COLLECTION, SPECIATION AND AEROSOL MODELLING FOR VOLATILE ORGANIC COMPOUNDS

by

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Abstract

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Volatile organic compounds (VOCs) are collected on the integrated organic gas and particle sampler (IOGAPS) to measure particle loss and collection efficiency. Particle loss increases with increasing flow rate while collection efficiency is a function of alkane volatility. Unresolved complex mixtures (UCMs) are then analyzed and quantified using the novel technique supersonic molecular beam gas chromatography/mass spectrometry (SMB-GC/MS), to develop accurate inputs in modelling the formation of secondary organic aerosol (SOA). Alkanes were segregated by carbon number ($N_C$), number of double bond equivalents ($N_{DBE}$), and chemical structure. With the most explicit compositional knowledge to date, these mixtures were modelled for their affinity towards formation of SOA. Unsaturated alkanes formed the most and relatively equal amounts of aerosol based on their $N_{DBE}$ while branched species formed the least. Increasing specificity in chemical structure led to increased computational demands while only general structural motifs were needed to form an accurate picture of aerosol formation.
Dedication

For my niece Shefali, because you went all the way to Guam and no one gave you a degree.
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# Contents

1 Introduction .................................................. 1

2 Collecting VOCs: The integrated organic gas and particle sampler (IOGAPS) ................................. 4
   2.1 Abstract .................................................... 4
   2.2 Experimental Methods ...................................... 5
      2.2.1 Particle loss experiment .............................. 5
      2.2.2 Collection efficiency experiments .................... 5
   2.3 Results and Discussion ..................................... 7
      2.3.1 Particle loss in IOGAPS denuders ..................... 7
      2.3.2 Standard collection efficiency in IOGAPS denuders .... 9
   2.4 Figures and Tables ......................................... 13

3 Speciating and quantifying complex mixtures using supersonic molecular beam –
gas chromatography/mass spectrometry, SMB-GC/MS .......................................................... 19
   3.1 Abstract .................................................... 19
   3.2 Experimental Methods ...................................... 20
      3.2.1 Supersonic molecular beam, (SMB)-GC/MS ............ 20
      3.2.2 Quantification of VOCs ............................... 22
   3.3 Results and Discussion ..................................... 22
      3.3.1 Speciation of saturated, $N_{DBE} = 0$, alkanes ........ 22
      3.3.2 Speciation of unsaturated, $N_{DBE} \geq 1$, alkanes ..... 25
      3.3.3 Quantification of VOCs ............................... 26
   3.4 Figures and Tables ......................................... 27
4 Explicit kinetic modelling of the formation of secondary organic aerosol from complex mixtures

4.1 Abstract

4.2 Experimental Methods

4.2.1 Model design and mechanism

4.2.2 Rate constants and partitioning coefficients

4.3 Results and Discussion

4.3.1 Model comparison to other studies

4.3.2 Modelled SOA formation from individual VOCs

4.3.3 Modelled SOA formation from diesel fuel

4.4 Figures and Tables

5 Conclusions

Bibliography
List of Tables

3.1 Kováts retention index comparison ....................................................... 27

4.1 OH radical rate constants for ALKH, AP11 and AP12 oxidation mechanisms ......................................................... 45

4.2 Fragmentation and isomerization rate constants for the alkoxy radical ......................................................... 46
List of Figures

2.1 IOGAPS experimental set-up ........................................... 13
2.2 Particle size distribution fits with flow rate .......................... 14
2.3 IOGAPS particle transmission efficiency ............................... 15
2.4 Particle number, volume and area concentrations with flow rate .... 16
2.5 Deuterated alkane calibration curves .................................. 17
2.6 Deuterated alkane recovery comparison ................................ 18

3.1 The supersonic molecular beam mass spectrometer ................. 28
3.2 Electron impact mass spectra with and without SMB ............... 29
3.3 TIC of HC and diesel fuel mixtures .................................. 30
3.4 Molecular ion traces across carbon numbers ........................ 31
3.5 Branching regions of saturated alkanes in diesel fuel .............. 32
3.6 B1 branching region of saturated alkanes in diesel fuel .......... 33
3.7 B2 branching region of \( m/z \) 184 in the HC mixture ............... 34
3.8 Monocyclic alkane comparison in diesel fuel ....................... 35
3.9 Pearson correlation data for informative fragments in \( N_{DBE} = 1 \) regions .......... 36
3.10 Relative quantification of two unresolved complex mixtures .. 37

4.1 Modelled mechanism of SOA formation .............................. 47
4.2 SOA model product list ................................................. 48
4.3 Product distributions for oxidation of two modelled VOCs .......... 49
4.4 Model comparison to other studies ................................ 50
4.5 Modelled linear \( n \)-alkane SOA yield comparison ................ 51
4.6 Individual VOC precursor SOA yields ............................... 52
4.7 VBS distribution of diesel fuel ....................................... 53
List of Acronyms

**DBE**  double bond equivalent

**EI**  electron impact

**GC/MS**  gas chromatography/mass spectrometry

**GECKO-A**  Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere

**HC**  hydrocarbon

**IOGAPS**  integrated organic gas and particle sampler

**IVOC**  intermediate volatility organic compound

**OA**  organic aerosol

**PAH**  polycyclic aromatic hydrocarbon

**PM**  particulate matter

**POA**  primary organic aerosol

**QFF**  quartz fibre filter

**SAR**  structure activity relationship

**SIC**  selected ion chromatogram

**SIF**  sorbent impregnated filter

**SMB**  supersonic molecular beam

**SMPS**  scanning mobility particle sizer

**SOA**  secondary organic aerosol

**SPI**  single-photon ionization
SVOC semivolatile organic compound
TIC total ion chromatogram
UCM unresolved complex mixture
VBS volatility basis set
VOC volatile organic compound
VUV vacuum ultraviolet
VVOC very volatile organic compound
Chapter 1

Introduction

Organic matter comprises a major fraction of the aerosol encountered in the atmosphere.\cite{1} This organic aerosol (OA) can be either directly emitted as primary organic aerosol (POA) or form chemically as secondary organic aerosol (SOA).\cite{2} The chemistry of atmospheric SOA is highly complex and remains poorly understood.\cite{3} Despite recognition of the cardiovascular and respiratory health impacts of atmospheric particulates,\cite{4,5,6} as well as the net cooling effect OA has on global climate,\cite{7,8} models routinely underpredict atmospheric SOA budgets.\cite{9,10,11,12} At the centre of this problem is the lack of understanding in SOA precursors. A complex myriad of volatile organic compounds (VOCs) is emitted into our atmosphere every day from both anthropogenic and biogenic sources.\cite{13,14} These important SOA precursors, including very volatile organic compounds (VVOCs), intermediate volatility organic compounds (IVOCs), and semivolatile organic compounds (SVOCs), are chemically complex and difficult to collect and speciate. These unspeciated compounds, often representing the majority of the mass, are collectively known as the unresolved complex mixture (UCM).

These UCMs\cite{15,16,17} of VOCs contain thousands of organic isomers and are immediately subjected to oxidation driven primarily by the hydroxyl radical, ozone and the nitrate radical under photolytic conditions.\cite{18} With each successive oxidative generation each VOC will follow a different reactive pathway based on its own molecular structure giving each VOC a different affinity for SOA formation.\cite{19} As the VOC reacts its molecular structure changes and grows – functionalization processes lead to a decrease in volatility and the potential to partition to the condensed phase, thereby forming SOA. Reactions may also occur within the particle once it has formed.\cite{20}

Scientists routinely use air sampling systems combined with gas chromatography/mass spectrometry (GC/MS), and subsequent computational modelling to develop a clearer understanding of what is both
a thermodynamic and kinetic process. Off-line collection of VOCs provides hourly to daily time resolution of the ongoing oxidation process. Alternatively, on-line means such as gas analyzers and aerosol mass spectrometers offer minute time resolution but less information on aerosol composition. The integrated organic gas and particle sampler (IOGAPS) is an off-line technique that has been developed over two decades.\textsuperscript{[21,22,23]} The instrument uses two multichannel annular glass denuders upstream of a filter pack to segregate gas- and particle-phase VOCs. The denuders with their high surface area are coated with a polymer resin wherein gas-phase compounds, such as polycyclic aromatic hydrocarbons (PAHs), will adsorb. The particles are then expected to travel through the denuders without significant diffusive losses before striking quartz fibre (QFF) and sorbent impregnated (SIF) filters held in sequence.\textsuperscript{[23,24,25]} Ideally, no breakthrough would occur in either the denuders (positive artefacts) or the filter pack (negative artefacts). In practice however, the instrument experiences these breakthroughs given the high flow rates necessary to collect enough sample for analysis over a time period of hours.\textsuperscript{[21,26]} Sample UCMs are collected from both the denuders and filter pack for later GC/MS analysis. However, traditional GC/MS techniques use electron impact electron impact (EI) with 70 eV ionization energy, thereby inducing extensive fragmentation and producing virtually identical fragmentation patterns for typical aliphatic compounds. As the myriad of compounds present in the UCM elute simultaneously from the GC column, the fragmentation signals obfuscate one another and render any precise molecular speciation impossible.

Recently, soft ionization, which limits fragmentation and retains the molecular ion, has been seen as a new direction for resolving UCM compounds. Previous work in this area has seen the use of single-photon ionization (SPI),\textsuperscript{[27,28,29]} field ionization,\textsuperscript{[30]} Cold EI\textsuperscript{[31]} and chemical ionization by NO\textsuperscript{+} ions\textsuperscript{[32]} to minimize hydrocarbon fragmentation. Under SPI, photon production is achieved using gas-filled lamps, synchrotron radiation, or laser methods.\textsuperscript{[33,34,35,36]} Current research into UCMs using vacuum ultraviolet (VUV)-GC/MS has resolved alkanes by carbon number ($N_C$), degree of unsaturation or double bond equivalents ($N_{DBE}$), and resolved branched alkanes from linear isomers,\textsuperscript{[27,37,38]} but exact molecular structures such as branching position and ring structure are not known.

