New Portable Flow Tube Technique to Investigate the Formation and Aging of Secondary Organic Aerosol

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Abstract

A new portable flow tube technique, the Toronto Photo-Oxidation Tube v2.0 was developed and characterized to explore its potential to control and monitor the OH-initiated formation and chemical aging of secondary organic aerosol (SOA) in-situ. The first study investigated the different operational parameters of this flow tube technique. TPOT v2.0 can generate oxidizing conditions equivalent to ambient OH exposures of 2.3 – 10.8 days. The transmission efficiency of a model organic aerosol indicated negligible losses in the oxidation tube. Differences in the residence time distribution curves measured for a gas and model organic aerosol showed that particles were subjected to approximately half of the OH exposure compared to gases.

The second study examined the capacity of the TPOT technique to generate secondary aerosols due to OH oxidation. High aerosol yield was observed for H$_2$SO$_4$ particles, whereas a low aerosol yield was observed for α-pinene SOA.
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CHAPTER 1: INTRODUCTION

1 Formation and Chemical Aging of Secondary Organic Aerosol (SOA)

1.1 Motivation

An aerosol is a suspension of solid or liquid in a gas. However, this elementary description shadows the variability in chemical compositions, sizes, and concentrations of atmospheric aerosol, both spatially and temporally. Particle sizes range from $10^{-9}$ to $10^{-5}$ m in diameter and mass concentrations can range from $10^{-2}$ to $10^4$ mg m$^{-3}$. Atmospheric aerosol comprises of mainly inorganic (e.g. sulfate, nitrate), carbonaceous matter (organic matter and elemental carbon/soot), and water. Organic species are ubiquitous in the atmosphere as they constitute more than 20 – 90% of aerosol by mass. In this text, the term atmospheric “organic aerosol (OA)” refers to the organic fraction of the total aerosol mass.

Atmospheric aerosol plays an important role in the environment. They affect climate directly by scattering and absorbing incoming solar radiation, thereby changing the radiative balance of the Earth. They affect climate indirectly by acting as cloud condensation nuclei (CCN) and ice nuclei (IN). This indirect effect on radiative forcing is one of the largest uncertainties in climate models, restricting the ability to accurately predict climate change. Atmospheric aerosol also has an important impact on human health as exposure to aerosol has been linked to respiratory and cardiovascular illnesses. Despite the importance of aerosol on climate forcing and human health, there is a lack of understanding on the mechanisms of formation and aging processes. These processes affect aerosol composition and ultimately, their properties. In fact, in addition to size,
chemical properties of aerosol are the key influences on the health and climate implications as mentioned above. Driven by the need to better predict the impacts of aerosol, the formation and chemical aging of organic aerosol and how these processes change their properties need to be better studied.

1.2 Formation and Aging Processes of SOA.

Organic aerosol (OA) components include primary organic aerosol (POA) and secondary organic aerosol (SOA), in which the latter constitute a large fraction of the total organic aerosol mass. POA are directly emitted into the atmosphere while SOA are formed from the oxidation of volatile organic compounds (VOCs) where oxidation products of sufficiently low volatility will partition to the condensed phase. In addition, SOA are subjected to other physical and chemical transformations, such as heterogeneous oxidation, condensed-phase reactions, and evaporation - altering their chemical composition and properties. Near source regions, the formation of SOA dominates; however, as an air mass travels away from its source, SOA aging processes start to play a significant role in changing the chemical composition of SOA. In the atmosphere, many organic carbon-containing molecules are of a semi-volatile nature, which indicates that they are present in significant concentrations in both gas and condensed-phase. As a result, changes in the composition in one phase will lead to a corresponding change in the other phase. In fact, the chemical composition of SOA is subject to continual changes due to the multiphase nature of the formation and aging processes. As such, it is important to understand these formation and aging processes of SOA individually but to note that these are intrinsically coupled processes.
1.2.1 Formation of SOA

Both biogenic and anthropogenic sources of VOCs can form SOA, however, biogenic VOCs (BVOC; e.g. monoterpenes) are thought to be the predominant source of SOA on the global scale, whereas anthropogenic VOCs (AVOC; e.g. aromatic carbons) are the dominant source of SOA in urban areas.\textsuperscript{5} SOA formation is initiated by the oxidation of gas phase precursors (see Figure 1.1). The vapour pressure of these oxidation products plays an important role in determining their potential to form SOA.

