2 ())	$M(-CH_3C)^+$	43	2
		M(-CHO) ⁺	41	78
		$M(-CH_3.O)^+$	39	15
hexanal (100)	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CHO	$M(-H)^+$	99	3
		$M(-C_2H_5)^+$	71	15
		$M(-CH_3CH_2CH_2CH_2)^+$	43	43
		$M(-C_{3}H_{5}O.H_{2})^{+}$	41	30
		$M(-C_{3}H_{5}O.2H_{2})^{+}$	39	3
		$M(-C_4H_7O.H_2)^+$	27	5
Ketones				
acetone (58)	CH ₃ COCH ₃	M.NO ⁺	88	78
		$M(-CH_3)^+$	43	22
butanone (72)	CH ₃ CH ₂ COCH ₃	$M.NO^+$	102	28
		\mathbf{MH}^{+}	73	59
		M^+	72	2
		$M(-CH_3)^+$	57	3
		$M(-CH_2CH_3)^+$	43	3
		$M(\text{-COCH}_3.H_2)^+$	27	1
hexan-2-one (100)	CH ₃ CH ₂ CH ₂ CH ₂ COCH ₃	$\mathbf{M.NO}^+$	130	26

² Ion present due to PTR from hydronium. Low levels of hydronium were present due to residual water contamination of the ion source. ³ Peak may also contain some contribution from the $CH_3CH_2^+$ ethyl ion. ⁴ Peak may also contain some contribution from the CH_2CHO^+ acylium ion.

Appendix				Chapter 3
Molecule / molecular weight	Formula	Product Ion	m/z	Relative Abundance
		$M.NO(-CH_3.H_2)^+$	112	4
		MH^+	101	15
		M^+	100	2
		$M(-H)^+$	99	2
		$M(-CH_3)^+$	85	13
		$M(-CH_3CH_2)^+$	71	6
		N/I	70	3
		$M(-CH_2CHCH_3)^+$	58	16
		$M(-CH_3CH_2CH_2CH_2)^+$	43	5
hexan-3-one (100)	CH ₃ CH ₂ CH ₂ COCH ₂ CH ₃	$M.NO^+$	130	8
		MH^+	101	16
		M^+	100	15
		$M(-CH_3)^+$	85	2
		$M(-CH_2CH_2)^+$	72	19
		$M(-CH_3CH_2)^+$	71	5
		$M(-CH_3CH_2CH_2)^+$	57	4
		$M(-COCH_2CH_3)^+$	43 ⁵	16
		$M(-COCH_2CH_3H_2)^+$	41	5
		$M(-CH_3CH_2CH_2CO.H_2)^+$	27	3
MVK (70)	CH ₂ CHCOCH ₃	$M.NO^+$	100	6
		$M(-H).NO^+$	99	7
		N/I	98	8
		$M(-H)^+$	69	10
		$M(-CH_3)^+$	55	30
		$M(-CH_2CH)^+$	43	33
		$M(-CH_3CO)^+$	27	6
Alcohols				
ethanol (46)	CH ₃ CH ₂ OH	M(-H) ⁺	45	97
		$M(-OH)^+$	29	1
		$\mathrm{M(-H)}^{+}(\mathrm{-H}_{2}\mathrm{O})$	27	2
Esters		· · · · · · · · · · · · · · · · · · ·		
ethyl acetate (88)	CH ₂ CHCOCH ₃	M.NO ⁺	118	4
		$M(-CH_2CH)^+$	61	42
		$M(-CH_5O)^+$	55	1
		$M(-CH_3CO)^+$	45	2
		$M(-C_2H_5O)^+$	43	51
methyl benzoate	CH ₃ OCOC ₆ H ₆	N/I	107	2
(130)		$M(-CH_3O)^+$	105	88
		N/I	104	2
		N/I	103	2

 $^{^5}$ TOF-MS accurate mass data shows a double peak, which also contains contribution from the $\rm CH_2CHO^+$ acylium ion.

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Molecule / molecular weight	Formula	Product Ion	m/z	Relative Abundance
		N/I	102	1
		$M(-CH_3OCO)^+$	77	3
		N/I	45	2
Non-oxygenated				
1-butene (56)	CH ₂ CHCH ₂ CH ₃	$M.NO^+$	86	12
		M^+	56	24
		$M(-H)^+$	55	2
		N/I	44	9
		$M(-CH_2)^+$	42	12
		$M(-CH_3)^+$	41	2
		$M(-CH_2CH)^+$	29	33
		$M(-C_2H_4)^+$	28	6
benzene (78)	C_6H_6	\mathbf{M}^+	78	100
toluene (92)	CH ₃ C ₆ H ₆	\mathbf{M}^{+}	92	100
acetonitrile (41)	CH ₃ CN	\mathbf{M}^+	41	87
	-	$M(-H).NO^+$	71	13

Table A3.10: Product ion distribution for reaction of $O_2^{+\bullet}$ with a range of atmospherically significant VOCs

Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
Aldehydes				
acetaldehyde (44)	CH ₃ CHO	$M(-H)^+$	43	100
methacrolein (70)	CH ₂ C(CH ₃)CHO	M^+	70	3
		$M(-H)^+$	69	3
		$M(-CH_3C)^+$	43	16
		$M(-CHO)^+$	41	58
		$M(-CH_3.O)^+$	39	18
hexanal (100)	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CHO	$\mathrm{MH}^{+}(-\mathrm{H}_{2}\mathrm{O})$	83 ⁶	10
		$M(-H_2O)^+$	82	3
		N/I	72	4
		$M(-C_2H_5)^+$	71	1
		N/I	67	5
		$M(-C_{3}H_{4})^{+}$	60	3
		$M(-CH_2CHO)^+$	57	8
		$M(-C_{3}H_{9})^{+}$	55	24
		N/I	45	3
		$M(-C_4H_9)^+$	43	12

⁶ Ion present due to PTR from hydronium. Low levels of hydronium present due to residual water contamination of the ion source.

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Molecule (molecular weight)	Formula	Product Ion	m/z	Relative Abundance
		$M(-C_{3}H_{5}O.H_{2})^{+}$	41	10
		$M(-C_5H_{11})^+$	29^{7}	4
		$M(\text{-}C_4H_7O.H_2)^+$	27	1
Ketones				
acetone (58)	CH ₃ COCH ₃	$M(-CH_3)^+$	43	100
MVK (70)	CH ₂ CHCOCH ₃	\mathbf{M}^{+}	70	1
		$M(-H)^+$	69	18
		$M(-CH_3)^+$	55	18
		$M(-CH_2CH)^+$	43	47
		$M(-COH)^+$	41	10
		$M(-CH_3CO)^+$	27	6
Alcohols				
ethanol (46)	CH ₃ CH ₂ OH	$M(-H)^+$	45	66
		$M(-CH_3)^+$	31	34
Esters				
ethyl acetate (88)	CH ₂ CHCOCH ₃	$M(-CH_2CH)^+$	61	61
		$M(-CH_5O)^+$	55	5
		$M(-CH_3CO)^+$	45	12
		$M(-C_2H_5O)^+$	43	22
methyl benzoate (136)	CH ₃ OCOC ₆ H ₆	M^+	136	3
		$M(-H)^+$	135	3
		$M(-CH_3O)^+$	105	88
		$M(-CHO_2)^+$	91	6
Non-oxygenated				
1-butene (56)	CH ₂ CHCH ₂ CH ₃	M^+	56	25
		$M(-CH)^+$	43	10
		$M(-CH_3)^+$	41	41
		$M(-CH_2CH)^+$	29	24
benzene (78)	C_6H_6	\mathbf{M}^{+}	78	100
toluene (92)	$CH_3C_6H_6$	\mathbf{M}^{+}	92	100
acetonitrile (41)	CH ₃ CN	\mathbf{M}^+	41	100

 $^{^7}$ Peak may also contain some contribution from the $\rm CH_3CH_2CH_2CH_2CH_2^+$ alkyl ion.