Detailed knowledge of molecular structures is needed to properly model the formation of SOA from these complex hydrocarbon mixtures as molecular structures, such as carbon number, number of non-aromatic rings, degree of substitution on rings, and alkane branching positions have been experimentally shown to significantly affect final yields.\textsuperscript{[3,18,39,40,41]} Generally, fragmentation propensity is enhanced in branched alkanes while cyclic species fragment once to ring open, and then continue reacting to ultimately partition to the condensed phase.\textsuperscript{[3,39,40]} In bicyclic species there exist two potential C-C bond scission
steps that can lead to no reduction in carbon number; this implies bicyclic compound oxidation products have a higher affinity to enter the particle phase. However, Hunter et al. (2014)\cite{42} recently showed that alkanes with multiple rings have similar SOA yields as monocyclic species, suggesting that only one ring opening is needed before partitioning to the condensed phase. Additionally, rate constants for isomerization, fragmentation, carbonyl formation, and OH radical reaction are often missing and must be assumed or calculated based on the molecular structure.\cite{43,44,45,46} These pathways have been modelled in detail in explicit models such as the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) model.\cite{47,48,49} Vast quantities of reaction products are considered explicitly for their molecular structure and group contribution partition theories are applied to each. To date, only a single precursor is modelled owing to lack of knowledge of mixture composition. Alternatively, organic compounds are grouped into volatility bins and the change in overall volatility during aging is modelled by redistributing organic mass without consideration of specific molecular structures.\cite{50}

In Chapter 2 the IOGAPS’ capacity for gas-phase VOC collection and particle breakthrough is measured. Off-line sampling is performed over a period of several hours whereupon solvent extracts are obtained containing standard solutions used. Particle breakthrough is measured by way of scanning mobility particle sizer (SMPS) over a range of flow rates. In Chapter 3, two relevant UCMs are studied using a novel soft-ionization technique, supersonic molecular beam (SMB)-GC/MS, capable of elucidating and quantifying the VOCs present in an atmospheric sample. We employ GC/MS with SMB to identify molecular structures in the UCM. This Cold-EI of vibrationally cooled molecules in SMB technique modifies the column effluent prior to ionization.\cite{31,51} Using Cold EI technology developed about 25 years ago,\cite{52,53} electron ionization provides an effective soft ionization method in which the molecular ion is largely enhanced while retaining the standard EI fragments for library identification and isomer structural elucidation. Subsequently, in Chapter 4, knowledge of exact VOC molecular structures and relative amounts therein are then applied to an SOA box model recently developed by Jordan et al. (2008)\cite{54} to better understand the overall affinity the UCM has for the condensed phase. Models historically under-predict SOA levels observed in the atmosphere. It is hoped that the development of new analytical instrumentation will improve modelled results by providing insight into the fundamental processes occurring during aerosol formation and inform bulk modelling efforts, such as the volatility basis set (VBS) framework,\cite{50,55} and provide fundamental insights into the evolution of complex organic mixtures in the atmosphere.\cite{56}
Chapter 2

Collecting VOCs: The integrated organic gas and particle sampler (IOGAPS)

2.1 Abstract

The integrated organic gas and particle sampler (IOGAPS) is studied for its denuder particle loss and collection efficiencies. The instrument is a continuous flow system with two multichannel annular denuders held in sequence upstream of a filter pack. The denuders are designed to collect gas-phase samples while the filter pack collects the particle phase. In these experiments the filter pack was left empty and only the denuders were analyzed. One particle sizing experiment was performed using a scanning mobility particle sizer (SMPS) and aerosol atomizer as well as two standard collection efficiency experiments using a deuterated hydrocarbon standard. Particle transmission was found to be mostly unaffected by flow rate but smaller diameter particles ($D_p \leq 100$ nm) were more greatly affected while overall particle mass decreased with increasing flow rate. Standard collection efficiency was more complex but appeared to be a strong function of compound volatility and chemical structure where less volatile, non-aromatic compounds gave lower recoveries.
2.2 Experimental Methods

2.2.1 Particle loss experiment

Particle loss was measured through the long (44 cm) and short (22 cm) IOGAPS multichannel annular glass denuders\cite{25,57,58} using the set-up depicted in Fig. 2.1 where the inlet was an aerosol atomizer (3076, TSI) using compressed air to generate a polydisperse aerosol from a 30 mmol L$^{-1}$ aqueous ammonium sulfate solution. Aerosol was blown from the atomizer through a three-way plug valve connecting either the IOGAPS denuders in sequence or a bypass line. A rotameter was used to measure the flow rate generated by a rotary vane pump (1023-318Q-G274X, GAST). A custom SMPS system was used to measure the size distribution of aerosol. The overall flow rate was adjusted by opening or closing a relief needle valve connecting the rotary pump to the room to lower or raise the flow rate respectively. The instrumentation was initiated and allowed to stabilize before final readings were taken. Four flow rates of 33, 40, 49 and 60 LPM, and ten scans were taken over forty minutes for both IOGAPS and bypass flows. The ten scans were arithmetically averaged and particles were separated into 100 size bins by their diameter (Fig. 2.2, inset). Curves were then fit to log-normal distributions using IGOR Pro (6.35A5, Wavemetrics), (Fig. 2.2). From these fits particle transmission efficiency in the denuders was calculated for each flow rate as a function of particle size (Fig. 2.3). Additionally, counts of total particle number, volume and surface area per unit volume were taken in the ten averaged scans for all flow rates and results are compared for the IOGAPS and bypassing set-ups in Fig. 2.4.

2.2.2 Collection efficiency experiments

Collection efficiency of the IOGAPS denuders was measured through two experiments using a deuterated hydrocarbon standard in chloroform containing (from most to least volatile) n-pentadecane-d$_{32}$ (n-C$_{15}$D$_{32}$), phenanthrene-d$_{10}$ (C$_{14}$D$_{10}$), n-eicosane-d$_{42}$ (n-C$_{20}$D$_{42}$), n-pentacosane-d$_{52}$ (n-C$_{25}$D$_{52}$), chrysene-d$_{12}$ (C$_{18}$D$_{12}$), n-triacontane-d$_{62}$ (n-C$_{30}$D$_{62}$) and n-hexatriacontane-d$_{74}$ (n-C$_{36}$D$_{74}$). However hexatriacontane-d$_{74}$ was deemed too non-volatile to be confidently resolved during GC separation and so its collection efficiency could not be calculated.

In the first experiment the set-up in Fig. 2.1 was used where the inlet was a syringe pump. The two multichannel annular denuders were coated with a previously ground cross-linked styrene-divinylbenzene copolymer (XAD-4, Amberlite) and suspended into a 70:30 (by volume) hexanes/acetone solvent. Two aliquots of 70 mL (140 mL) were used to coat the longer of the two denuders while two of 40 mL (80 mL)
were used for the shorter denuder to be connected downstream in sequence. The solvent was evaporated by flowing a steady stream of nitrogen through the denuders for several hours. 500 µL of 10 ng µL⁻¹ hydrocarbon standard (5000 ng) was injected into 120 cm long, 1/4” polymer tubing connected to the IOGAPS at a rate of 10 µL min⁻¹ for 50 minutes at an air flow rate of 60 LPM pulling from room air. Following this, the denuders were washed using two aliquots of 70 mL and 40 mL of the hexane/acetone solvent for the long and short denuders, respectively. The two extract solutions were then transferred to 250 mL volumetric flasks for concentrating. An evaporator system (Turbovap II, Caliper Life Sciences) was used for concentrating both solutions over a period of roughly 1.5 hours in a 37 °C water bath under nitrogen flow. Extract flasks were washed with 2 mL isooctane solution and final volumes were 2.3 ± 0.5 mL and 1.6 ± 0.5 mL for long and short denuder extracts, respectively. Both extracts were analyzed by GC/MS (7890B and 5977A, Agilent) quadrupole scanning between 35 and 600 m/z. A 1 µL injection into a 250 °C inlet using splitless helium flow was used. The column was a Rxi-5sil ms with dimensions (length, internal diameter, film thickness) of 29 m × 250 µm × 0.25 µm (Restek). The temperature ramping program was 50 °C initial temperature held for 5 minutes followed by a ramp of 10 °C per minute for 27 minutes to 320 °C and held for 5 additional minutes. Five calibration standards were made in chloroform and run as 1 µL injections using the aforementioned method, these were concentrations of 0, 1, 5, 10 and 25 ng µL⁻¹. Calibration curves were prepared for each of the alkanes sought (Fig. 2.5) where R² correlation values were between 0.996 and 0.976. m/z 66, m/z 188, and m/z 240 were used to quantify deuterated n-alkanes, phenanthrene-d₁₀, and chrysene-d₁₂, respectively. In this way, alkane concentrations in both extracts were interpolated using instrument response and calculated using final volumes. Final recoveries were calculated using Eq. 2.1.

\[
\text{Recovery} = \frac{\text{Extract Mass}}{\text{Input Mass}} = \frac{\text{Extract Mass}}{5000 \text{ ng}}
\]

In the second experiment, the syringe pump was removed as the inlet and instead a charcoal denuder was affixed upstream of the IOGAPS denuders (Fig. 2.1). The procedure was repeated as before except where 5 µL of 1000 ng µL⁻¹ (5000 ng) deuterated hydrocarbon standard was applied directly to the top of the long denuder before pulling room air for 4 hours at 60 LPM, simulating an 8 hour sampling period. The charcoal denuder was expected to remove any gas-phase contaminants from the air. The extraction, concentration, and analysis procedures were then repeated as in the first experiment and final volumes were 2.0 ± 0.5 mL for both long and short denuder extracts in isooctane.
2.3 Results and Discussion

2.3.1 Particle loss in IOGAPS denuders

Using the aerosol atomizer as the inlet, the set-up depicted in Fig. 2.1 was constructed. The atomizer was capable of providing a stable and easily measurable flow of aerosol. In comparison, when sampling untreated room air, the particle counts were near the limit of detection and particle sizing measurements could not be confidently made. Changes of the size distribution due to dilution of the ammonium sulphate solution were considered negligible. Although the atomizer recycles water through the nebulizer system as it operates, the volume of solution made was 500 mL and so any changes in salt concentration would have been minimal during the course of the experiment. The fitting results of the experiment are shown in Fig. 2.2 where colour denotes a given flow rate and solid (IOGAPS in line) or hashed (bypassing flow) denotes denuded versus non-denuded air. Inset is the log-normal fit of a typical size distribution.

Overall, the particle size distribution was not significantly impacted by the denuders but smaller particles (diameter $\leq 100$ nm) were affected more (either positively or negatively) than larger particles. This result makes sense given the denuders are supposed to trap only gas-phase compounds and is in agreement with Fan et al. (2004) and Lane et al. (2000), aerosol phase compounds should effectively transmit through the denuders to be collected by the filter pack. Fan et al. (2004) found that at 16.7 LPM a laminar flow was produced and negligible particle losses in the denuder were experienced from small particles diffusing. Using their 8-channel denuders they calculate a 3.5% particle loss for particles of $D_p$ 100 nm at their 16.7 LPM flow rate. In our 4-channel glass denuder lined with stainless steel and at our higher flow rates we would expect even lower losses due to diffusion. Indeed we observed this at $D_p = 100$ nm where particle losses are all exceedingly low at the three lower flow rates. As particles smaller than 100 nm will diffuse more easily we expect to see greater losses and in fact do observe this in 33, 40 and 49 LPM flow rates. In calculating Reynolds numbers it was found that at the three lower flow rates the flow through the IOGAPS denuders should be laminar while at 60 LPM it should be transitioning to turbulent flow. Under these turbulent conditions larger particles would be expected to impact and be lost in the denuders while diffusional losses for smaller particles should be minimized. Indeed this is observable in the reverse trend seen in 60 LPM blue curve (Fig. 2.2). Larger particles $D_p \geq 71$ nm are lost in the IOGAPS denuders. The enhancement of smaller particles ($\leq 71$ nm) at 60 LPM was attributed to two factors. First, the possibility of larger particles breaking up in the IOGAPS denuders would have led to an artificially lower signal for larger bin sizes and a concordantly higher signal in
smaller bins as is seen. Second, the experiments were run from lowest to highest flow rate, potentially smaller particles were deposited in the IOGAPS denuders from diffusing at the lower, laminar, flow rates. Then, when the flow was increased and became turbulent these particles may have dislodged thereby increasing the signal during the 60 LPM experiments.