![Figure 1.1](image)

**Figure 1.1** A generalized illustration of the SOA formation pathway (adapted from Seinfeld & Pankow\textsuperscript{10}).

The gas phase oxidation of SOA precursors initiated by OH, O\textsubscript{3} and NO\textsubscript{3} is the primary process by which the volatility of organic molecules in the atmosphere changes. Shown in Figure 1.2, there are several key branching points in the oxidation mechanism that dictates the resulting volatility distribution of the oxidation products.\textsuperscript{8} These oxidation reactions result in the addition of one or more oxygenated polar functional groups that tend to make the products less volatile, favouring the partitioning to the condensed phase.
However, these reactions, along with photolysis, also lead to the fragmentation of the carbon backbone, resulting in an increase in volatility, increasing the likelihood for products to remain in the gas phase.\textsuperscript{8, 9} These oxidation products are of semi-volatile nature, thus, the formation of SOA is a competition of oxidation products between the partitioning to the condensed phase and further oxidation in the gas-phase.\textsuperscript{8-10}

As suggested above, the polarity of the added functional group and size of the oxidation products governs their potential to form SOA.\textsuperscript{11} In fact, a significant decrease in vapour pressure is resulted from the addition of hydroxyl, hydroperoxyl, nitrate, and acid functional groups. Therefore, the reaction pathways leading to the addition of these functional groups are the most important reactions to consider for SOA formation and aging.\textsuperscript{8}

\textbf{Figure 1.2} A simplified depiction of the oxidation mechanism of a VOC. The reactions that lead to a significant decrease in the volatility are denoted with thick black arrows, whereas reactions that lead to a significant increase in volatility are denoted with grey arrows. The reaction mechanism involving the oxidation by O\textsubscript{3} has been omitted for simplicity (adapted from Kroll & Seinfeld\textsuperscript{8}).
1.2.2 Heterogeneous Oxidation

Oxidation of organic aerosol can occur heterogeneously by gas phase oxidants (e.g. OH, NO$_3$, O$_3$). The mechanism of heterogeneous oxidation is likely similar to those for VOC oxidation (Figure 1.2), however, with differences in the branching ratios of the different reactions. The kinetic processes involved in heterogeneous oxidation can be summarized by the reactive uptake coefficient ($\gamma$), which describes the probability of a reaction following gas-surface collision. The overall reactive uptake coefficient is governed by several processes: i) the diffusion of the gas to the surface of the aerosol; ii) diffusion and solubility of solvated radical species in the particle bulk phase; iii) reaction on the surface; and iv) bulk phase reactions.

Reactive uptake coefficients of $\gamma \geq 0.1$ for OH have been measured experimentally for various model organic aerosol/surfaces by monitoring the decay of condensed phase species as a function of radical exposure. Some studies have observed $\gamma \geq 1$, where the derived reaction uptake coefficient is greater than unity due to the secondary chemistry driven by radical uptake. Collectively, these experimental observations indicate that the reactive uptake of radicals is highly efficient.