Figure A4.1: Ozone concentration and water vapour pressure within the SAPHIR simulation chamber during (a) experiment 2, (b) experiment 3 and (c) experiment 4. Taken from (Apel *et al.*, 2008).

Compound	Mass / Da	Mixing Ratio / ppbV
methanol	32	522
acetaldehyde	44	453
ethanol	46	542
acrolein	55	468
butane	58	548
propanal	58	480
acetone	58	536
1-propanol	60	532
methacrolein	70	432
methyl vinyl ketone	70	511
butanal	72	504
methyl ethyl ketone	73	510
1-butanol	74	491
2-methyl-3-buten-2-ol	86	540
pentanal	86	481
hexanal	100	476

Table A4.1: Air Environmental, Inc. multi gas component mixture S1 (University of Bristol, UK). Target compounds of the OVOC intercomparison exercise are highlighted in red.

Compound	Mass / Da	Mixing ratio / ppbV
acetaldehyde	44	1000
methanol	33	1000
ethanol	46	1000
isoprene	68	200
acetone	58	200
toluene	92	200
cis-3-hexanol	102	100
α-pinene	136	200

Table A4.2: Air Environmental, Inc. multi component gas mixture S2 (Paul Scherrer Institut, Ch.). Target compounds of the OVOC intercomparison exercise are highlighted in red.

Table A4.3: Air Environmental, Inc. multi component gas mixture S3 (Paul Scherrer Institut, Ch.). Target compounds of the OVOC intercomparison exercise are highlighted in red.

Compound	Mass / Da	Mixing ratio / ppbV
propene	42	200
acetaldehyde	44	1000
propenal	42	200
acetone	58	200
MVK	70	200
toluene	92	200
1,3,5 TMB	120	200
benzaldehyde	106	100

Table A4.4: Permeation tube gas mixture S2 (FAL, Ch.). Target compounds of the OVOC intercomparison exercise are highlighted in red (not used in this instance for calibration).

Mass / Da	Mixing ratio / ppbV
69	8.85
70	9.17
70	19.17
78	21.67
93	10.50
100	19.54
102	39.9
	Mass / Da 69 70 70 78 93 100 102



Figure A4.2: CIR-TOF-MS mass spectra of multicomponent gas standards employed for calibration during the OVOC intercomparison exercise

Determination of Analyte Concentration in the Presence of Water Vapour utilising Proton Transfer Reaction Kinetics

If hydrated hydronium ions are present within the drift cell reactor, the ionisation potential of the system for a particular analyte, M, will not be only determined by reaction (R3.3) and equation (E3.9) of Chapter 3. Consequently, equation (E3.9) must be modified to account for reactions (R5.2) – (R5.4). First consider the fraction of analyte M ionised to MH^+ *via* reaction (R5.2):

$$[\mathbf{M}_{1}] = \sum_{n \to \infty} \chi_{1} \left(F \frac{i(\mathbf{MH}^{+})}{i(\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n})_{0}} \frac{1}{k_{1} t} \frac{\mu_{\mathbf{MH}^{+}}}{\mu_{\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n}}} \right)$$
(EA5.1)

Where, χ is a branching ratio, which ranges from 0 to 1, used to scale equation (EA5.1) according to the ability of M to react with H₃O⁺.(H₂O)_{*n*} *via* reaction (R5.2). For example for a compound that does not react with hydrated hydronium *via* reaction (R5.2), χ would be set to 0, whereas for a compounds which would readily react with hydrated hydronium, χ would be set to 1. Similarly, for the fraction of analyte M ionised to MH⁺ *via* reaction (R5.3):

$$[M_{2}] = \sum_{n \to \infty} \chi_{2} \left(F \frac{i(MH^{+})}{i(H_{3}O^{+}.(H_{2}O)_{n})_{0}} \frac{1}{k_{2} t} \frac{\mu_{MH^{+}}}{\mu_{H_{3}O^{+}.(H_{2}O)_{n}}} \right)$$
(EA5.2)

Finally, for those compounds that are also able to undergo ligand switching with hydrated hydronium, the fraction of M ionized *via* reaction (R5.4) must be accounted for:

$$[M_{3}] = \sum_{n \to \infty} \chi_{3} \left(F \frac{i(MH^{+}.(H_{2}O)_{n})}{i(H_{3}O^{+}.(H_{2}O)_{n})_{0}} \frac{1}{k_{3}t} \frac{\mu_{MH^{+}.(H_{2}O)_{n}}}{\mu_{H_{3}O^{+}.(H_{2}O)_{n}}} \right)$$
(EA5.3)

Combining equations (E5.4) - (E5.6) the expression giving the concentration of analyte M, within the sample matrix becomes:

$$[\mathbf{M}] = \left(F\frac{i(\mathbf{M}\mathbf{H}^{+})}{i(\mathbf{H}_{3}\mathbf{O}^{+})_{0}}\frac{1}{kt}\frac{\mu_{\mathbf{M}\mathbf{H}^{+}}}{\mu_{\mathbf{H}_{3}\mathbf{O}^{+}}}\right) + \sum_{n \to \infty} \chi_{1}\left(F\frac{i(\mathbf{M}\mathbf{H}^{+})}{i(\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n})_{0}}\frac{1}{k_{1}t}\frac{\mu_{\mathbf{M}\mathbf{H}^{+}}}{\mu_{\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n}}\right) + \frac{1}{k_{1}t}\frac{\mu_{\mathbf{M}\mathbf{H}^{+}}}{\mu_{\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n}}}\right) + \frac{1}{k_{1}t}\frac{\mu_{\mathbf{M}\mathbf{H}^{+}}}{\mu_{\mathbf{H}_{3}\mathbf{O}^{+}.(\mathbf{H}_{2}\mathbf{O})_{n}}}$$

$$\sum_{n \to \infty} \chi_2 \left(F \frac{i(\mathrm{MH}^+)}{i(\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n)_0} \frac{1}{k_2 t} \frac{\mu_{\mathrm{MH}^+}}{\mu_{\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n}} \right) + \sum_{n \to \infty} \chi_3 \left(F \frac{i(\mathrm{MH}^+.(\mathrm{H}_2\mathrm{O})_n)}{i(\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n)_0} \frac{1}{k_3 t} \frac{\mu_{\mathrm{MH}^+.(\mathrm{H}_2\mathrm{O})_n}}{\mu_{\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n}} \right) + \sum_{n \to \infty} \chi_3 \left(F \frac{i(\mathrm{MH}^+.(\mathrm{H}_2\mathrm{O})_n)}{i(\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n)_0} \frac{1}{k_3 t} \frac{\mu_{\mathrm{MH}^+.(\mathrm{H}_2\mathrm{O})_n}}{\mu_{\mathrm{H}_3\mathrm{O}^+.(\mathrm{H}_2\mathrm{O})_n}} \right) \right)$$

(EA5.4)

As the presence of hydronium-water cluster ions will perturb the ionisation potential of the reactor, it is important that their behaviour be well characterised across a range of conditions and for all species of analyte.