Increasing the flow rate decreased particle number roughly uniformly across all size bins, but not linearly with flow rate. Nearly doubling the flow rate more than halved the total particle volume. This is contrary to the results of Zhang et al. (2012) who found that particle number size distribution was enhanced at a higher (74 LPM) flow rate over a lower (30 LPM) flow rate. This may have come from the differences in how the particle size distributions are measured. Whereas we measured particles through a bypass line as our non-denuded reference, they took particle measurements upstream and downstream of the IOGAPS denuders in what was a single flow path. However, similar to this study they found the shape of the size distribution was mostly maintained by changing flow rates and that smaller particle counts were impacted to a greater extent. In literature the IOGAPS is generally connected to a cyclone upstream of the denuders. At or above a given flow rate the cyclone is capable of removing particulate matter (PM) greater than a certain size region which is typically desired as small particles show a greater detriment on human health. Our IOGAPS cyclone is designed to operate at flow rates of 60 LPM or above in order to effectively remove PM greater than 2.5 µm in diameter, and so the experiments performed in literature likely see losses of particle due to the necessity of these higher flow rates; however the collected samples should be size-representative of the particle in the atmosphere. In Zhang et al. (2012) mass losses for 74 LPM and 30 LPM were calculated as 10% and 24% respectively under the assumption of spherical particles with equal density. In doing the same calculations we find a particle mass enhancement of 2% at 60 LPM and mass losses of 18%, 3% and 10% for 49, 40 and 33 LPM sampling rates, respectively.

Using the data in Fig. 2.2, the total particle transmission through the IOGAPS was calculated (Fig. 2.3). Marker style denotes flow rate while marker colour denotes the particle diameter. Only at the highest 60 LPM flow rate (marker circles) was particle count greater through the IOGAPS than through bypassing the denuders, but values are considered within reasonable estimates of error. Again this observation was considered to be due to possible dislodging of previously deposited particles from lower flow rate experiments, or the possibility of larger particles breaking up in the turbulent flow regime. Particle transmission was mostly unaffected by flow rate but had some dependence on particle diameter. Smaller particles (≤ 200 nm) appeared to transmit at or near 90% under a laminar flow regime. Under turbulent flow (marker circles) larger particles (≥ 300 nm) transmit less effectively from impaction losses. Finally,
total particle number, volume and area concentrations are compared in Fig. 2.4. Denuding the particles at a given flow rate produced little change in these three metrics as all changes were within one standard deviation (denoted by error bars).

2.3.2 Standard collection efficiency in IOGAPS denuders

Initial attempts at standard collection efficiency were performed using a linear \( n \)-alkane standard. Experiments were performed in both the syringe pump and direct injection set-ups and contamination was observed in both. For this reason a deuterated hydrocarbon standard was used. The standard compounds were placed on the denuder through either the syringe pump injecting into a 120 cm, 1/4” polymer tubing with a room air flow of 60 LPM for 50 minutes or through directly injecting the standard onto the long denuder (first in sequence, Fig. 2.1), followed by pulling room air for four hours at 60 LPM. The calibration curve data (Fig. 2.5) was generated using five standards made (0, 1, 5, 10 and 25 ng \( \mu \text{L}^{-1} \)) diluted from a stock standard solution. Correlation values were good and ranged from 0.976 to 0.996 for the six compounds sought, indicative of minimal error in final recoveries.

Results are shown in Fig. 2.6 where compounds are arranged from left to right by decreasing volatility. \( n \)-C\(_{25}\)D\(_{52}\), Chrysene-d\(_{12}\) and \( n \)-C\(_{30}\)D\(_{62}\) were the least volatile compounds and showed very low recovery in both methods, although some of these were recovered from the long denuder during the direct injection experiments and marginal breakthrough to the small denuder can be seen. Comparatively recoveries were almost zero for these low volatility compounds during the syringe pump experiment. It is likely the compounds were too non-volatile to effectively evaporate from the syringe pump needle during the experiment. Heating the syringe needle could have potentially overcome this issue. In injecting these compounds directly, their oily nature allowed them to adhere at least somewhat to the long denuder while some broke through and were collected from the short denuder over the four hour period. As the denuders are designed for gas-phase VOC collection the poor recoveries of these non-volatile compounds are expected.

\( n \)-C\(_{15}\)D\(_{32}\), phenanthrene-d\(_{10}\) and \( n \)-C\(_{20}\)D\(_{42}\) are more volatile and their collection efficiencies were notably higher than the previous three compounds. The two linear alkanes showed a similar trend, their collection was enhanced in the syringe pump method over the direct injection method while they were primarily collected from the long denuder. Interestingly, they both show similar recovery in the direct injection experiment while the more volatile \( n \)-C\(_{15}\)D\(_{32}\) shows a stronger (over 95%) recovery in the syringe pump method. It is believed both compounds partitioned to the gas-phase from the syringe solution given
their higher vapour pressures but that the deuterated \textit{n}-pentadecane did so more effectively as it lies in the center of the IVOC range while \textit{n}-eicosane nears the transition between IVOC and SVOC volatility ranges. In the direct injection experiment, these two linear alkanes likely dislodged from the denuders over the four hour sampling period where the extent of the losses was functionalized by the intermolecular interactions between the XAD-4 polymer resin and the alkanes themselves. Because the alkanes are of such similar molecular structure, their adherence to the resin and thus their losses were similar. This implies that a knowledge of UCM composition is needed to accurately quantify VOCs using the IOGAPS as certain VOCs may be collected more effectively based on their molecular structure and volatility.

Phenanthrene-\textsubscript{d\textsubscript{10}} (C\textsubscript{14}D\textsubscript{10}) showed an opposite trend to the linear alkanes. The compound showed 80\% recovery in the direct injection experiment where it was found almost entirely on the long denuder while very poor (12\% cumulatively) recovery from the syringe pump experiments. Likely the improved intermolecular interactions afforded to phenanthrene-\textsubscript{d\textsubscript{10}} by its aromaticity resulted in improved collection efficiency over the linear alkanes in the direct injection experiment. Because the volatility of phenanthrene lies between the pentadecane and eicosane compounds, the argument for insufficient gas-phase partitioning from the syringe needle cannot be made. Instead Eqns. 2.2 – 2.5 were used to calculate the possible diffusional losses of phenanthrene-\textsubscript{d\textsubscript{10}} under the turbulent 60 LPM flow regime.

\[ Sc = \frac{\mu}{\rho_{\text{air}} D} \quad (2.2) \]

\[ Sh = 2 + 0.552 \frac{Re_{\text{tube}}^{1/2}}{D} Sc^{1/3} \quad (2.3) \]

\[ 1 - \frac{N}{N_o} = 1 - exp \left( -\frac{Sh \pi D L}{Q} \right) \quad (2.4) \]

Where first the Schmidt number (\(Sc\)) was calculated (Eq. 2.2) as the ratio of viscous to molecular diffusion rates using a diffusion coefficient, \(D\), of \(6.54 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}\),\textsuperscript{[59]} a dynamic viscosity, \(\mu\), of \(1.81 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}\), and a density of air, \(\rho_{\text{air}}\), of \(1.29 \text{ kg m}^{-3}\). Subsequently the Sherwood number (\(Sh\), ratio of mass transfer to diffusion rates, Eq. 2.3) was calculated given a Reynolds number (\(Re\)) of almost twenty-thousand, indicative of turbulent flow. Finally the molecular losses were calculated as one minus the ratio of outgoing, \(N\), to incoming, \(N_o\), molecules. The ratio is equivalent to the negative exponential ratio of the product of Sherwood number, \(\pi\), molecular diffusion coefficient in air and tubing length, \(L\),
to flow rate, $Q$ (Eq. 2.4). Flow was assumed as immediately turbulent in the narrow 1/4” tubing as entry length ($L_h$) calculations (Eq. 2.5) showed turbulent flow would develop in just a few centimeters.

$$L_h = 1.359D_{\text{tube}}Re^{1/4} \quad (2.5)$$

Using these equations the total losses of phenanthrene-d$_{10}$ were estimated as $92\%$. This would suggest that no losses occurred due to improper gas-phase partitioning from not heating the syringe needle as the remaining phenanthrene-d$_{10}$ was collected. Repeating these calculations for $N_C = 15, 20, 25$ and $30$ linear deuterated alkanes, losses were estimated from diffusional constants found in Elliott and Watts (1971).$^{[60]}$ As molecular weight increases diffusion coefficient decreases and fewer losses are expected. Diffusional losses were calculated as $70\%$, $59\%$, $47\%$ and $35\%$ for these alkanes, respectively. However, the collection efficiency of C$_{15}$D$_{32}$ was nearly $100\%$ leading us to believe that gas-phase VOCs lacked diffusional accommodation on the tubing walls and diffusional losses could not have played an important role in compound recoveries. Given that both the expected gas-phase partitioning, and the diffusional loss calculations cannot adequately explain the incongruous result for the phenanthrene-d$_{10}$ PAH, we believe the result must originate from the molecular structure of the PAH and its intermolecular adsorption interactions with the XAD-4 resin whilst in the gas-phase.

Gundel et al. (1995)$^{[58]}$ found increasing flow rate and sampling period led to lower recoveries of PAHs including phenanthrene in what was a previous version of the IOGAPS apparatus. Using lower flow rates ($5-20$ LPM) they were able to achieve phenanthrene recoveries in excess of $70\%$ from laboratory room air. Using three 22 cm denuders held in sequence (as opposed to the two denuders of length 44 cm and 22 cm used here), their argument was that at higher PAH concentrations the XAD-4 sorbent material will saturate before any breakthrough occurs. Under lower gas-phase concentrations however, they expect the volumetric capacity (the maximum sampling volume beyond which VOC breakthrough is expected) to be achieved before the sorbent material saturates and lower sample recovery occurs in the form of VOC breakthrough. Later, both Peters et al. (2000)$^{[61]}$ and Lane et al. (2000)$^{[57]}$ found that the hydrophobic XAD-4 resin is highly capable of trapping PAHs at 16.7 LPM under ambient atmospheric concentrations with minimal VOC breakthrough over several hours. Ideally the experimental design should be adjusted for flow rate and sampling time so as to cease sampling before volumetric capacity is reached thus avoiding denuder saturation. Gundel et al. (1995)$^{[58]}$ estimate a volumetric capacity of 2000 L for these denuders and under our 60 LPM flow regime used here, this capacity would be reached in 33.3 minutes. Furthermore, given our 5000 ng sample loading and 50 minute runtime, the
mean concentration of phenanthrene-d_{10} in sampled air would have been 1.67 ng L^{-1}, roughly 1600 times higher than the ambient concentrations used in these ambient air studies.\textsuperscript{[57,58,61]}

Based on these results and calculations it seems our low collection efficiency for the phenanthrene-d_{10} PAH was not heavily functionalized by diffusional tubing losses or lack of gas-phase partitioning, given the high recoveries and similarly calculated losses for n-alkanes of comparable volatilities. Instead it likely originated from insufficient gas-phase VOC adsorption in our high flow and highly concentrated regime.