Heterogeneous oxidation may add oxygenated functional groups to the condensed phase species or may lead to their decomposition and volatilization. Using squalane as a model organic species, Kroll et al. observed an increase in oxygen content (O:C ratio) at low OH oxidation whilst a decrease in the amount of carbon was observed at high OH oxidation - suggesting that functionalization is the dominant reaction pathway for less oxidized organic species, and fragmentation for more oxidized organic species. Therefore, both functionalization and fragmentation increase the O:C ratio of SOA. Since the dissociation of alkoxy radical intermediates is the only known reaction that can lead to fragmentation and
the formation of small, volatile species, this study, amongst others, suggests that the fate of alkoxy radicals is important in the evolution of SOA due to heterogeneous oxidation.\textsuperscript{18, 19}

Given the high oxidizing capacity of the atmosphere and the efficiency of heterogeneous oxidation of organic aerosol, this aging mechanism has the potential to lead to a large change in the chemical composition, and hence, properties of SOA.

### 1.2.3 Condensed-Phase Reactions

The atmospheric oxidation mechanism of a VOC shown in Figure 1.2 indicates that low volatility products such as peroxides and nitrates form. However, high molecular weight (MW) chemical species such as HULIS (humic like substances) and oligomers have been detected in ambient aerosol.\textsuperscript{10} Reactions in the gas-phase are unlikely to lead to the formation of these species, suggesting reactions in the condensed-phase are important to consider for the chemical aging of SOA.\textsuperscript{8}

![Figure 1.3 Reaction pathways that can lead to the formation of oligomers and other high MW species found in SOA (adapted from Halliqust et al.\textsuperscript{10}).](image)
Oligomers and high MW species in SOA are likely formed by non-oxidative association reactions, also known as accretion reactions (Figure 1.3). Dimerization reactions between organic species of 6-8 carbon atoms can lead to a decrease of two-orders of magnitude for vapour pressure.\textsuperscript{8}

The importance of aqueous-phase oxidation for SOA formation and aging has been investigated in numerous studies as water constitutes a large volume in which chemical processing can occur in the atmosphere. This work has shown that aqueous phase processing of water soluble organic compounds yields products that are highly oxidized and of low volatility.\textsuperscript{10, 20, 21} The formation of carboxylic acids and other small diacids has been observed for the aqueous OH-initiated oxidation of various organic compounds.\textsuperscript{10} Particle acidity has also been observed to enhance SOA formation, suggesting the importance of acid-catalyzed condensed-phase reactions. These reactions include (hemi)acetal formation, aldol condensation and hydration.\textsuperscript{22} Formation of low-volatility products via oligomerization, acid-catalyzed and OH-initiated reactions changes the chemical makeup of the condensed-phase. As discussed in section 1.2.3, changes in the chemical composition of the condensed-phase affect the uptake of semi-volatile compounds, thereby affecting SOA formation and aging.\textsuperscript{8}

1.2.4 Gas Phase Oxidation

During the chemical aging of a SOA, products that are of sufficiently high vapour pressure will partition into the gas phase from the condensed phase. However, once in the gas phase, they are subject to further gas phase oxidation that may generate products of sufficiently low vapour pressure to condense back onto the particle. The SOA formation pathway and the chemical aging due to gas phase oxidation are analogous processes. SOA is formed from the partitioning of low-volatility oxidation products to the condensed phase.
However, chamber studies have shown that the oxygenated component of SOA does not reach values representative of aged aerosol in the atmosphere. On the other hand, SOA is aged by the condensation of semi-volatile organic compounds that have repartitioned back into the gas phase and have been further oxidized, thereby increasing the O:C ratio.

1.3 Experimental Methods to Study SOA Formation and Chemical Aging

1.3.1 Techniques to Study SOA Formation and Aging

The immense range of chemical species that are detected in SOA makes it difficult to properly characterize the processes leading to aerosol formation and aging. Smog chambers have been used in the past two decades to develop a mechanistic understanding of these processes by simulating atmospheric conditions. More recently, flow tube reactors have been used to study atmospheric aerosol chemistry. Neither technique provides ideal simulation of the atmosphere, however, the use of smog chambers and flow tube reactors to study SOA formation and aging are complementary to one another. Other techniques to study the formation and aging of SOA have also been employed, such as the oxidation or photolysis of organic aerosol collected on filter samples. However, this type of approach does not allow the investigation of these aging processes on suspended particles – therefore not reflective of the ambient gas-particle collision frequencies, unlike smog chambers and flow tube techniques. The following is a brief overview of these two techniques in which their application to study SOA formation and aging will be explored and evaluated. Analytical techniques to measure the chemical composition of SOA will be briefly discussed as well.
1.3.1.1 Smog Chambers