Table A6.1: CIR-TOF-MS calibration details. The measured compound is given along with the method employed for calibration, the relative humidity of the sample matrix during calibration and, where appropriate the surrogate compound employed. The instrument sensitivity to each given compound is provided along with an uncertainty/error estimate for the measurement.

Target	Method	Relative Humidity /	Calibration Compound	Sensitivity ¹ / ncps ppbV ⁻¹	Calibration Error ² / %
2,4,6-trimethyl phenol	Gas Standard ³	0	phenol	226.35 – 372.54	11.04 - 21.78
3,5-dimethyl benzaldehyde	Gas Standard	0	<i>m</i> -tolualdehyde	98.65 - 145.35	9.35 - 17.20
O ₂ -bridged nitrate (TM135BPNO3) ⁴	Gas Standard	0	<i>m</i> -tolualdehyde	98.65 - 145.35	9.35 - 17.20
O ₂ -bridged diol (TM135BP2OH) ⁴	Gas Standard	0	<i>m</i> -tolualdehyde	98.65 - 145.35	9.35 - 17.20
O_2 -bridged ketone (TM135OBPOH) ⁴	Gas Standard	0	<i>m</i> -tolualdehyde	98.65 - 145.35	9.35 - 17.20
bicyclic marker ⁴	Gas Standard	0	<i>m</i> -tolualdehyde	98.65 - 145.35	9.35 - 17.20
<i>m/z</i> 129	Permeation Tube	50	methacrolein	9.46 - 19.27	3.95 - 4.20
furanones (<i>m/z</i> 111 & 113)	Teflon Bag ⁵	50	citraconic anhydride	32.53 - 119.90	27.60 - 27.63
hydroxy acetic acid	Permeation Tube ⁶	50	acetic acid	17.43 - 45.93	2.93 - 5.96
hydroxy acetone	Permeation Tube	50	acetone	55.60 - 104.04	3.25 - 4.87
methyl glyoxal	Permeation Tube	50	isoprene	9.46 - 19.27	6.53 - 11.56

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Target	Method	Relative Humidity / %	Calibration Compound	Sensitivity ¹ / ncps ppbV ⁻¹	Calibration Error ² / %
acetic acid	Permeation Tube	50	acetic acid	17.43 - 45.93	2.93 - 5.96
acetone	Permeation Tube	50	acetone	55.60 - 104.04	3.25 - 4.87
formic acid	Permeation Tube	50	formic acid	5.14 - 9.52	3.77 - 6.78
acetaldehyde	Permeation Tube	50	acetaldehyde	57.01 - 107.33	3.17 - 3.31
carbonyl marker	Permeation Tube	50	acetone	55.60 - 104.04	3.25 - 4.87
methanol	Permeation Tube	50	methanol	22.25 - 46.06	3/94 - 6.76

¹ Instrument sensitivity is given as a range covering all drift cell conditions employed during the study (see **Table 1** in Chapter 6 for further information).

² Measurement uncertainty/error is given as a range covering all drift cell conditions employed during the study (see **Table 1** in Chapter 6 for further information).

³ Gas standards provided by Air Environmental Inc. (US) and courtesy of PSI. Compound mixing ratio accuracy: 5 %.

⁴Calibrated values used only to calculate "pseudo" VOC yields

⁵ Calibration conducted by injecting liquid citraconic anhydride (Sigma Aldrich, 99%) into an 80 L Teflon sample bag (SKC, Ltd). Sticking factors employed to adjust for deposition/wall loss.

⁶ Permeation tubes supplied by Ecoscientific (UK) and Vici Inc. (US). Compound emission rate accuracy: 2.02 – 11.24 %



Figure A6.1: Variation of $[O_3]$ with [1,3,5-TMB] and (a) $[NO_x]$, (b) [NO] and (c) $[NO_2]$ during high NO_x experiment 6



Figure A6.2: Variation of $[O_3]$ with [1,3,5-TMB] and (a) $[NO_x]$, (b) [NO] and (c) $[NO_2]$ during low NO_x experiment 7

Atmospheric Simulation Chamber Wall Loss Corrections

Within an atmospheric simulation chamber some fraction of the particulate matter formed will deposit upon the chamber walls, hence the SOA number and volume concentrations measured (and thus the corresponding aerosol mass and yield determined) will constitute a lower limit.

Providing that a number of simple assumptions are made, deposition of particles to the interior of the simulation chamber, or *wall loss* as it is often known, can be accounted for using a suitable model. In this instance the PARticle Growth And Nucleation (PARGAN) model, developed by Verheggen and Mozurkewich (Verheggen and Mozurkewich, 2006) was employed^a. When used to adjust a measured data set for wall losses, particle growth and nucleation rate determining models such as PARGAN employ two first order loss rate coefficients in order to account for: (i) particle loss by diffusive motion ($k_D(r)$, EA6.1) and (ii) particle loss by gravitational settling ($k_G(r)$, EA6.2),:

$$k_D(r) = C_D \sqrt{D_B(r)} \tag{EA6.1}$$

$$k_G(r) = \mathcal{M}\,\mu(r)g\frac{S}{V}F_s \tag{EA6.2}$$

where, C_D = a chamber specific constant (empirically derived from a series of characterisation experiments), $D_B(r)$ = Brownian diffusion coefficient, r = particle radius, M = SOA mass, $\mu(r)$ = particle mobility, g = acceleration due to gravity (9.81 ms⁻¹), S = chamber surface area, V = chamber volume and F_s = a second chamber specific constant (projected horizontal surface area/total chamber surface area ratio). As can be seen from observation of equations (EA6.1) and (EA6.2), the values of $k_D(r)$ and $k_G(r)$ are dependent upon particle size (hence as is the overall loss of SOA particles to the chamber walls). Within the PSI simulation chamber, $k_D(r)$ is the dominant term in controlling wall loss for particles of diameter < 100 nm, whereas $k_G(r)$

If values for $k_D(r)$ and $k_G(r)$ can be determined, the measured SOA volume concentration (and hence mass) can be scaled in order to compensate for the proportion of particles lost to the chamber walls. Following the completion of this thesis, wall loss coefficients were determined for those experiments described within Chapter 6^a. **Figure A6.3** gives an example plot showing the temporal evolution of SOA mass measured during TMB experiment 6 (VOC/NO_x ~ 2:1) along with the corresponding 'wall loss corrected' mass profile.

^a Determination of wall loss correction factors performed by, and supplied with permission of Axel Metzger (PSI, Ch.)



Figure A6.3: SOA mass and corresponding 'wall loss corrected' mass obtained during TMB experiment 6 (VOC/NO_x \sim 2:1)

As can be seen from **Figure A6.3**, the maximum corrected SOA mass achieved during experiment 6 was ~ 35 μ g m⁻³ (*i.e.* some 13.5 % greater than the uncorrected value of ~ 31 μ g m⁻³), giving a wall loss corrected SOA yield (Y(corrected)) of 2.01 %. Similar increases in SOA mass and yield were obtained when applying wall loss correction factors to the data sets of each of the experiments detailed within Chapter 6, *e.g.* Y(corrected) = 2.98, 8.13 and 11.42 %, for experiments 4, 5 and 7, respectively. These corrected values confirm and support the discussions made and conclusions drawn within Chapter 6.