Imagining the adsorption/desorption mechanism as an equilibrium between the VOC and the XAD-4 resin, under the assumption of Langmuir adsorption kinetics, the VOCs will compete for adsorption sites to form a non-interacting monolayer in the denuders. The direct injection experiment can be thought of as measuring only desorption over four hours while the syringe pump experiment measured both adsorption and desorption over fifty minutes. Here phenanthrene-d_{10} appears to adsorb and desorb less effectively than the n-alkanes. It was desorbed less effectively than the n-alkanes in the direct injection experiment (80% recovery), while it also adsorbed less effectively when volatilized (12% recovery). Desorption appears less important than adsorption for the PAH as only 20% desorbed in what was a simulated eight hour sampling period. This indicates insufficient PAH-resin adsorption at high flow rate and concentration was the controlling factor in poor PAH recovery.

Further work for the IOGAPS should focus on characterizing VOC recovery at known, atmospherically relevant concentrations, and over long sampling periods with varied flow rates. This could potentially implicate the PM cyclone’s necessity for higher flow rates and the possibility of varied VOC adsorption affinities as negative aspects in atmospheric VOC quantification with the IOGAPS apparatus.
2.4 Figures and Tables

Figure 2.1: Set-up of IOGAPS. The inlet was fitted as an ammonium sulphate atomizer, 10 µL syringe pump, or charcoal denuder for particle sizing and two standard collection efficiency experiments, respectively. The large 60 LPM pump is depicted at bottom right while the SMPS (custom) and backing pump separate at a T-junction.
Figure 2.2: Fits of particle size distributions as a function of sampling flow rate through and bypassing the IOGAPS set-up using 30 mmol L$^{-1}$ ammonium sulphate solution. Inset shows a typical log-normal fit function. Total particle concentration decreased with increasing flow rate. Particle size distribution was mostly unaffected by connecting the IOGAPS denuders but smaller particles (diameter ≤ 100 nm), appeared to be more affected than larger particles. The reverse trend observed at 60 LPM is attributed to a transition to turbulent flow. Under the assumption of constant density and particle sphericity, mass losses from the denuders for 33, 40, 49 and 60 LPM were 10%, 3%, 18% and -2%, respectively.
Figure 2.3: Total particle number transmission for IOGAPS set-up using 30 mmol L$^{-1}$ ammonium sulphate solution. Points below hashed black line (slope = 1) indicate less than 100% transmission through IOGAPS denuders under various flow regimes (marker style) and for various sized particles (colour scale). Black dotted lines indicate 110% and 90% transmission.
Figure 2.4: Particle number, volume and area concentrations with flow rate through and bypassing the IOGAPS set-up using 30 mmol L$^{-1}$ ammonium sulphate solution, error bars represent ±1 standard deviation. Increasing flow rate reduced all three metrics while connecting or disconnecting IOGAPS apparatus had little effect on particle measurements.
Figure 2.5: Calibration curves for deuterated hydrocarbon standards during direct injection experiment. Denuder extract concentrations were interpolated between 1, 5, 10 and 25 ng μL⁻¹ standard concentrations. m/z values of 66, 188 and 240 were used in quantifying n-alkanes, phenanthrene-d₁₀ and chrysene-d₁₂. $R^2$ values ranged between 0.996 and 0.976.
Figure 2.6: Comparison of recoveries for deuterated alkanes in order of most to least volatile (left to right) between direct injection and syringe pump experiments in the long and short denuders. More volatile IVOCs were collected more effectively than less volatile SVOCs while PAH phenanthrene-d$_{10}$ had an opposing trend in recovery from the linear $n$-alkanes.
Chapter 3

Speciating and quantifying complex mixtures using supersonic molecular beam – gas chromatography/mass spectrometry, SMB-GC/MS

3.1 Abstract

Two atmospherically relevant unresolved complex mixtures (UCMs) are analyzed by supersonic molecular beam – gas chromatography/mass spectrometry (SMB-GC/MS), one, a hydrocarbon mixture of petrogenic origin, the second – a sample diesel fuel diluted in chloroform. Hydrocarbons present are speciated by carbon number ($N_C$), number of double bond equivalents ($N_{DBE}$), and structural motifs such as degree of branching, branch position, or degree of ring substitution. The first mixture is found to be composed primarily of saturated hydrocarbons in which linear $n$-alkanes are predominant. Branched alkanes are found and volatility trends based on branching are predictable. Explicit branch positions are elucidated and constitutional isomers are quantified relative to each other. The diesel mixture is found to be comparatively similar save for the presence of unsaturated compounds. These are hypothesized as cyclohexyl-based volatile organic compounds (VOCs) and their degree of ring substitution follows a predictable trend. The procedure of quantification is repeated for the diesel fuel where alkane mass between
C₈ and C₂₁ is found to be heavily dependent on N\text{DBE}. The number and variety of compounds present in these anthropogenic mixtures underscores the need to better understand the emission of precursors to atmospheric aerosol.

3.2 Experimental Methods

3.2.1 Supersonic molecular beam, (SMB)-GC/MS

The SMB-GC/MS technique has been described elsewhere.\cite{31,51,52,53,62} In Fig. 3.1 the gaseous effluent of the GC column expands into vacuum through a small nozzle, cools concordantly and forms a beam of supersonic velocity. A helium make-up gas is added to tune the extent of adiabatic expansion. This cooling by expansion reduces internal molecular energy prior to collimation via a skimmer lens of 0.8 mm. The central portion of the beam is isolated and transferred to the differentially pumped ionization chamber. Ionization takes place at 70 eV and analyte is deflected 90° by ion mirror. The ionized and sample is then filtered in scanning mode by a quadrupole mass analyzer before detection by channeltron ion detector.

Because the gaseous effluent of the GC column is adiabatically cooled before ionization the lifetimes of molecular ions (M⁺) are enhanced. Characteristic molecular fragments are also preserved and lifetimes of especially stable fragments are also enhanced in comparison to traditional EI methods without cooling (Fig. 3.2). As the mass spectrum is plotted relative to the most abundant ion, the molecular ion and characteristic fragment ion signals become pronounced while other ionic fragment signals are still clearly observed. Changing the flow of helium make-up gas tunes the relative strength of the molecular ion signal by controlling the extent of vibrational de-excitation. As increased introduction of helium make-up gas increases cooling effects and leads to an increase in M⁺ signal. In this way the SMB-GC/MS can be returned to a typical EI-GC/MS set-up by minimizing the make-up gas flow rate and the additional vacuum chamber after column separation can be released. Mass spectra can be compared to literature databases\cite{63} yielding strong matches with good matching factors and probabilities despite the enhanced M⁺ signal.\cite{31,64}

Samples and standards were analyzed between 50–500 m/z scanning by GC (7890 Series, Agilent) equipped with quadrupole mass selector (5975 Series, Agilent) and upgraded with a supersonic molecular beam interface and fly-through ion source (5975-SMB, Aviv Analytical Ltd.). Two samples are analyzed in this work: the first (hereafter referred to as the HC mixture) is a relevant petrogenic mixture and the
second (hereby referred to as diesel) is a diesel fuel sample collected at a Californian gas station. Both samples described are diluted and analyzed by 1 µL direct injection into an inlet held at 250 °C and at a 9:1 split flow. The GC column was a DB-5ms with dimensions (length, internal diameter, film thickness) of 27.8 m × 250 µm × 0.25 µm (Agilent). For the hydrocarbon (HC) mixture, the temperature program was 50 °C for 1 min, ramp 50 °C to 300 °C at 10 °C per minute, and held at 300 °C for four minutes. For the diesel mixture, the temperature program was a 40 °C initial column temperature held for 0.3 minutes, followed by a ramping program at 15 °C per minute to 320 °C held for two minutes (Fig. 3.3). Additionally, two standards were analyzed under identical conditions to that of the diesel fuel. The first standard was a hydrocarbon standard containing known C₈-C₄₀ linear alkanes, phytane, pristane, and n-pentadecylcyclohexane and was used for sensitivity comparison across carbon numbers. The second standard was a sample of N_C = 10 isomers used for comparisons of response between different numbers of N_{DBE}.[28]

Chromatographic data were analyzed using custom code in IGOR Pro (6.35A5, Wavemetrics) and ChemStation (G1701EA E.02.02, Agilent). Molecular ion peaks were first classified by carbon number (N_C) and by N_{DBE}. A double bond equivalent (DBE) is an unsaturation in the form of a ring or olefin moiety leading to empirical formulae with two fewer H atoms than that of a saturated alkane. Here the hydrocarbon $i$ of mass $m_{(i)}$ is reduced by the mass of two protons ($2 \times m_H$) compared to the mass of a saturated hydrocarbon of equal N_C, $m(C_{N_C(i)}H_{2N_C(i)+2})$, for each double bond equivalent (Eq. 3.1).

$$N_{DBE}(i) = \frac{m(C_{N_C(i)}H_{2N_C(i)+2}) - m_{(i)}}{2 \cdot m_H}$$ (3.1)

Alkenes are generally more reactive, and therefore less abundant, than cyclic species under ambient conditions and are not considered in the samples. It is therefore expected that most compounds with N_{DBE} ≥ 1 contain one or more rings. Cyclohexanes were hypothesized to represent the bulk of N_{DBE} = 1 species as the six membered ring is sterically most relevant, although it is likely cyclopentanes were present in small amounts. Branched alkanes were differentiated based on their characteristic fragmentation mass spectra and overall alkanes were speciated into five main groups: linear, singly methyl branched, doubly methyl branched, mono-substituted cyclohexanes, and cyclohexanes of higher substitution where the two latter groups are considered unsaturated in that they have N_{DBE} ≥ 1.
3.2.2 Quantification of VOCs

Species were quantified from C$_8$ to C$_{21}$ by N$_C$, degree of branching and position of methyl branch, or by degree of ring substitution, or number of rings. Ionization, fragmentation, and transfer efficiencies of each species were accounted for through molecular ion comparisons within the linear alkane and C$_{10}$ standards. For this purpose 4-methylnonane, n-decane, n-butylcyclohexane, decalin, adamantane, 1,2,3,5-tetramethylbenzene, and tetralin were used to represent branched, linear, and N$_{DBE}$ = 1, 2, 3, 4, or 5 species, respectively. In brief, the ratio of M$^+$ signals between a non-linear (for example B1, B2, or monocyclic) and a linear alkane of the same N$_C$ are taken. This ratio is then divided into all M$^+$ signals for species of the same non-linear structure. This augments the intensity of the non-linear alkane’s M$^+$ signal to correct for the different propensities for ionization and fragmentation at 70 eV imparted by its non-linearity. Branched alkanes fragment more easily so their M$^+$ signals require enhancement while cyclic compounds maintain their structure more readily and will have stronger M$^+$ ion signals that require reduction.

Signal intensities were also corrected for transfer efficiencies using the linear alkane standard by normalizing to the most abundant n-alkane (C$_{21}$, n-heneicosane). Transfer efficiency through the instrument is functionalized by alkane volatility (and therefore size). Less volatile VOCs tend to traverse the instrument more easily than more volatile VOCs and so signals are further corrected by adjusting to the n-alkane of greatest signal within a standard of equally concentrated n-alkanes. Standard linear alkanes of N$_C$ < 21 showed a varied response from the instrument despite being in equal concentrations. The ratio of their signals to the most abundant n-alkane produced an N$_C$ dependant correction factor that was applied to all alkanes in both the HC and diesel mixtures.