As mentioned previously, smog chambers have been traditionally used to study SOA formation and aging processes. There are outdoor and indoor smog chambers, however, only indoor chambers will be discussed in this text. These stationary chambers are of large volumes (0.01 - 90 m$^3$), and they can be operated in batch or continuous flow mode, which provides aerosol residence times of hours to a day. The large volume of chambers increases the volume-to-surface-area ratios (V/S) that range from 0.5 to 4.0 m, in order to minimize wall effects, such as loss of gas-phase species and deposition of particles onto the walls. Teflon® films are used for the walls of these chambers, which leads to electrostatic wall losses of charged particles. Broad spectrum artificial light sources, placed outside the chamber, are usually used to simulate the actinic spectrum, even though the relative intensities and wavelengths may not be fully representative of natural sunlight. Typical oxidant concentrations for chambers are similar to those in the atmosphere, with ozone concentrations up to hundreds of ppb and OH in the $10^6$ - $10^7$ molecules cm$^{-3}$ range. While the average lifetime of tropospheric aerosol is approximately one week, ambient oxidant exposures up to several days can be attained in a smog chamber, as the level of oxidant exposure is limited by particle residence time.

1.3.1.2 Flow Tube Reactors

While not as commonly used, flow tube reactors employed to study organic aerosol are of small volume, typically in the range of 0.001 – 0.02 m$^3$ with residence times of several minutes. The smaller volume-to-surface-area ratios of flow tube reactors range from 0.01 to 0.035 m, which suggest that significant wall effects may be present. Flow tube reactors are generally made of Pyrex®, which allows electrostatic built-up, leading to wall losses of charged particles. In addition, semi-volatile gases more frequently encounter the
wall than in a chamber. Mercury lamps, placed inside the reactors, have been used to generate light in the UV region that leads to the formation of the oxidant of interest but other light sources are possible. High concentrations of oxidants can be generated, with ozone concentrations up to 40 ppm and OH concentrations up to $10^{10}$ molecules cm$^{-3}$. Short residence times and high oxidant concentrations result in high oxidant exposure, where atmospheric processing of up to two weeks is attainable. This results in accelerated chemical and physical processing compared to the rate at which it occurs in the atmosphere. Besides the ability to attain higher oxidant exposures compared to chambers, the use of flow tube reactors is advantageous due to their portability, rendering their use in the field plausible.

1.3.2 Chemical Analysis of SOA

The chemical makeup of SOA is complex, due to a large number of factors, such as (but not limited to): variations in sources, phase, and reactivity - both temporally and spatially. This complexity renders the complete characterization of the chemical composition of SOA practically impossible. Nonetheless, recently developments in analytical techniques have permitted advances in our scientific understanding of SOA. The following is a brief overview of the online instrumentation and techniques used to characterize the chemical composition of SOA.

Given the variability in mass loading and chemical composition of ambient SOA, mass spectrometry (MS) is a useful analytical technique to characterize atmospheric aerosol in real time. Aerosol mass spectrometers have the ability to quantify both organic and inorganic aerosol components with low detection limits, high sensitivities and high time resolution.
Single particle mass spectrometers, such as the TSI Aerosol Time of Flight Mass Spectrometer (ATOFMS) and Single Particle Analysis and Sizing System (SPASS) provide real time qualitative information of both the inorganic and organic components of particles. The use of a laser to both vapourize and ionize single particles allows the measurement of refractory compounds (e.g. soot, metals, and minerals). The biggest advantage of single particle mass spectrometers is their ability to probe mixing states of aerosol directly, while other online measurement techniques can only do this indirectly, or to a limited degree.\textsuperscript{28, 29} However, the major limitation of this technique is that the instrument response is species-dependent due to matrix effects which affect the resulting mass spectrum in ways that are difficult to calibrate or account for.\textsuperscript{28}