Figure A6.4: SOA time-dependent growth curves for all high NO_x TMB experiments. (b) focuses on the nucleation point for each curve



Figure A6.5: SOA time-dependent growth curves for both low NO_x TMB experiments

Experiment						Volatile	Organi	c Compo	ound Pro	oduct Yi	ield / %					
-	meth	lanol	carbo	slynd	acetald	le hyde	formi	c acid	acet	one	acetic	acid	methyl	glyoxal	hydr	oxy-
															acet	one
1	1.74	6.53	6.25	17.44	3.75	96.6	11.51	30.06	n/m	u/m	19.47	38.97	13.48	22.49	0.56	0.89
7	0.98	3.66	8.69	24.26	10.43	27.82	13.12	34.27	0.38	0.79	14.72	29.46	24.30	40.53	0.47	0.75
3	0.98	3.67	8.72	24.35	7.33	19.53	32.48	84.81	3.29	6.80	11.86	23.73	31.10	51.88	1.06	1.69
4	0.74	2.79	5.56	15.54	3.39	9.05	15.32	40.00	1.42	2.95	10.03	20.07	28.80	48.03	0.99	1.58
v	2.78	10.43	4.06	11.33	1.62	4.33	48.68	127.10	3.11	6.44	33.08	66.20	21.31	35.54	1.45	2.33
9	1.44	5.41	4.05	11.30	3.32	8.85	10.88	28.41	1.31	2.72	16.01	32.05	22.48	37.49	0.64	1.02
2	2.56	9.63	69.9	18.68	3.85	10.26	m/n	m/n	1.54	3.18	32.23	64.51	21.02	35.06	1.20	1.92
n/m: Not me	easured															

Table A6.2: VOC yields for various compounds measured by the CIR-TOF-MS during experiments 1 – 7. Mass percent yield (*i.e.* mass formed per mass reacted) given in white columns, molar yield (*i.e.* ppbV formed per ppbV reacted) given in shaded columns. Red text signifies low NO_x experiment.

Experiment						Volatile	Organi	c Compo	ound Pr	oduct Yie	eld / %					
	hydrox ac	y acetic sid	3me.5n (2H) fu	ne thyl.5 ranone	2/W	113	3,5-dir benzalc	me thyl Ie hyde	2,4,6-tri phe	imethyl nol	O ₂ Bri Did (TM13B	idged ol P2OH)	O ₂ Bri Kete (TMI35C	idge d one DBPOH)	O ₂ Bri Nitr (TM1351	idged ate 3PNO3)
-	3.09	4.88	5.70	6.23	15.61	16.74	1.28	1.15	0.87	0.77	0.24	0.17	0.70	0.46	1.75	16.0
5	m/n	m/n	10.29	11.24	46.64	50.01	2.45	2.20	2.52	2.23	0.26	0.19	0.64	0.42	2.84	1.47
ю	1.99	3.15	8.79	9.60	37.15	39.84	1.56	1.40	1.57	1.39	m/n	m/n	0.96	0.50	2.69	1.40
4	3.08	4.86	7.85	8.85	38.37	41.15	2.57	2.30	2.69	2.38	0.40	0.29	1.10	0.17	2.93	1.52
N)	18.61	29.41	3.59	3.92	33.28	35.69	1.89	1.70	n/m	u/m	0.82	0.85	2.97	1.94	4.32	2.24
9	5.85	9.25	8.13	8.88	39.64	42.51	2.70	2.42	3.79	3.45	0.19	0.13	0.79	0.52	3.71	1.93
Ч	8.33	13.17	8.89	9.71	26.51	28.43	2.20	1.97	2.42	2.14	0.90	0.64	2.30	1.50	5.05	2.64
n/m: Not me	easured															

Table A6.2 continued: VOC yields for various compounds measured by the CIR-TOF-MS during experiments 1 - 7. Mass percent yield (*i.e.* mass formed per mass reacted) given in white columns, molar yield (*i.e.* ppbV formed per ppbV reacted) given in shaded columns. Red text signifies low NO_x experiment.

Table A7.1: CIR-TOF-MS calibration details for all isoprene and a-pinene experiments. The measured compound is given along with the method employed for calibration, the relative humidity of the sample matrix during calibration and the compound employed (or where appropriate the surrogate compound employed) for calibration purposes. The instrument sensitivity to each given compound is provided along with an uncertainty/error estimate for the measurement.

Target	Calibration	Relative	Calibration	Sensitivity ¹ /	Calibration
	Method	Humidity	Compound	ncps ppbV ⁻¹	Error ² / %
		/ %			
	Isoj	orene Oxidat	ion Products		
4-hydroxy-2-methyl- but-2-enoic acid	Gas Standard	0	cis-3-hexenol	16.89 - 59.32	12.08 – 25.99
C5-alkenediols / C4- hydroxydialdehydes	Gas Standard	0	cis-3-hexenol	16.89 - 59.32	12.08 - 25.99
C5-hydroxycarbonyls	Permeation Tube	50	methacrolein	9.46 - 19.27	3.95 - 4.20
C4-hydroxycarbonyls	Permeation Tube	50	methacrolein	9.46 - 19.27	3.95 - 4.20
C5-carbonyls	Permeation Tube	50	methacrolein	9.46 - 19.27	3.95 - 4.20
3-methyl furan	Teflon Bag ³	50	furan	31.69 - 123.89	26.00 - 30.03
hydroxy acetone	Permeation Tube	50	acetone	55.60 - 104.04	3.25 - 4.87
methacrolein / MVK	Permeation Tube	50	methacrolein / MVK	35.74 - 83.97	3.95 - 17.20
methyl glyoxal	Chamber / Permeation Tube	50	methyl glyoxal / isoprene	15.04 - 24.58	6.53 – 11.56
glycoaldehyde / acetic acid	Permeation Tube	50	acetaldehyde	57.01 - 107.33	3.25 - 4.87
propanal / glyoxal	Gas Standard /	0	propanal /	57.50 - 107.33	3.17 - 3.31

Appendix Target	Calibration	Relative	Calibration	Sensitivity ¹ /	Chapter Chapter
C	Method	Humidity	Compound	ncps ppbV ⁻¹	Error ² / %
		/ %			
	Permeation		acetone		
	Tube				
acrolein	Gas Standard	0	acrolein	40.07 - 116.95	9.20 - 18.30
acetaldehyde	Permeation Tube	50	acetaldehyde	57.01 - 107.33	3.25 - 4.87
carbonyls- acylium ion	Permeation Tube	50	acetone	55.60 - 104.04	3.25 - 4.87
methanol	Permeation Tube	50	methanol	37.32 - 56.11	3.94 - 6.76
	α-р	inene Oxidat	ion Products		
4-oxopinonaldehyde	Gas Standard	0	benzaldehyde	48.8 - 80.62	10.45 - 18.30
pinonaldehyde	Gas Standard	0	benzaldehyde	48.8 - 80.62	10.45 - 18.30
trioxoheptanal	Teflon Bag ³	50	hexanal	10.91 - 22.23	18.7 - 31.4
norpinaldehyde	Gas Standard	0	benzaldehyde	48.8 - 80.62	10.45 - 18.30
pinene oxide / norpinonic acid / pinanediol	Gas Standard	0	benzaldehyde	48.8 - 80.62	10.45 - 18.30
trimethyl-cyclohex-2- en-1-ol	Gas Standard	0	cis-3-hexenol	16.89 - 59.32	12.08 - 25.99
3,4-dioxopentanal / 3- oxo pentanal	Permeation Tube	50	methacrolein / MVK	35.74 - 83.97	3.95 - 17.20
dioxobutanal	Gas Standard	50	propenal	42.6 - 57.5	10.01 - 17.50
2-oxomalonaldehyde	Gas Standard	50	propenal	42.6 - 57.5	10.01 - 17.50
hydroxy-butane-2,3- dione	Permeation Tube	50	methacrolein / MVK	35.74 - 83.97	3.95 - 17.20
methyl glyoxal /	Chamber /	50	methyl glyoxal	14.46 – 17.11	6.53 - 11.56