3.3 Results and Discussion

3.3.1 Speciation of saturated, N$_{DBE} = 0$, alkanes

The HC and diesel mixtures are found to exhibit some striking similarities in isomer distribution across carbon numbers, shown in Figs. 3.3 and 3.4. The HC mixture facilitated the elucidation of the trend in constitutional isomer elution for saturated (N$_{DBE} = 0$) compounds given its abundance of these alkanes and the clarity in which they appear in the region of 5 – 15 minutes (Fig. 3.3). We are able to directly associate the molecular ions with fragment ions. The peaks are found to be ordered by
degree of branching on the alkane backbone, and the branches that occur are almost entirely pendant methyl groups save for one 3-ethyl isomer observed at higher carbon numbers. The earliest constitutional isomers to elute are those of highest degree of branching (hereafter referred to as B2), followed by singly branched alkanes (B1), and finally the linear \( n \)-alkane (B0), for the same molecular formula (and thus molecular weight), an alkane \( (N_C \leq 9) \) with a larger number of methyl branches has a shorter chain length and higher vapour pressure\(^{65}\), (Fig. 3.3, inset).

Therefore, the earliest eluting B2 alkanes are predominantly saturated alkanes with two methyl branches (Fig. 3.3, inset), and the B1 alkanes are isomers with a single methyl branch. Fig. 3.4 shows the molecular ion traces for alkanes across several carbon numbers and the trends are present in both the HC and diesel mixtures. For B1 and B2, the distribution of peak areas is highly consistent, progressing from a few resolved peaks at \( N_C = 8 \) to finally an unresolved region of many overlapping peaks at \( N_C > 21 \). As the carbon number increases the number of potential isomers increases exponentially\(^{14}\). For this reason, specific isomeric quantification was only pursued up to \( N_C = 21 \).

Basic theories of fragmentation are used to identify molecular ions by overlaying their signals with informative fragment ions\(^{66}\). The B1 isomers have a methyl branch, and C-C bond scission is favoured on either side of the methyl branch, owing to a more stable secondary carbocation. For example, peak B in Fig. 3.5, is most consistent with 3-methyldecane, since the favourable losses are either \(-\text{CH}_2\text{-CH}_3\), (loss of 29 amu) or \(-(\text{CH}_2)_6\text{-CH}_3\), (loss of 99 amu), where the two secondary carbocation fragments that result show the highest intensity in the mass spectrum (127 \( m/z \) and 57 \( m/z \), respectively). The lack of fragment signal corresponding to a loss of three carbons (113 amu, or loss of 43 amu) reinforces this conclusion.

The identification of all peaks can be made in this way, for example, peak E has a clear molecular ion signal \((m/z \ 156)\) and two strong fragments at \( m/z \ 85 \) and \( m/z \ 99 \) which correspond to the loss of \(-\text{CH}_3\text{-(CH}_2)_4\) and \(-\text{CH}_3\text{-(CH}_2)_3\), respectively. These two fragments of roughly equal intensity betray the location of the pendant methyl group as charge formation on the secondary carbon of the resulting larger fragment is favoured after C-C bond scission between the methyl- and \( \alpha \)-carbons. Two weaker fragments are observable at \( m/z \ 71 \) and \( m/z \ 57 \) and result from the positive charge instead moving to the primary carbon of the smaller fragment (a less favourable process) and then likely redistributing to a secondary carbon via hydride shift\(^{66}\).

The order from longest retention time and least volatile to shortest retention time and most volatile was linear (B0), 3-methyl, 2-methyl, 4-methyl, 5-methyl, 6-methyl, 7-methyl (where possible). Figure
3.6 shows the elution trends of B1 isomers at low N
C
where isomer elution order was determined. As
carbon number increases so too do the number of potential isomers with a single methyl branch however
their elution order remains consistent. The isomers became less resolved as the number of carbon atoms
increased and the methyl branch approached the centre of the alkane backbone.

Speciation of doubly branched species (B2) was more difficult as the complexity of adding a second
tertiary carbon to the alkane backbone increases the number of relevant fragmentation pathways, (Fig.
3.7). The number of potential isomers is also greater and adds to the obfuscated mass spectra, however
some patterns were extracted and species have been proposed. In almost all cases the isomers were found
to contain two methyl branches one of which was on the 2-carbon, evidenced by the propensity to lose
a fragment of m/z 43 (B, Fig. 3.7) or m/z 15. These fragments correspond to the terminal isopropyl
group or loss of the terminal CH
3
(m/z 15) forming the secondary carboxation. Subsequently, lighter
fragments were used to determine the position of the second methyl branch (C, Fig. 3.7). Tentatively,
the B2 peaks are being assigned (in order of least to most volatile, highest to lowest retention time)
to 2,3-dimethyl and 3-ethyl alkanes preceded by 2,10-dimethyl (where possible) and progressing to 2,6-
and 2,5-dimethyl isomers which coelute right after the 2,4-dimethyl isomer. Interestingly, 2,6-dimethyl
peaks were noticeably larger than other peaks possibly owing to isoprenoid backbones remnant of ancient
biological material in fossil fuels.[27]

As a worked example, the peak in Fig. 3.7 at retention time = 9.99 minutes has been assigned to
2,4-dimethylundecane (m/z 184). According to fragmentation theory[66] this alkane should favourably
fragment to lose either a terminal isopropyl group (loss of 43 amu), a terminal isobutyl group (loss of
57 amu), or the large linear -CH
3
-(CH
2
)6
 group (loss of 99 amu). These three losses correspond to
fragment m/z ratios of 141, 127, and 85, respectively. In looking at Fig. 3.7, these m/z ratios appear
most abundant after the molecular ion (m/z 184) at time t = 9.99 minutes.

\[
I = 100 \times \left[ n + \left( \left\{ N - n \right\} \times \frac{t_u - t_n}{t_{N} - t_{n}} \right) \right]
\]

(3.2)

Where available Kováts retention indices[67] were used as guidelines for comparisons.[63] Retention in-
dices measured in the HC mixture and diesel fuel correlated well with those found in the database,
further supporting these isomeric assignments although not all proposed isomers were present in the
database for comparison (Table 3.1). The indices were measured using Eq. 3.2. Linear n-alkanes of
identical N
C
and N
C
- 1 were used as internal standards (t
N
and t
n
, respectively) from which all B1
and B2 isomers could be interpolated using their retention times (t
u
). The bounding carbon numbers
NC and NC - 1 are represented as N and n in this equation where I is the Kováts retention index. Table 3.1 shows this correlation between retention indices for NC = 13 isomers using n-tridecane and n-dodecane as internal standards. Isomers of other carbon numbers showed similarly strong correlations with literature but lacked entries in the database particularly for the variety of B2 isomers found in our samples.

### 3.3.2 Speciation of unsaturated, \(N_{\text{DBE}} \geq 1\), alkanes

The HC mixture contained primarily saturated alkanes so here we focus on the diesel fuel sample, for this the following approach was applied: individual isomers at lower (NC = 8) carbon numbers were first identified based on fragmentation patterns, and the isomer distribution was then extrapolated to higher NC. Fig. 3.8 shows a comparison of \(N_{\text{DBE}} = 1\) chromatograms at NC = 8 and 9 to NC = 16. The rings in all cases were considered to be six-membered cyclohexane structures as this represents the most stable conformation and little or no evidence was found for the presence of five-, seven-, or eight-membered rings. For NC = 8, there are only four possible constitutional isomers with a six membered ring: ethylcyclohexane and three dimethyl cyclohexanes. The major fragment ion of C\(_8\) cyclohexanes are \(m/z\) 97, and \(m/z\) 83; \(m/z\) 97 (C\(_7\)H\(_{13}\)) likely originated from a dimethylcyclohexane, and \(m/z\) 83 (C\(_6\)H\(_{11}\)) is likely a fragment ion of ethylcyclohexane since the favoured loss is one that forms a secondary carbocation on the hexane ring. By overlaying the ion traces of \(m/z\) 97 and \(m/z\) 83 with the molecular ion trace (\(m/z\) 112), the peaks in the molecular ion trace can clearly be assigned. At NC = 9, the number of isomers increases but the peaks in the molecular ion trace can still be assigned to mono-, di-, and tri-substituted cyclohexanes using the characteristic ions \(m/z\) 83, 97, and 111, respectively. Extending these assignments to higher carbon numbers (NC = 16 is shown in Fig. 3.8 as an example), the chromatograms were divided into regions with the latest eluting, proposed to represent mono-substituted ring species, the intermediate region di-substituted, and the earliest eluting region to represent tri-substituted and higher monocyclic species.

\[
\begin{align*}
  r &= \frac{\sum_{i=1}^{n} X_i Y_i - \frac{1}{n} \sum_{i=1}^{n} X_i \sum_{i=1}^{n} Y_i}{\sqrt{\left(\sum_{i=1}^{n} X_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} X_i\right)^2\right)\left(\sum_{i=1}^{n} Y_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} Y_i\right)^2\right)}} \\
  sr &= \sqrt{\frac{1 - r^2}{n - 2}}
\end{align*}
\]  

The proposed identification is further supported by Pearson’s linear correlation tests of identified regions.
with mass fragments, $m/z$ 83, 97 and 111 for higher $N_C$, $N_{DBE} = 1$ species (Fig. 3.9). Equations 3.3 and 3.4 were used to test the correlation of these three indicative fragments with all of the mass spectra collected over the time of the cyclic alkane elution from Fig. 3.8. A value of +1 indicates an exact correlation, 0, a non-correlation response, and -1 indicates an exactly inverse correlation. These three ions were found to correlate well with the sum of ions in the mass spectra given their enhanced signal as stable and characteristic fragment ions in the SMB. It should be noted the 'cut-offs' for these elution regions were made visually by the experimenter (as in Fig. 3.8). In all cases the 83 $m/z$ fragment correlated best with the proposed mono-substituted region, the 97 $m/z$ fragment showed best correlation with the intermediate regions. Lastly, the 111 $m/z$ corresponded well to the earliest elution of isomers in all cases except for $N_C = 11$. These results provide confidence in our interpretations of molecular structures.

### 3.3.3 Quantification of VOCs

Both mixtures were analyzed quantitatively through use of analytical standards described in the Experimental section 3.3. The procedures described in Chan et al. (2013)\cite{28} were used to correct for ionization and fragmentation efficiencies across different alkane types. The transfer efficiency through the column as a function of retention time was accounted for by the $n$-alkane standard where $N_C = 21$ $n$-heneicosane produced the largest signal. Quantification results for diesel fuel are shown in Fig. 3.10 A and B, while the analogous HC mixture quantification is shown in Fig. 3.10 C and D. Linear $n$-alkanes comprise 47% of the $N_{DBE} = 0$ mass in diesel and 18% of that in the HC mixture. Both mixtures have similar relative amounts of highly branched B2 saturated alkanes at 30% and 22%. However, the HC mixture is more abundant in singly branch B1 saturated alkanes (Fig. 3.10, C) at 59% and only 23% in the diesel relative to all $N_{DBE} = 0$ compounds. Shown in Fig. 3.10 A and C, the number of potential B1 isomers increases as the carbon backbone lengthens and the single methyl branch migrates towards the centre of the alkane. $N_C = 16$ and 17 appear to be the dominant saturated alkane in diesel while $N_C = 12, 13$ and 16 dominate the HC mixture.