On the other hand, aerosol mass spectrometers (AMS) provide quantitative information about the particle ensemble. Commercially developed by Aerodyne Inc., AMS provides size-resolved mass spectra of the non-refractory components (chemical components that vapourize at temperatures $\leq 600^\circ$C) of fine mode aerosol, with fast time resolution. Particle size information is obtained using particle flight times through the sizing chamber. Thermal desorption and electron impact (70eV electrons) are employed to vapourize and ionize particles, respectively, followed by detection using either a quadrupole or time-of-flight mass spectrometer.\textsuperscript{30} Later developments of this instrument have allowed for chemical speciation of single particles, and determination of the elemental composition of particles.\textsuperscript{30} However, the use of EI means that information regarding the parent species is lost due to extensive fragmentation. Moreover, information regarding the functionality of the organic components is qualitative, and apportioning sources is best done using factor analysis of the time series of the electron impact mass spectrum.\textsuperscript{29}
1.4 Overview of SOA Studies

Given the ubiquitous nature of SOA and its health and climate implications, understanding SOA formation and transformation processes, as well as properties is important in order to adequately predict its overall impact. Global climate models have significantly underpredicted the amount of SOA that has been measured in the atmosphere.\(^3\) In fact, the disparity between the amount of SOA measured and modeled increases significantly with photochemical age, indicating a need to further study the fundamental processes governing SOA formation and chemical aging, both in a laboratory setting as well as field measurements, in order to reduce the involved uncertainties.\(^{34-39}\)

1.4.1 Field Observations

The widespread use of the Aerodyne AMS, coupled with factor analysis, has provided quantitative information on the chemical composition of ambient aerosol around the world. Regardless of location, SOA dominated the overall organic fraction of ambient aerosol.\(^{11}\) In addition, SOA can be further described by their level of oxygenation as well as their volatility and/or source: LV-OOA (low volatility oxygenated organic aerosol), SV-OOA (semi-volatile OOA), BBOA (biomass burning OA), and HOA (hydrocarbon-like OA). SV-OOA and LV-OOA are determined by the mass fraction of AMS mass spectra fragments to total organic species, where \(m/z\) 44 arises from the \(\text{CO}_2^+\) ion, and \(m/z\) 43 from the \(\text{C}_3\text{H}_7^+\) and \(\text{C}_2\text{H}_5\text{O}^+\) ions.\(^{31}\) An increase in the fraction of 44 (f44) is indicative of atmospheric aging, rendering this a useful approach to separate SV-OOA and LV-OOA.

At Mexico City in 2003, as part of the MILAGRO field campaign, aircraft measurements of OA were taken downwind of the city – to examine changes in chemical composition due to aging (see Figure 4).\(^{11}\) A few key observations are illustrated in this figure:
1) a decrease (from T0→T1), then stable (T1→T2) OA mass concentration

2) rapid increase in oxygen-to-carbon (O:C) ratio of OA from T0→T1, slow increase from T1→T2

3) increasing mass fraction of LV-OOA

4) oxygenated organic aerosol (OOA) constitutes a large fraction of the total organic mass

These observations suggest that there is no net SOA formation once the air mass has travelled away from the source - indicated by a decrease in mass and an increasing O:C ratio. Moreover, the mass fraction of LV-OOA increases while SV-OOA decreases, suggesting a conversion of less oxygenated to more oxygenated species. Taken together, the observations indicate chemical aging, in particular, the gas-phase oxidation aging mechanism, dominates the chemical evolution of SOA once the air mass moved away from the source.