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Target	Calibration	Relative	Calibration	Sensitivity ¹ /	Calibration
	Method	Humidity	Compound	ncps ppbV ⁻¹	Error ² / %
		/ %			
propanedial	Permeation		/ isoprene		
	Tube				
acetic acid	Permeation	50	acetic acid	17.43 - 45.93	2.93 - 5.96
	Tube				
acetone	Permeation	50	acetone	55.60 - 104.04	3.25 - 4.87
	Tube				
formic acid	Permeation	50	formic acid	5.14 - 9.52	3.77 - 6.78
	Tube				
acetaldehyde / methyl	Permeation	50	acetaldehyde	57.01 - 107.33	3.25 - 4.87
glyoxal	Tube				
carbonyls- acylium ion	Permeation	50	acetone	55.60 - 104.04	3.25 - 4.87
	Tube				
methanol	Permeation	50	methanol	37.32 - 56.11	3.94 - 6.76
	Tube				

¹ Instrument sensitivity is given as a range covering all drift cell conditions employed during the study (see Chapters 6 and 7 for further information).

² Measurement uncertainty/error is given as a range covering all drift cell conditions employed during the study (see Chapters 6 and 7 for further information).

³ Calibration conducted by injecting liquid furan/hexanal (Sigma Aldrich, 99%) into an 80 L Teflon sample bag (SKC, Ltd). Sticking factors employed to adjust for deposition/wall loss.

• Gas standards provided by Air Environmental Inc. (US) and courtesy of PSI. Compound mixing ratio accuracy: 10 %.

• Permeation tubes supplied by Ecoscientific (UK) and Vici Inc. (US). Compound emission rate accuracy: 2.02 -11.24~%

Measured m/z	Tentative Assignment			Expe	riment Nu	mber		
	0	1	2	3	4	5	6	7
249.45	N/I			27	37			
162.17	N/I		70	28	20			
160.16	N/I		40	127	32			
157.23 / 157.28*	N/I	-	40	115	105	40		
146.15 -	N/I		120	55	55			

Table A7.2: Major spectral features recorded by CIR-TOF-MS during isoprene experiments 1 - 7, tentative assignment and exact mass given. Columns 1 - 7 give: peak signal / concentration / yield (where possible).

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Measured m/z	Tentative Assignment			Expe	riment Nu	mber		
		1	2	3	4	5	6	7
146.19								
127.17 – 127.22	N/I			100	120	70		
117.14	C5-trihydroxy- carbonyls	398 / 23.6 / 2.4	343 / 5.8 / 1.2	169 / 2.8 / 1.8	270 / 4.6 / 1.7	78 / 3.5 / 1.4		
115.13	N/I	180	625	305	275	158		
113.11	N/I	1400	1000	375	1315	935		
103.12 (102.13) (102.09) (103.10)	C5-alkenediols / C4 hydroxy- dialdehyde / MPAN (F)	124 / 7.3 / 0.7	262 / 4.4 / 0.8	294 / 1.3 / 0.7	135 / 2.3 / 0.7	94 / 1.6 / 0.6	90 /	
101.13 (100.12)	C5-hydroxycarbonyls	338 / 35.8 / 3.3	673 / 45.3 / 8.2	464 / 24.1 / 13.4	524 / 31.0 / 10.4	277 / 16.4 / 5.93	181 / 19.1 / 1.8	
99.12	N/I	640	756	360	630	505	140 /	67
97.09	N/I	1000	520	70	568	316		
87.11 (86.09)	C4-hydroxycarbonyls / methacrylic acid	1519 / 37.3 / 2.8	1349 / 20.1 / 3.5	966 / 8.3 / 4.0	1444 / 13.5 / 3.9	1295 / 12.1 / 3.7	2520 / 61.9 / 4.9	1690
86.09	Potential organic nitrate	195	164	136	328	156		
85.12 (84.12)	C5-carbonyls	1167 / 32.7 / 2.7	1095 / 23.3 / 4.0	280 / 3.5 / 1.9	609 / 7.3 / 2.1	372 / 4.4. / 1.6	960 / 26.3 / 2.8	579
83.11 (82.10)	3-methyl furan	3094 / 95.1 / 7.0	1612 / 17.0 / 2.5	384 / 7.0 / 3.1	1682 / 14.5 / 3.9	841 / 7.0 / 2.4	259 / 8.0 / 0.7	303
77.08	N/I	180 /	694	350	665	448	200 /	
75.09 (74.08)	hydroxy acetone	1925 / 30.8 / 10.0	3358 / 38.6 / 5.1	1351 / 16.0 / 6.3	1729 / 16.6 / 3.9	1217 / 11.7 / 2.9	820 / 13.1 / 0.9	
73.08 (72.06)	methyl glyoxal	1593 / 93.1 / 5.8	1563 / 63.6 / 8.1	550 / 23.2 / 9.0	654 / 43.5 / 9.8	590 / 39.2 / 9.6	1697 / 99.2 / 6.5	508
71.10 (70.09)	methacrolein / MVK	24044 / 672.8 / 47.5	17441 / 370.8 / 53.1	9260 / 117.2 / 51.0	20644 / 245.8 / 65.9	19944 / 237.5 / 64.7	24419 / 683.2 / 45.9	
61.07 (60.05)	acetic acid / glycoaldehyde	3005 / 60.7 / 3.2	4456 / 2.9 / 0.3	2193 / 25.3 / 8.1	3550 / 33.1 / 6.2	3493 / 32.6 / 6.5	2027 / 51.2 / 2.8	521

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Measured	Tentative			Expe	riment Nu	mber		
m/z	Assignment	1	2	3	4	5	6	7
59.09**	acetone /		1598 /	1394 /	1607 /	4319/	2925 /	11225
(59.04)	propanal / glyoxal		18.4 /	16.5 /	15.5 /	41.5 /	57.6 /	
(58.08/	1 1 0 5		1.9	5.1	2.8	8.3	3.1	
58.04)								
57.10*	acrolein	4178 /	1423 /	504 /	1294 /	1373 /	1111 /	1772
(57.07)		102.7 /	21.2 /	4.3 /	12.1 /	12.9 /	27.3 /	1,1,2
(56.06)		5.1	2.1	1.3	2.1	2.4	1.5	
55.08	CH_2CCHO^+ (inc.	2058	1621		1150	660	930	833
	Methac. + MVK)							
47.04 -	formic acid	3644	2149	1013	1590	1453	5879	
47.07								
(46.03)								
46.02**	organic nitrate	21641	8670	925	3291	2493	625	
(46.01)	marker $(NO_2^+)(F)$							
45.06	acetaldehyde /	5511 /	1875 /	479 /	1814 /	1509 /	6170 /	
(44.05)	methyl glyoxal (F)	111.4 /	25.1 /	5.5 /	16.9 /	14.1 /	124.7 /	
		4.3	2.0	1.3	2.3	2.1	5.0	
43.04	acylium ion	25513 /	11181 /	1715 /	8747 /	5710/	13920 /	
(43.05)		502.4 /	128.4 /	20.3 /	84.1 /	54.9 /	274.1 /	
		18.7	9.7	4.6	11.6	8.0	10.7	
33.05	methanol		347 /	212 /	843 /	1159 /	1396 /	
(32.04)			6.2 /	5.7 /	18.3 /	25.2 /	33.7 /	
			0.4	1.0	1.8	2.7	1.0	
31.03	formaldehyde	1555	662	241	567	536	1558	
(30.03)								