Quantification by $N_{DBE}$ is shown in Fig. 3.10 B and D for the diesel and HC mixtures. The HC mixture contains mostly saturated alkanes between $N_C = 12$ and 17, as well as a a group of unsaturated compounds that are in relatively equal proportion to each other over this volatility range. At higher volatility the saturated alkanes dominate as was expected given the relative cleanliness of the early part of the chromatogram (5 – 15 minutes, Fig. 3.3) where saturated alkane branching was elucidated. This
early part of the chromatogram contains $N_C = 8 - 12$ VOCs (VOCs). In diesel, the relative mass fraction of $N_{DBE} = 1$ compounds remains relatively constant across carbon numbers while $N_{DBE} \geq 3$ compounds are not a significant component (Fig. 3.10, B). These results are in agreement with Gentner et al. (2012) who found that alkanes of $N_{DBE} \leq 2$ and some aromatic species dominate diesel fuel carbon mass. Overall these findings indicate the HC mixture is of similar average volatility to the diesel fuel but within a narrow range of carbon numbers and its $N_{DBE} = 0$ alkane fraction is heavy in B1 alkanes while diesel contains more linear, B0 alkanes.

### 3.4 Figures and Tables

Table 3.1: Example Kováts retention indeces (calculated by Eq. 2.4) comparison for a single saturated alkane ($N_C = 13$). Where indicated literature values vary from the PDMS stationary phase used. Indeces calculated through interpolation using $n$-alkanes as internal standards with retention indeces of $I = N_C \times 100$ and Eq. 3.4.

<table>
<thead>
<tr>
<th>C_{13}H_{28}</th>
<th>Name</th>
<th>Calculated Retention Index</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>$n$-tridecane</td>
<td>1300</td>
<td>1300 (by definition)</td>
</tr>
<tr>
<td>B1</td>
<td>3-methyldodecane</td>
<td>1272</td>
<td>1270</td>
</tr>
<tr>
<td></td>
<td>2-methyldodecane</td>
<td>1266</td>
<td>1263</td>
</tr>
<tr>
<td></td>
<td>4-methyldodecane</td>
<td>1260</td>
<td>1259</td>
</tr>
<tr>
<td></td>
<td>5-methyldodecane</td>
<td>1255</td>
<td>1254</td>
</tr>
<tr>
<td></td>
<td>6-methyldodecane</td>
<td>1253</td>
<td>1251</td>
</tr>
<tr>
<td>B2</td>
<td>2,3-dimethyldodecane</td>
<td>hypothesized</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3-ethylundecane</td>
<td>1234</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,10-dimethyldodecane</td>
<td>1228</td>
<td>1228 (DC-200)</td>
</tr>
<tr>
<td></td>
<td>2,9-dimethyldodecane</td>
<td>hypothesized</td>
<td>1233</td>
</tr>
<tr>
<td></td>
<td>2,8-dimethyldodecane</td>
<td>1222</td>
<td>1223 (DC-200)</td>
</tr>
<tr>
<td></td>
<td>2,7-dimethyldodecane</td>
<td>1217</td>
<td>1216</td>
</tr>
<tr>
<td></td>
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Figure 3.1: Cutaway of the SMB-GC/MS taken from Amirav et al., 2001. [51] The analyte travels from the GC column at right through the gas mixing zone where it is adiabatically cooled by expansion into vacuum created by a large rotary pump and mixed with helium make-up gas. The sample is then collimated into a fly-through EI ion source held at 70 eV for ionization and ultimately detected using a quadrupole mass analyzer and channeltron ion detector.
Figure 3.2: Mass spectra comparison for \( n \)-undecane \((m/z \ 156)\), between traditional EI-GC/MS and SMB-GC/MS showing pronounced molecular ion peak in the SMB method. The linear fragmentation pattern is observable in the progressively increasing fragment ion intensity with reduced carbon number.
Figure 3.3: Total ion chromatogram (TIC) of HC and diesel fuel mixtures. Backgrounds show detected fragment masses with time. Colour spectrum indicates low (grey) to high (red) signal intensities for normalized $m/z$. Inset: SIC of $m/z$ 142 showing elution order trends of $C_{10}H_{22}^+$ by branching in the HC mixture.
Figure 3.4: Molecular ion traces across a range of carbon numbers for A) saturated (N_{DBE} = 0) alkanes in the HC mixture and B) cyclic (N_{DBE} = 1) alkanes in diesel fuel. In A), regularity in linear (B0), singly branched (B1), and doubly branched (B2) regions can be seen. As carbon number increases, early eluting B1 isomers begin to coelute and B2 regions become less resolved. In B), three regions pertaining to cyclohexane substitution are resolved at lower N_C and blend together at higher retention times.
Figure 3.5: Linear (B0) and singly branched (B1) regions of $N_C = 11$ SIC ($m/z$ 156), overlaid onto spectrometric results. Colour spectrum indicates low (grey) to high (red) signal intensities for normalized $m/z$. Peak assignments are A) $n$-undecane, B) 3-methyldecane, C) 2-methyldecane, D) 4-methyldecane, E) 5-methyldecane. Fragmentation in B1 isomers led to their elucidation; formation of secondary car-bocations through C-C bond scission at the methyl branching site was favoured.
Figure 3.6: Elution pattern of B1 regions by increasing $N_C$. A) $N_C = 8$, with 4- and 2-methyl isomers coeluting B) $N_C = 9$, 4-methyl isomer is beginning to resolve C) $N_C = 10$, 4- and 5-methyl isomers coeluting and D) $N_C = 11$ with all 3-, 2-, 4-, and 5-methyl isomers resolved. As $N_C$ increases so too does the number of possible methyl positions; the elution order follows a predictable trend according to isomer volatility and the peaks are quantifiable.
Figure 3.7: HC mixture B2 region of m/z 184, N\textsubscript{C} = 13, N\textsubscript{DBE} = 0 alkanes (black trace) showing colour intensity spectra in background (normalized, red = 100%) where each horizontal strip represents the loss of a carbon atom from the molecular ion. A) Molecular ions at m/z 184. B) Favourable loss of CH\textsubscript{3}-CH-CH\textsubscript{3} indicates 2-methyl branch save for the rightmost peak (3-ethylundecane, retention time = 10.35 min). C) Informative fragment ions elucidate the position of the second methyl branch. From top left to bottom right, losses of four, five, six, seven, and eight carbons tentatively indicate secondary methyl branching at 4-, 5-, 6-, 7-, and 8- positions leading to assignments of 2,4-dimethylundecane (retention time = 9.99 min), 2,5-dimethylundecane, 2,6-dimethylundecane (coeluting with previous forming the largest peak, retention time = 10.04 min), 2,7-dimethylundecane (retention time = 10.11 min), and 2,8-dimethylundecane (retention time = 10.17 min); 2,10-dimethylundecane (retention time = 10.26 min) shows a distinct loss of 3 carbons followed by a linear fragmentation pattern; the 2,9-isomer appears absent.
Figure 3.8: Comparison of NDBE = 1 diesel cyclohexanes for NC = 8, 9, and 16. At low NC the number of potential isomers are fewer and their elution patterns can be assigned in order of least to most volatile as mono-, di-, and (where possible) tri-substituted cyclohexanes by overlaying molecular ion trace with cyclohexyl (m/z 83), methylocyclohexyl (m/z 97), and dimethylocyclohexyl (m/z 111) ions. As carbon number increases the isomers begin to coelute, but their order is maintained facilitating quantification by degree of ring substitution across a range of carbon numbers.
Figure 3.9: Pearson linear correlation data comparing informative fragment ion signals $m/z$ 83, 97, and 111 for each of the three region’s TIC defining ring substitution in $N_{DBE} = 1$ cyclic species. Under the hypothesis of favourable fragmentation occurring at the ring-C bond, these ions correspond to mono-, di-, and tri-substitution, respectively. $m/z$ 83 correlates best with the mono-substituted region across carbon numbers, while $m/z$ 97 and $m/z$ 111 correlate best with di-substituted and $\geq$ tri-substituted cyclic regions. Correlation and error equations are shown in equations 3.3 and 3.4.
Figure 3.10: UCM quantification: A and C) Relative quantification of \( N_{\text{DBE}} = 0 \) alkanes showing individual B1 isomers and their evolution with \( N_{\text{C}} \) for diesel (A) and HC mixtures (C). B2 isomer signals were deemed too weak and unresolved to confidently quantify individual isomers. B and D) Relative quantification by \( N_{\text{DBE}} \) showing \( N_{\text{DBE}} \leq 2 \) as the dominant fraction in diesel fuel (B) and \( N_{\text{DBE}} = 0 \) as the dominant fraction in the HC mixture (D). \( N_{\text{DBE}} \geq 4 \) were typically aromatic species while \( N_{\text{DBE}} = 1, 2 \) or 3 were typically ring species.
Chapter 4

Explicit kinetic modelling of the formation of secondary organic aerosol from complex mixtures

4.1 Abstract

A model based on Jordan et al. (2008)\(^{[54]}\) was constructed simulating high NO\(_x\) conditions. Previously quantified volatile organic compounds (VOCs) were treated individually for oxidation chemistry over three generations using the SIMPOL.1 group contribution method developed by Pankow and Asher (2008)\(^{[68]}\) for \(t = 3\) hours, \([\text{OH}] = 1 \times 10^7\) molecules cm\(^{-3}\), \(M_o = 10\) µg m\(^{-3}\), \([\text{Alkane}] = 5\) ppb. Highly substituted cyclic alkanes formed the most secondary organic aerosol (SOA) and yields were insensitive degrees of unsaturation (\(N_{DBE}\)) greater than one (\(N_{DBE} \geq 1\)); this was followed by less substituted cyclic alkanes, linear \(n\)-alkanes, and branched alkanes formed the least SOA. Changes in specific branching position led to only small (< 1%) changes in SOA yield. Unresolved complex mixtures (UCMs) were modelled as mixtures and the rate of volatility reduction was delineated under the volatility basis set (VBS) framework. Current parameterizations in functionalization rate were found to agree with explicitly modelled results.
4.2 Experimental Methods

4.2.1 Model design and mechanism

To model SOA formation, a box kinetic model was formulated using custom code in Matlab (R2012b, Mathworks). We opt to use the oxidation mechanism compiled by Jordan et al. (2008)\textsuperscript{[54]} while adding modifications for branched and cyclic compounds. We assume urban high NO\textsubscript{X} conditions and that RO\textsubscript{2} reacts with NO only. It is likely RO\textsubscript{2} may react to some extent with other peroxy radicals (RO\textsubscript{2} and HO\textsubscript{2}) but these pathways are likely negligible for reactions of hydrocarbons in the UCM.\textsuperscript{[69]} No particle-phase oxidation is considered. One limitation of this oxidation mechanism is that the nominal case overpredicts SOA yields measured by Lim and Ziemann (2005)\textsuperscript{[70]} at high initial VOC concentrations.\textsuperscript{[54]} No attempt is made here to adjust vapour pressures or activity coefficients to match data by Lim and Ziemann (2005), as was done by Jordan et al. (2008).\textsuperscript{[54,70]}

The modelled mechanisms are shown in Fig. 4.1. The OH rate constants and branching ratios were derived from Lim and Ziemann (2009a) and Atkinson and Arey (2003).\textsuperscript{[19,39]} Each linear or branched hydrocarbon reacts to form eighteen products, which can partition to the particle phase (only gas-phase chemistry was considered). As an extension of the mechanism proposed by Jordan et al. (2008),\textsuperscript{[54]} each monocyclic hydrocarbon (N\textsubscript{DBE} = 1) forms twenty-eight additional products (Fig. 4.2) as a second peroxy radical is formed after ring-opening, and follows an analogous mechanism. For simplicity, N\textsubscript{DBE} ≥ 2 were not considered separately but instead grouped with the monocyclic precursors; initial attempts at modelling their oxidation led to significant model complexity with similar SOA yields to those of monocyclic systems.