Shown in Figure 1.5 Ng et al. summarized the chemical composition of ambient aerosol from 43 field campaigns using the f44 to f43 approached mentioned earlier. It can be seen that LV-OOA is most dominant OOA form, indicating ambient aerosol was highly oxygenated.
Figure 1.4 Chemical aging of OA above the city (T0), and downwind sites (T1, T2), which corresponds to 0, 3, and 6 hours from the urban area. ΔCO accounts for dilution of air mass during transport (adapted from Jimenez et al.\textsuperscript{11}).

Figure 1.5 AMS dataset of 43 field measurements (includes urban, urban downwind, and rural locations), illustrating the chemical composition of ambient aerosol. The black dotted lines define the triangular area of which most of these ambient data lie. The plot can be
qualitatively divided into two, indicated by the solid grey line, to show the range of f44 vs. f43 that corresponds to LV-OOA and SV-OOA (adapted from Ng et al. 31).

1.4.2 Laboratory Investigations

Most studies examining SOA formation processes have used smog chambers, until more recently, flow tube reactors were employed. In general, laboratory studies examine the SOA formation and aging processes using individual precursors to understand their relative contributions in regional and global SOA budgets. For SOA formation, a mass balance approach is used where SOA formation is expressed as a yield (Equation 1.1):\[ Y_{SOA} = \frac{\Delta M_{OA}}{\Delta M_{HC}} = \sum_i \frac{\alpha_i}{1 + \frac{C_i}{C_{OA}}} \] where $\Delta M_{OA}$ is the mass of SOA produced; $\Delta M_{HC}$ is the mass of the precursor gas reacted; $\alpha_i$ is the mass-based stoichiometric yield for a specific compound $i$; $C_i$ is the mass concentration of species $i$ in the gas phase; and $C_{OA}$ is the mass concentration of species $i$ in the particle phase. As expected, when most of species $i$ exist in the particle phase, the SOA yield should be the value of one. Equation 1.1 shows that the degree to which semi-volatile oxidation products partition into the particle phase depends on the amount of particle mass present. The greater the amount of particulate matter, the greater the likelihood for a given oxidation product to condense onto the particle phase. Similarly, a critical concentration of semi-volatile products in the gas phase needs to be generated before nucleation can occur. These thermodynamic and kinetic processes lead to the observation of an induction period for a typical SOA formation experiment where the oxidation of SOA precursors needs to proceed for a certain period of time before particle formation can be observed. Moreover, SOA yield is observed to be dependent on initial precursor concentration. Other reasons for the wide disparity of yields reported for a single precursor include different chemistry based on the oxidants used, different wall effects, and whether or not a seed aerosol is
Therefore, a range of SOA yields for the same precursor is reported amongst smog chamber studies. An even larger discrepancy is observed when comparing SOA yields between those obtained using smog chambers and flow tube reactors.

While a yield is an important parameter to describe the SOA formation ability for specific precursors, the relative changes in chemical composition provide information on the chemical aging of SOA. The chemical composition of laboratory generated SOA is summarized in Figure 1.6. It can be seen in this figure that the chemical composition of biogenic SOA generated in smog chambers is different than SOA generated in flow tube reactors, and to a smaller extent, for anthropogenic SOA. A larger range of f44 and f43 values was observed in SOA generated in flow tube reactors as well. However, it is important to note that differences in SOA yields and chemical composition observed in smog chambers and flow tube reactors can be attributed to the differences in their physical design and operational conditions. As mentioned in sections 1.3.1.1. and 1.3.1.2., it is important to study SOA formation and chemical aging processes using both complementary techniques to explore a range of parameters, to better understand the atmospheric processes. The specific differences in these processes will be described later in the thesis. Despite of this importance, there is still a paucity of laboratory SOA studies using flow tube reactors.
1.4.3 Connecting Field and Laboratory Measurements