Notes: * Shoulder ** Minor shoulder at low ECC energy (F) Fragment ion



Figure A7.1: Principal component analysis (PCA) conducted on VOC data recorded during isoprene experiment 4



Figure A7.2: Principal component analysis conducted on VOC data (excluding m/z 71, methacrolein and methyl vinyl ketone) recorded during isoprene experiment 4

Figures A7.1 and A7.2 show the results obtained from the principal component analysis conducted on the CIR-TOF-MS VOC product data recorded during isoprene experiment 4. Figure A7.1 gives the results obtained from the PCA conducted on all product data, whereas Figure A7.2 gives the corresponding results obtained from the PCA conducted on the product data set excluding the dominant signal at m/z 71 (methacrolein and methyl vinyl ketone). In both instances the first principal component (PC1) is primarily composed of m/z 43 (acylium

ion), 61 (acetic acid/glycoaldehyde), 113 (not identified) and when included, m/z 71 (methacrolein and MVK). The second principal component (PC2) is composed of m/z 43, 83 3-methyl furan), 85 (C5-carbonyls), 87 (C4-hydroxycarbonyls/methacrylic acid) and 101 (C5-hydroxycarbonyls), *i.e.* those compounds associated with SOA formation (see Chapter 7). The third (PC3) and fourth (PC4) principal components account for little of the variance and are composed primarily of m/z 43, 46, 83 and 113.

Table A7.3: Major spectral features recorded by CIR-TOF-MS during α -pinene experiments 8 – 11, tentative assignment and exact mass given. Columns 8 – 11 give: peak signal (number in brackets gives signal from the sum of all fragment ions) / concentration / yield, where possible.

Measured	Tentative Assignment		Experime	nt Number	
m/2,		8	9	10	11
185.26 (184.23)	pinonic acid /	30 / (275)	28 (472)	86 (530)	30 (500)
183.25 (182.22)	4-oxo-pinonaldehyde	33 (55) / 1.1 / 1.52	75 (103) / 1.3 / 0.94	73 (123) / 1.5 / 1.24	60 (71) / 0.9 / 0.60
169.26 (168.23)	pinonaldehyde	141 (981) / 20.1 / 25.1	347 (1751) / 21.7 / 16.8	421 (1792) / 22.2 / 16.5	323 (1951) / 24.2 / 15.4
167.23 (167.22)	pinonic acid (F ₁)	92	158	133	189
165.21 (165.22)	4-oxo-pinonaldehyde (F ₁)	28	145	55	38
157.16 / 157.22** (156.14 / 156.22)	trioxoheptanal / 1-(3-hydroxyme2,2- dimecyclobutyl)- ethanone	(86) / 7.9 / 8.2	42 (170) / 7.7 / 4.7	(131) / 5.9 / 3.8	34 (159) / 7.2 / 4.2
155.22 (154.21)	norpinaldehyde	46 / 0.9 / 1.0	112 / 1.4 / 0.9	113 / 1.4 / 0.9	62 / 0.8 / 0.5
153.22 (152.23)	pinene oxide / pinanediol (F ₁) / norpinonic acid (F ₁) / pinalic-4-acid (F ₁)	133 (295) / 6.0 / 6.8	254 (578) / 7.2 / 4.8	279 (595) / 7.4 / 5.8	256 (599) / 7.4 / 4.3
151.23 (151.23)	pinonaldehyde (F1)	460	881	806	1016
141.19** (141.14)	5-hydroxy-3,6-dioxo- heptanal (F_1) / 3- hydroxy-5,6-dioxo- heptanal (F_1) / trimethyl-cyclohex-2- en-ol	59 / 5.5 / 5.7	142 / 6.4 / 4.0	113 / 5.1 / 3.3	105 / 4.7 / 2.8

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	Measured m/7	Tentative Assignment		Experime	nt Number	
			8	9	10	11
	139.15 / 139.20 ** (139.13 / 139.21)	trioxoheptanal (F ₁) / 1-(3-hydroxyme2,2- dimecyclobutyl)- ethanone (F ₁)	86	134	131	126
	125.18	pinonic acid (F)	93	196	212	189
	115.15	3.4-dioxo-pentanal / 3-	48 /	106 /	102 /	73 /
	(114.10)	oxo-pentanedial	1.4 /	1.9 /	1.9 /	1.3 /
	~ /	1	1.0	0.9	0.9	0.6
	113.14	N/I	67	217	428 [#]	80
	111.15	N/I	62	100	284 [#]	97
	109.18	pinene oxide (F ₂)	175	332	317	350
	107.16	pinonaldehyde $(F_2)^{\$}$	404	579	639	674
	101.12	2.3-dioxobutanal	(58) /	80 (199) /	93 (222) /	60 (225) /
	(100.07)	<u>,</u>	1.4 /	3.5 /	3.9 /	3.9 /
	~ /		0.9	1.4	1.6	1.5
	99.15	N/I	98	229	249	222
	97.14 (97.09)	3,4-dioxo-pentanal (F ₁) / 3-oxo-pentanedial (F ₁)	68	150	164	140
	87.10	2-oxo-malonaldehyde	67 /	161 /	222 /	73 /
	(86.05)	- 0110 11101010100113	1.6 /	2.8 /	3.9 /	1.3 /
	()		0.9	0.9	1.4	0.4
	85.12	1-hydroxy-butane-2,3-	56 /	156 /	154 /	135 /
	(85.08)	dione (F_1)	1.6 /	2.9 /	2.8 /	2.5 /
	· · · ·		1.1	1.2	1.2	1.0
	83.13 (83.07)	2,3-dioxobutanal (F ₁)	58	135	132	165
	73.08	me_glvoxal/	83 /	188 /	471 /	111 /
	(72.06)	propanedial	4.9 /	13.0 /	32.6 /	7.7 /
	(/2:00)	propulsion	2.3	3.7	10.3	2.1
	71.10	N/I	411	745	702	951
	69.11	N/I	117	232	191	162
	61.07	acetic acid	57 /	1771 /	1218 /	310 /
	(60.05)		32.7 /	86.1 /	59.2 /	15.1 /
			13.1	19.9	14.7	3.4
	59.09	acetone	1173 /	1819 /	2027 /	1745 /
	(58.08)		23.1 /	24.1 /	26.8 /	23.1 /
			9.3	5.5	6.4	6.8
	47.05	formic acid	498 /	1173 /	821 /	605 /
	(46.03)		64.1 /	134.2 /	94.0 /	69.2 /
			19.6	23.9	17.9	12.1
	46.02*	organic nitrate marker	802	1727	2560	2614

Measured <i>m/z</i>	Tentative Assignment		Experime	nt Number	
	—	8	9	10	11
(46.01)	$(NO_2^+)(F)$				
45.06	acetaldehyde	292 /	551 /	1055 /	453 /
(44.05)		5.9 /	8.8 /	16.8 /	7.2 /
		1.7	1.5	3.1	1.2
43.04	acylium ion (F)	1407 /	2769 /	2622 /	1306 /
(43.04)	-	27.7 /	36.7 /	34.7 /	17.3 /
~ /		7.9	6.1	6.0	2.8
33.05	methanol		720 /	283 /	
(32.04)			17.6 /	6.9 /	
			2.2	0.9	
31.03	formaldehyde	116	92	96	235

Notes: § Potential identity: M(-OH.CH₃CO)⁺

* Shoulder

** Shoulder not resolved

Oxidation product of 1,3,5-TMB oxidation

(F) Fragment ion

(F₁) Fragment ion = $MH^+(-H_2O)$

Peak signal given in parentheses provides the peak signal summed over all contributing mass channels.