4.2.2 Rate constants and partitioning coefficients

Equation 4.1 was used to calculate partitioning coefficients, $K_{p,i}$, where $MW_i$ is the molecular weight of $i$, $\gamma_i$ is the activity coefficient assumed as unity, $p_i^o$ is the liquid vapour pressure at temperature $T$, and $R$ is the gas constant. Liquid vapour pressures were estimated using the SIMPOL.1 model developed by Pankow and Asher (2008).\textsuperscript{[68]} Gas/particle partitioning equilibrium is assumed to be instantaneous.

$$K_{p,i} = \frac{RT}{10^6 \cdot MW_i \cdot \gamma_i \cdot p_i^o} \quad (4.1)$$
The reaction sequence is shown in Fig. 4.1 and relevant rate constants are provided in the tables 4.1 and 4.2, branching ratios of NO reaction and correction factors were taken from Jordan et al., (2008).[54] Briefly, hydrogen abstraction occurs first on the ALKH precursor, acronyms given by Griffin et al. in the Caltech Master Chemistry Model, CACM, (2002).[71] This forms the peroxy radical RO232. Subsequent reaction with NO forms either the AP11 alkynitrate or the alkoxy radical and NO2. This alkoxy radical has three potential sinks, isomerization, carbonyl formation, and fragmentation. In all cases carbonyl formation was treated as a terminating step. Attempts to model the further oxidation of this ketone led to only small changes in SOA yield owing to the relatively small value of k_carb (0.05 × 10^6 s^-1). The ALKH series leads to the formation of terminal products (AP13 and UR36), and AP11 and AP12 which follow a similar oxidation/isomerization scheme leading to the formations of UR37-40, and UR41-43, respectively.

OH radical rate constants (Table 4.1, Eq. 4.3) were calculated using structure activity relationships (SARs) outlined in Kwok and Atkinson (1995) and compared to those from Lim and Ziemann (2009a).[39,43] The branching ratios of alkoxy radical fragmentation, isomerization, and carbonyl formation are based on their first order rate constants (k_frag, k_isom, k_carb respectively). k_carb is 0.05 × 10^6 s^-1.[39] k_frag depends on the identity of the α-carbon (the carbon atom where H-atom abstraction occurred) k_frag,tert > k_frag,sec > k_frag,prim, and their values for k_frag are taken from Peeters et al. (2004).[72] We then calculate a weighted average k_frag defined by Eq. 4.2, where N_CH3, N_CH2, and N_CH are the number of primary, secondary, and tertiary carbon atoms in the parent hydrocarbon molecule, and 0.04, 0.31, and 0.65, are the relative rate constant ratios of OH abstraction from carbon atoms of each of these respective degrees of substitution.[43,44,45]

\[ k_{frag} = \frac{0.65 \, N_{CH} \, k_{frag,tert}}{N_C} + \frac{0.31 \, N_{CH_2} \, k_{frag,sec}}{N_C} + \frac{0.04 \, N_{CH_3} \, k_{frag,prim}}{N_C} \quad (4.2) \]

k_isom depends on the identity of the δ-carbon. As a simplification, an intermediate value of 3.3 × 10^6 s^-1 was used,[46] corresponding to k_isom for a secondary δ-carbon. This is likely more relevant for larger N_C where -CH2- is the most likely moiety in a long carbon backbone.

For linear alkanes, fragmentation was assumed to halve the molecule, while for branched species fragmentation reduced molecular size according to methyl branch position such that fragmentation was equally likely to occur on either side of the tertiary carbon. During sensitivity analysis, reducing carbon number between one and N_C – 1 carbon atoms during fragmentation led to only small differences in final yields and O:C ratios. This was attributed to isomerization being the dominant RO2 pathway during
the first few generations of oxidation modelled such that fragmented alkanes contributed little to final aerosol mass (Fig. 4.3). This is consistent with alkoxy radical formation being more predominant on more substituted carbon atoms. For doubly branched species, the abundance of 2-methyl isomers present in our samples led us to treat fragmentation as occurring on either side of the second tertiary carbon whose position varied on the alkane backbone. For cyclic species, fragmentation of the alkoxy radical was assumed to lead to a ring-opened peroxy radical which can further react following the same mechanisms as the initial RO$_2$ radical, (formation of the nitrate, hydroxynitrate, and alkoxy radical). Branching ratios of further fragmentation and isomerization of the ring-opened alkoxy radical were taken to be the same as those of singly or doubly branched alkanes of the same carbon number. In all, the three reaction schemes including the further reaction of ring-opened peroxy radical from cyclic species produce an additional 28 products for a total of 46.

Simulations were run for a time $t = 3$ h at $T = 298$ K with $[\text{OH}] = 1 \times 10^7$ molecules cm$^{-3}$ and an initial organic aerosol of 10 $\mu$g m$^{-3}$ simulating an urban environment. For single hydrocarbon simulations initial concentrations were 5 ppb while for diesel, the total mixture concentration was 5 ppb.

### 4.3 Results and Discussion

#### 4.3.1 Model comparison to other studies

The extension of the Jordan et al. (2008) model to cyclic and branched precursors was tested by comparing to the previous smog chamber studies of Presto et al. (2010), Loza et al. (2014), and Tkacik et al. (2012) in Fig. 4.4. We then compared further to Lim and Ziemann (2005, 2009a) for linear $n$-alkanes across a range of carbon numbers (Fig. 4.5). Our model shows good agreement with other studies under their respective conditions, but like Jordan et al. (2008), still over-predicts OA yields for linear $n$-alkanes when modelling high initial VOC concentrations as used in Lim and Ziemann (2005, 2009a).

#### 4.3.2 Modelled SOA formation from individual VOCs

Using explicit chemical structures, linear, branched, and cyclic compounds over a range of $N_C$ were modelled individually for their SOA formation (Fig 4.6). Highly substituted cyclic precursors showed the greatest affinity for SOA formation as their ring-opening led to more functionalized, heavier, less
volatile products. In contrast, mono-substituted cyclic precursors were calculated as having smaller ring opening rate constants, thereby limiting the formation of the additional twenty-eight products that have lower volatilities and leading to lower SOA yields. This effect was also noted initially for modelling species of $N_{\text{DBE}} \geq 2$. The calculated rate constants for isomerization and fragmentation were similar to that of the highly substituted monocyclics leading to similar SOA yields (Table 4.2). In all cases, an expanded product set after two instances of C-C bond scission led to only marginal differences in SOA formation, likely because only one instance of C-C bond scission is necessary before partitioning to the condensed phase.\textsuperscript{[42]} For this reason $N_{\text{DBE}} \geq 2$ were not distinguished from $N_{\text{DBE}} = 1$ when modelling the diesel mixture.

Linear alkanes showed predictably higher yields than branched structures and were comparable to Presto et al. (2010)\textsuperscript{[76]} (agreeing to $\leq 5\%$, Fig. 4.4) upon simulating their conditions. For branched alkanes, the lower SOA yields are associated with their fragmentation to more volatile products. Degree of branching was found to have little effect on SOA formation as branching ratios between isomerization and fragmentation were not significantly changed by the addition of a second methyl branch. Moreover, specific branching position did not play a significant role in SOA yields for B1 and B2 alkanes. Only a small change in yield (generally less than 1\%) was noted in comparing 2-methyl isomers to those who branched in the middle of the alkane backbone (the latter of which had lower yields). This result agrees with Carrasquillo et al. (2014)\textsuperscript{[78]} who found that SOA yields of branched alkoxy radicals varied little with relative position of methyl branch and oxygen radical. In comparison to Aumont et al. (2013)\textsuperscript{[79]} and the explicit GECKO-A mechanism, our results are in agreement in that the difference in yields between singly and doubly branched alkanes is minimal and the methyl branch position does not contribute significantly to final SOA composition; however they posit a vicinal effect whereby SOA is dramatically reduced from precursors containing methyl branches adjacent along the carbon backbone. The fragmentation rate should be enhanced in these precursors leading to lower SOA formation. This effect was not considered in our more simplified mechanism and so is not observed here.

Tkacik et al. (2012)\textsuperscript{[41]} found experimentally that SOA yields did depend on methyl branch position amongst B1 isomers. They compared $N_C = 12$ and 14 branched and linear alkanes and found a larger disparity in yields between 7-methyltridecane and modelled $n$-tetradecane as compared to 2-methylundecane and $n$-dodecane. They cited differences in volatilities of fragmentation products. As fragmentation occurs most readily at the tertiary carbon position, the 7-methyltridecane was thought to form two fragments of relatively equal but moderate volatility while the 2-methylundecane was thought to only lose up to 3 carbons upon fragmenting and still have enough mass to partition to the condensed
phase. In repeating this procedure with our model we found similar trends in yields but a smaller difference between $N_C = 14$ isomer yields (difference of 4\% as compared to 28\% in Tkacik et al. (2012)). \cite{41}

We hypothesize that at lower $N_C$, any fragmentation will substantially preclude SOA formation as both products formed are too volatile to partition into the particle phase. As carbon number increases there may exist some threshold volatility whereupon the loss of 3 carbon atoms does not preclude particle formation of the larger fragment, but fragmentation at the centre of this alkane forms two fragments of intermediate volatility, both of which are still too volatile to form particle. Within this volatility region branching position may be important to aerosol formation. For most of the carbon numbers relevant to diesel fuel, modelled SOA formation is not sensitive to branching position.

4.3.3 Modelled SOA formation from diesel fuel

The VBS framework is often used to model complex mixtures and their evolution by grouping compounds by volatility (saturation concentration, $c^*$). \cite{50} Initial gas-phase precursors undergo oxidation and decrease in volatility and ultimately partition to the particle phase. Jathar et al. (2014) \cite{56} recently modelled UCM oxidation for a range of fuels including several diesel fuel samples. They found that accounting for molecular size ($N_C$) and structure (cyclic, linear, or branched alkanes) was critical in accurately predicting the SOA formation of these mixtures. Here we compare the evolution in volatilities in our explicit framework with detailed molecular structures to those in current implementations which make assumptions about rates of evolution without detailed UCM composition. \cite{80,81,82,83}

Figure 4.7 shows the evolution in volatility distributions from diesel fuel. Here species were lumped based on similarities in SOA yields shown previously. For each carbon number, the branched alkanes were lumped into a single species, and $N_{DBE} \geq 2$ were lumped into $N_{DBE} = 1$. The composition of diesel fuel speciated by SMB was used to define the starting mixture for this base case simulation. From our explicit model, the decrease in median volatility from the diesel mixture is 1.03 bins per hour over 3 hours, which is a relevant urban oxidation timescale, \cite{84} but is 1.25 bins per hour for the first two hours.