Table A7.4: VOC yields for various compounds measured by the CIR-TOF-MS during isoprene experiments 1 - 6. First number in each column gives mass percent yield (*i.e.* mass formed per mass reacted), the second gives molar yield (*i.e.* ppbV formed per ppbV reacted).

Measured	Tentative			Experime	nt Numbo	er	
m/z	Assignment	1	2	3	4	5	6
117.14	C5-trihydroxy- carbonyls	2.4 / 1.4	1.2 / 0.7	1.8 / 1.0	1.7 / 1.0	1.4 / 0.8	
103.12	C5-alkenediols / C4-hydroxy- dialdehyde / MPAN (F)	0.7 / 0.4	0.8 / 0.5	0.7 / 0.5	0.7 / 0.5	0.6 / 0.4	
101.13	C5 hydroxycarbonyls	3.3 / 2.2	8.2 / 5.6	13.4 / 9.1	10.4 / 7.1	5.93 / 4.0	1.8 / 1.3
87.11	C4 hydroxycarbonyls / methacrylic acid	2.8 / 2.2	3.5 / 2.3	4.0 / 3.2	3.9 / 3.0	3.7 / 2.9	4.9 / 3.9
85.12	C5-carbonyls	2.7 / 2.2	4.0 / 2.3	1.9 / 1.5	2.1 / 1.7	1.6 / 1.3	2.7 / 2.2
83.11	3-methyl furan	7.0 / 5.8	2.5 / 2.1	3.1 / 2.5	3.9 / 3.2	2.4 / 2.0	0.7 / 0.6
75.09	hydroxy acetone	10.0 / 9.2	5.1 / 4.7	6.3 / 5.8	3.9 / 3.6	2.9 / 2.7	0.9 / 0.8
73.08	methyl glyoxal	5.8 / 5.5	8.1 / 7.7	9.0 / 8.5	9.8 / 9.3	9.6 / 9.1	6.5 / 6.1
Appendix

Measured	Tentative Assignment	Experiment Number					
m/z		1	2	3	4	5	6
71.10	methacrolein / MVK	47.5 / 46.1	53.1 / 51.6	51.0 / 49.5	65.9 / 64.0	64.7 / 62.9	45.9 / 44.6
61.07	acetic acid / glycoaldehyde	3.2 /3.6	0.3 / 0.4	8.1 / 9.2	6.2 / 7.1	6.5 / 7.4	2.8 / 3.1
59.09** (59.04)	acetone / propanal / glyoxal		1.9 / 2.2	5.1 / 6.0	2.8 / 3.3	8.3 / 9.7	3.1 / 3.6
57.10* (57.07)	acrolein	5.1 / 6.2	2.1 / 2.6	1.3 / 1.6	2.1 / 2.6	2.4 / 2.9	1.5 / 1.8
45.06	acetaldehyde / methyl glyoxal (F)	4.3 / 6.5	2.0 / 3.0	1.3 / 2.0	2.3 / 3.6	2.1 / 3.2	5.0 / 7.7
43.04	acylium ion	18.7 / 29.6	9.7 / 15.4	4.6 / 7.3	11.6 / 18.3	8.0 / 12.7	10.7 / 16.9
33.05	methanol		0.4 / 0.8	1.0 / 2.1	1.8 / 3.9	2.7 / 5.7	1.0 / 2.1

(F) Fragment ion

Table A7.5: VOC yields for various compounds measured by the CIR-TOF-MS during α -pinene experiments 8-11. First number in each column gives mass percent yield (*i.e.* mass formed per mass reacted), the second gives molar yield (*i.e.* ppbV formed per ppbV reacted).

Measured <i>m/z</i>	Tentative Assignment	Experiment Number			
-	8	8	9	10	11
183.25	4-oxo-pinonaldehyde	1.5 / 1.1	0.9 / 0.7	1.2 / 0.9	0.6 / 0.5
169.26	pinonaldehyde	25.1 / 20.3	16.8 / 13.6	16.5 / 13.4	15.4 / 12.5
157.16 / 157.22**	trioxoheptanal / 1-(3-hydroxyme2,2- dimecyclobutyl)- ethanone	8.2 / 7.1	4.7 / 4.1	3.8 / 3.4	4.2 / 3.7
155.22	norpinaldehyde	1.0 / 0.8	0.9 / 0.8	0.9 / 0.8	0.5 / 0.4
153.22	pinene oxide / pinanediol (F ₁) / norpinonic acid (F ₁) / pinalic-4-acid (F ₁)	6.8 / 6.1	4.8 / 4.3	5.8 / 5.2	4.3 / 3.9
141.19**	5-hydroxy-3,6-dioxo- heptanal $(F_1) / 3$ - hydroxy-5,6-dioxo- heptanal $(F_1) /$ trimethyl-cyclohex-2- en-ol	5.7 / 4.9	4.0 / 3.4	3.3 / 2.8	2.5 / 2.4
115.15	3,4-dioxo-pentanal / 3- oxo-pentanedial	1.0 / 1.2	0.9 / 1.0	0.9 / 1.1	0.6 / 0.7

Appendix

Measured	Tentative	Experiment Number				
m/z.	Assignment					
		8	9	10	11	
101.12	2,3-dioxobutanal	0.9 / 1.0	1.4 / 1.8	1.6 / 2.2	1.5 / 2.0	
87.10	2-oxo-malonaldehyde	0.9 / 1.5	0.9 / 1.5	1.4 / 2.2	0.4 / 0.7	
85.12	1-hydroxy-butane-2,3- dione (F ₁)	1.1 / 1.4	1.2 / 1.5	1.2 / 1.6	1.0 / 1.3	
73.08	me. glyoxal / propanedial	2.3 / 4.4	3.7 / 6.9	10.3 / 19.4	2.1 / 4.0	
61.07	acetic acid	13.1 / 30.0	19.9 / 45.0	14.7 / 33.4	3.4 / 7.7	
59.09	acetone	9.3 / 21.8	5.5 / 12.8	6.4 / 15.0	6.8 / 16.0	
47.05	formic acid	19.6 / 58.1	23.9 / 70.6	17.9 / 52.9	12.1 / 35.6	
45.06	acetaldehyde	1.7 / 5.3	1.5 / 4.6	3.1 / 9.3	1.2/3.7	
43.04	acylium ion (F)	7.9 / 25.1	6.1 / 19.2	6.0 / 19.3	2.8 / 8.9	
33.05	methanol		2.2 / 9.2	0.9 / 3.9		

(F) Fragment ion (F₁) Fragment ion = $MH^+(-H_2O)$

Appendix A8

Publications

Parker, A.E., P. S. Monks, K. P. Wyche, J. M. Balzani-Lööv, J. Staehelin, S. Reimann, G. Legreid, M. K. Volmer and M. Steinbacher (2008), *Peroxy radicals in the summer free troposphere: Seasonality and heterogeneous loss*, Atmospheric Chemistry and Physics Discussions, 8, 17841 – 17889

Wyche, K. P., P. S. Monks, A. M. Ellis, R. L. Cordell, A. E. Parker, C. Whyte, A. Metzger, J. Dommen, J. Duplissy, A. S. H. Prevot, U. Baltensperger, A. R. Rickard, and F. Wulfert (2008). *Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation*, Atmospheric Chemistry and Physics Discussions, 8, 11685 – 11754. Accepted for publication in Atmospheric Chemistry and Physics, 9, in press

Apel, E. C., T. Brauers, R. Koppmann, B. Bandowe, J. Boßmeyer, C. Holzke, R. Tillmann, A. Wahner, R. Wegener, A. Brunner, M. Jocher, T. Ruuskanen, C. Spirig, D. Steigner, R. Steinbrecher, E. G. Alvarez, K. Muller, J. P. Burrows, G. W. Schade, S. J. Solomon, A. Ladstätter-Weißenmayer, P. Simmonds, D. Young, J. R. Hopkins, A. C. Lewis, G. Legreid, S. Reimann, A. Hansel, A. Wisthaler, R. S. Blake, A. M. Ellis, P. S. Monks, and K. P. Wyche (2008), *Intercomparison of oxygenated volatile organic compound measurements at the SAPHIR atmosphere simulation chamber*, Journal of Geophysical Research, 113(D20), doi: 10.1029/2008JD009865

Wyche, K. P., C. Whyte, R. S. Blake, R. L. Cordell, K. A. Willis, A. M. Ellis, and P. S. Monks (2007). *Atmospheric monitoring with chemical ionisation reaction time-of-flight mass spectrometry (CIR-TOF-MS) and future developments: Hadamard transform mass spectrometry*, Advanced Environmental Monitoring, 64 – 76

Cordell, R. L., K.A. Willis, K.P. Wyche, R. S. Blake, A. M. Ellis, and P. S. Monks (2007). *Detection of chemical weapon agents and simulants using chemical ionization reaction time-of-flight mass Spectrometry*, Analytical Chemistry, **79**(21), 8359 – 8366

Wyche, K. P., R. S. Blake, A. M. Ellis, P. S. Monks, T. Brauers, R. Koppmann, and E. Apel (2007). *Performance of Chemical Ionization Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS) for the measurement of atmospherically significant oxygenated volatile organic compounds*, Atmospheric Chemistry and Physics, 7(3), 609 – 620

Whyte, C., K.P. Wyche, M. Kholia, A. M. Ellis, and P. S. Monks (2007). *Fast fingerprinting* of arson accelerants by proton transfer reaction time-of-flight mass spectrometry. International Journal of Mass Spectrometry, 263(2-3), 222-232

Blake R. S., K. P. Wyche, A. M. Ellis, and P. S. Monks (**2006**). *Chemical ionization reaction time-of-flight mass spectrometry: Multi-reagent analysis for determination of trace gas composition*, International Journal of Mass Spectrometry, **254**(1 - 2), 85 – 93

Wyche K. P., R. S. Blake, K. A. Willis, P. S. Monks, and A. M. Ellis (2005). *Differentiation* of isobaric compounds using chemical ionization reaction mass spectrometry, Rapid Communications in Mass Spectrometry, 19(22), 3356 – 3362

Appendix A8

Conferences, Meetings and Presentations

Midlands' Universities Gas Phase Meeting, University of Birmingham, UK, 03/03/05 Oral presentation: "*Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry*"

Royal Meteorological Society, Special Interest Group, University of Leicester, UK, 11/03/05

Distributed Institute for Atmospheric Composition (DIAC) Meeting, University of Leeds, UK, 13 – 14/04/05 Poster presentation: "Chemical Ionisation Processes in Time-of-Flight Mass Spectrometry for Real-Time Analysis of Atmospheric Trace Species"

The First ACCENT Symposium, Urbino, It., 12 – 16/09/05 Poster presentation: "Performance of a Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer during the ACCENT OVOC Measurement Intercomparison, Jülich, 2005"

The British Academy Meeting, Leicester, UK, 28/11/05 Oral presentation: "*Atmospheric Monitoring*"

European Geosciences Union (EGU) Conference, Vienna, Au. 02 - 07/04/06

Poster presentation: "Detection of High Mass Gas Phase Oxidation Products of 1,3,5-Trimethylbenzene, Isoprene and α -Pinene and their Role in Seondary Organic Aerosol Formation"

Poster presentation: "Watching Paint Dry- Monitoring VOCs and OVOCs in the Indoor Environment"

EPSRC Meeting, the Crime Technology Program, London, UK, 30/05/06 "Detection of Arson Accelerants by Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry"

Advanced Environmental Monitoring Conference, Heidelberg, De., 27 - 30/06/06

Oral presentation: "Atmospheric Monitoring with Chemical Ionisation Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS) and Future Directions: Hadamard Transform CIR-TOF-MS"

National Centre for Atmospheric Science (NCAS) Meeting, University of York, UK, 05 – 06/04/07

Poster presentation: "Formation and Evolution of Potential Gas Phase Precursors to Secondary Organic Aerosol"

Institute for Climate and Atmospheric Science (ICAS), 2nd Online Particle Mass Spectrometry Workshop, University of Leeds, UK, 09-10/04/08

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Seminars Attended

Seminar Title	Speaker	Date
"The Chemistry of Interstellar Space"	Eric Herbst (Ohio State	15/10/04
	University, USA)	
"Fourier Transform Infra-Red Spectroscopy"	Stewart Mackenzie	01/11/04
	(University of Warwick,	
	UK)	
"Some Aspects of Ion-Molecule and Electron	Chris Mayhew (University	22/11/04
Attachment Processes"	of Birmingham, UK)	
		02/12/04
"The Mesosphere and Lower Thermosphere"	John Plane (University of East Anglia, UK)	02/12/04
	Last Aligna, OK)	
"Natures Detergent: Measurement of the OH	Dwayne Heard (University	14/03/05
Radical in the Atmosphere "	of Leeds, UK)	
"Electrochemistry of Single Walled Carbon	Julie MacPherson	09/05/05
Nanotube Based Devices and Scanning	(University of Warwick,	
Probes"	UK)	
<i>"What can we learn from current and future</i>	Paul Palmer (University of	01/02/06
satellite observations of Tropospheric	Leeds, UK)	
composition"		
		10/02/06
"Marine Antifouling Coating Technology"	Clayton Price (Akzo Nobel,	10/02/06
	0K)	
"Ion Mobility Spectroscopy: Shaping Up for	Collin Creaser (Nottingham	20/02/06
the Structural and Trace Analysis"	Trent University, UK)	
"Soft Ionisation Techniques for Analysis of	Robert Zenobi (Paul	08/03/06
Non-Covalent Interactions"	Scherrer Institut, Ch.)	

Appendix		Seminars
Seminar Title	Speaker	Date
"Chemistry and Giant Thunderstorms"	Geraint Vaughn (University	07/03/07
	of Manchester, UK)	
"The Earths Upper Atmosphere as a Natural	Terry Robinson (University	16/05/07
Plasma Laboratory"	of Leicester, UK)	
"Metal Layers in the Mesosphere and Lower	John Plane (University of	16/05/07
Thermosphere"	Leeds, UK)	
"Skating on Thin Ice- What's in he Universes	Helen Fraser (University of	16/05/07
Freezers"	Strathclyde)	
"Baltimore and Beijing: A Tale of Two Cities"	Russell Dickerson	08/11/07
	(University of Baltimore,	
	USA)	
"Exploring the Dynamics of Single Aerosol	Jonathan Reid (University of	12/11/07
Particles"	Manchester, UK)	
"Laser Studies of Photofragmentation	Grant Richie (University of	26/11/07
Dynamics"	Oxford, UK)	
"Synchrotron Radiation Studies of Processes	Chris Mayhew	10/12/07
Near Electrode Surfaces"	(University of Birmingham)	
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