For comparison, current VBS implementations use a rate of decrease of 1 bin per oxidation step, with an average OH rate constant of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. \cite{81} This translates to 1.4 bins per hour decrease in volatility under the conditions in Fig. 4.7. Also O:C increased from 0 to 0.40 after three generations of oxidation, and the total organic mass (gas + particle) increased by 23\% as a result of nitrogen and oxygen addition to the carbon backbone. The two approaches therefore show a strong agreement in the initial rate of functionalization, but diverge after two hours of oxidation which we attribute to limitations
in our oxidation mechanism. Shown in Fig. 4.1 and 4.3, a large fraction of the mass proceeds via the
isomerization route to form UR36, UR40 and UR43, which are assumed to be unreactive owing to the
lack of further understanding. Functionalization is therefore assumed to stop under this assumption.
Future work should study the fate of these compounds. Alternatively, generated mechanisms such as
those from GECKO-A, can be informative for further oxidation steps.

We also performed sensitivity analysis by varying the composition and the fragmentation rate constant
(branching ratio for the peroxy radical) in the modelled mechanism. Fig. 4.7 shows the change in
rate of functionalization as a result of increasing the fraction of branched alkanes or cyclic alkanes by
a factor of 10 (to increase and decrease fragmentation), or increasing $k_{\text{frag}}$ by a factor of 10 or 100
(to increase fragmentation and make it more competitive with isomerization). The rate of decrease in
log-median saturation concentration was mostly unaffected and these changes are insufficient to explain
the agreement between our explicit model and current VBS implementations. Therefore, based on the
rate of functionalization modelled detailed composition and oxidation mechanisms is consistent with
currently assumed VBS parameters, and is largely insensitive to changes in composition. Similar results
were found in Jathar et al. (2013)^{85} for diesel fuels. SOA yields for complex mixtures of low-volatility
alkanes were deemed less sensitive to changes in bulk mixture molecular structure than in more volatile
complex mixtures (gasoline). We simulated their study of SOA formation from diesel fuel. They found
an average O:C ratio of 0.23 over a range of experiments using an average OH exposure of $1.80 \times 10^7$
molecules cm$^{-3}$ hr while our model simulated 0.29 under the same conditions.

$$k_{OH} = [(N_C \times a) + b] \times c$$

(4.3)
### 4.4 Figures and Tables

Table 4.1: Oxidation rate constant values a, b, and c, used to calculate $k_{OH}$ for ALKH, AP11, and AP12 oxidation using Eq. 4.3 and structure activity relationships via factors $F(CH_3) = 1.00,$ $F(CH_2) = F(CH) = F(C) = 1.23,$ $F(NO_2) = 0.04.$

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Table 4.2: First order rate constants for alkoxy radical fragmentation ($k_{\text{frag}}$), carbonyl formation ($k_{\text{carb}}$), and radical isomerization ($k_{\text{isom}}$). $k_{\text{carb}}$ and $k_{\text{isom}}$ were treated as constant, (0.05 × 10$^6$ s$^{-1}$ and 3.3 × 10$^6$ s$^{-1}$, respectively).\cite{39,46,74} Using $k_{\text{prim}} = 1.36 \times 10^{-13}$ s$^{-1}$, $k_{\text{sec}} = 9.34 \times 10^{-13}$ s$^{-1}$, and $k_{\text{tert}} = 1.94 \times 10^{-12}$ s$^{-1}$, weights were calculated ($w_{\text{prim}} = 0.04$, $w_{\text{sec}} = 0.31$, $w_{\text{tert}} = 0.65$) of for rate constants 1.3×10$^3$ s$^{-1}$, 2.5×10$^2$ s$^{-1}$, 4.7×10$^4$ s$^{-1}$, and 1.6×10$^6$ s$^{-1}$ based on number of carbon atoms of the given substitution.\cite{43,44,72} For N$_{\text{DBE}}$ = 1, species were given two rate constants for ring opening and subsequent reaction steps where the second rate constant was equal to that of B1 or B2 alkanes for mono- or higher substituted cyclics, respectively.

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<td>3.3</td>
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</table>
In total, eighteen products are considered for linear (as shown) and branched alkanes while an additional twenty-eight are ascribed to cyclic alkanes (Fig. 4.2). Only terminal products are shown for AP11 and AP12 series. Fragmentation of alkoxy radical is shown for the five precursor groupings: linear, singly branched, doubly branched, mono-substituted cyclic, and highly substituted cyclic. Cyclic precursors may undergo one instance of fragmentation with no reduction in carbon number. NO reaction branching ratios are 0.3:0.7, 0.15:0.85, and 0.1:0.9 for first, second, and third generation products of nitrate formation to alkoxy radical formation, respectively.
Figure 4.2: Product list for ALKH, AP11, and AP12 series, eighteen products are considered for saturated alkanes ($N_{DBE} = 0$, Jordan et al. (2008)[54]), while an additional twenty-eight are afforded to cyclic species ($N_{DBE} = 1$, via FRAG suffix) given their potential to ring open and continue reacting. 'FRAG' refers to a fragmentation pathway while 'CARB' refers to carbonyl formation (treated as terminating chemistry).
Figure 4.3: Product fractions of organic species for simulated oxidation of 5 ppb \(n\)-decane and \(n\)-butylcyclohexane. Total gas and particle and particle-only formation represented. \([\text{OH}] = 1 \times 10^7\) molecules cm\(^{-3}\), \(M_o = 10\ \mu g\ m^{-3}\), \(T = 298\) K, \(t = 3\) hr, under high NO\(_x\) conditions. Isomerization pathways leading to terminal UR36, UR40 and UR43 dominated over fragmentation and carbonyl formation routes for ALKH, AP11 and AP12 series respectively.
Figure 4.4: SOA yield comparisons between individual organic precursors from previous smog chamber studies\textsuperscript{[41,76,77]} and our model adapted from Jordan et al.\textsuperscript{[54]} Hashed black lines represent slopes of two, one, and one-half. Linear $n$-alkanes are represented as triangles, branched alkanes as squares, and cyclic alkanes as circles. Loza et al.\textsuperscript{[77]} results reported as ranges.
<table>
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<th>Carbon Number</th>
<th>SOA Yield</th>
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<tr>
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<td>9</td>
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<td>0.8</td>
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<tr>
<td>16</td>
<td>0.9</td>
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</table>

**Figure 4.5:** Comparison of linear $n$-alkane secondary organic aerosol yields across carbon numbers from Lim and Ziemann $^{[39,70]}$ to modelled results for experimental conditions using our model based on Jordan et al. $^{[54]}$. Our modelled results also over-predict SOA formation despite using more explicit rate constants from SAR methods for fragmentation and isomerization steps.
Figure 4.6: Individual precursor yields of five alkane groups considered from C₈-C₁₇. [Alkane] = 5 ppb, [OH] = 1 × 10⁷ molecules cm⁻³, M₀ = 10 μg m⁻³, T = 298 K, t = 3 hr, simulated high NOₓ conditions. Change of B1 methyl branch position showed almost no effect on SOA formation (green squares overlapping orange circles). B2 species formed almost identical amounts of SOA as singly branched alkanes regardless of branching position (only 2,4-dimethyl isomers shown for this reason). Greater substitution on N_DBEX = 1 rings led to more ring opening fragmentation and enhanced SOA formation in comparison to mono-substituted rings.
Figure 4.7: VBS distribution over 3 hours of oxidation of 5 ppb diesel fuel, \([\text{OH}] = 1 \times 10^7 \text{ molecules cm}^{-3}, M_o = 10 \mu\text{g m}^{-3}, T = 298 \text{ K}, \) simulated high NO\(_x\) conditions. Reduction in log-median \(c^*\) indicated by curved black line. Other lines indicate median reduction in volatility under various scenarios: a tenfold increase in unsaturated alkanes (red), a tenfold increase in saturated branched alkanes (blue), a ten and one-hundredfold increase in fragmentation rate constant (pink and amber), and a rate of \(-1.4 \text{ bins per hour used in previous studies (green), (Robinson et al. (2007), Pye and Seinfeld (2010), Grieshop et al. (2009)). Colour scale indicates mass loading of each volatility bin. The rate of change in log-medians saturation concentration was } -1.03 \pm 0.06 \text{ bins per hour, for diesel fuel. Deviation from literature expectations after two hours was attributed to mechanistic limitations.}
Chapter 5

Conclusions

Sampling VOCs remains an active area of research as it provides means to gain a better understanding of the changing global climate. Proper collection and segregation is vital as these VOCs react and partition between the gas and particle phases. Sampling apparatus such as the IOGAPS provide an exciting direction in their capacity to sample large volumes of air and isolate gas-phase and aerosol-based compounds. Ultimately it appears the IOGAPS denuders are capable of effectively transmitting aerosol with an efficiency of nearly 100% based on particle size. Sampling flow rates appeared to have little consequence on the aerosol size distribution but fewer particles were detected at higher flow rates needed for upstream PM cut-off. Particles with $D_p \leq 100$ nm were lost due to diffusion in a laminar flow regime, their minor contribution to mass losses ranged acceptably between 0 – 20%. Standard collection of the denuders was more effective for more volatile VOCs and appeared to depend on compound adsorption affinity indicating compositional knowledge of collected UCMs would be required for quantifying VOCs in the atmosphere.

Recent years have seen significant progress in the ability to separate, identify and quantify organic compounds in complex environmental mixtures. Chromatographic separation combined with soft ionization is one of the most applicable approaches for source characterization in atmospheric chemistry. Here detailed speciation of previously unresolved emissions was achieved using a novel technique in soft-ionization GC/MS. Because GC/MS with Cold EI results in a strong molecular ion signal while simultaneously producing informative fragments, we are able to provide molecular details, such as branching position, ring structure, and degree of substitution on rings, which has not been possible previously. Exact chemical structures were elucidated and quantified for input into a box kinetic model and allowed treating...
subsequent chemistry with specific chemical structures in mind.

With such information we are now able to determine which molecular details are important for SOA formation such that they can be prioritized in chemical models. Results showed that the most important factors in determining SOA yields are carbon number, presence or absence of a ring moiety, and degree of ring substitution whereas precise knowledge of structural non-neighbouring branching positions, extent of branching, or degrees of unsaturation greater than one, may be of secondary importance.

While explicit modelling of SOA formation, and elucidation of exact chemical structures is computationally expensive for air quality models, it provides important information for bulk binned methods such as the VBS framework. The explicit modelling of SOA formation with detailed composition and mechanisms showed a rate of volatility decrease that is in agreement with current VBS implementations. Future work should continue to use detailed source characterization and explicit modelling to constrain these important parameters used in simplified frameworks. The modelled rate of functionalization appears to be insensitive to molecular composition of the mixture, but the lack of understanding in oxidation mechanisms of bulk organic mixtures limits the ability to accurately predict further ageing of products. Future laboratory studies should focus on elucidating the rates and products of later oxidation steps while maintaining knowledge of bulk precursor composition.
Bibliography