In the previous section, an overview of the results obtained from laboratory studies of SOA formation and aging processes was provided. These results are ultimately used to simulate SOA formation and aging processes in climate models, therefore, it is important that laboratory data are representative of ambient measurements. By comparing the chemical composition of laboratory generated and ambient SOA (Figures 1.5 and 1.6) it can be seen that majority of laboratory data fall within the lower half of the triangular region (of

**Figure 1.6** Summary of the AMS dataset of 27 laboratory generated SOA from the oxidation of biogenic and anthropogenic precursors using various oxidants (25 data sets obtained using smog chambers, 2 using flow tube reactors). Similar to Figure 1.5, the black dotted lines and the solid grey line define the areas of where most of the ambient measurements lie as well as the separation of the OOA based on their volatility (adapted from Ng et al.\textsuperscript{31} and Kang et al.\textsuperscript{36}).
which ambient data falls). This indicates laboratory generated SOA is less oxidized than ambient SOA. Several reasons are proposed to address the discrepancy observed:

1) indicated by Equation 1.1, high mass loadings used in most laboratory studies will favour the partitioning of less oxidized species to the particle phase. Under atmospherically relevant mass loadings, these species will remain in the gas phase instead;\(^8,31\)

2) limited oxidant exposures for smog chambers limit the maximum degree of oxidation attainable;\(^31\) and

3) the chemical matrix of laboratory generated SOA is simple compared to the complexity of ambient SOA as only identified SOA precursors are studied in the laboratory.\(^12\)

More recently, Jimenez \textit{et al.} examined the chemical evolution of SOA, POA and BBOA in a smog chamber and compared the corresponding AMS mass spectra to the ambient LV-OOA measurements made during the MILAGRO campaign. In their study, they illustrated that as chemical aging proceeds, the chemical composition of laboratory OA becomes increasingly similar to ambient OOA, regardless of aerosol source.\(^11\) The ability to make the connection between laboratory studies and ambient measurements is vital as it allows the evaluation of the current understanding of the SOA formation and aging processes, as well as highlighting the areas in which further studies are required.

### 1.5 Research Objective

Connecting laboratory studies and ambient measurements is still at its infancy, and additional studies are needed to explore the chemical processes of SOA formation and aging. Motivated by the need to address the discrepancy discussed in section 1.4.3., a new portable flow tube technique, the Toronto Photo-Oxidation Tube (TPOT) has been developed and characterized, in order to explore its potential to control and monitor the OH-initiated formation and chemical aging of SOA \textit{in-situ}. The first objective of this research is to understand the different parameters of this flow tube reactor that can potentially affect the
SOA measurements, including its oxidative capacity, particle transmission efficiency, and the flow dynamics of particles and gases in the reactor. The second objective is to evaluate the capacity of this technique to generate secondary aerosol (including SOA) under ambient conditions. While applicable, the performances of the two versions of TPOT are compared throughout the study.

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CHAPTER TWO:
INSTRUMENTATION

2 Aerosol Reactor Flow Tube Techniques at University of Toronto

2.1 General Overview of Principles

An ideal flow tube reactor used to address the discrepancies observed between laboratory and ambient measurements of SOA formation and aging processes (as discussed in the previous chapter) should fulfill the following requirements:

1) ability to generate and control a range of oxidant concentration;
2) time spent in the reactor by each volume element (residence time) is well defined;
3) ability to generate SOA under ambient conditions;
4) field deployable due to ease in shipment and transport (physical size, and weight comparable to other commonly used field-deployable instrumentations); and
5) it should also be free of wall effects.

In practice, reactors normally do not meet all the requirements listed above. However, it is important to determine the limiting conditions of a reactor and understand the impact these limitations have on experimental observations. For the TPOT technique, the characterization experiments will be discussed in the next chapter. The following is a description of the two versions of the TPOT in terms of their major components along with their functions, and physical configurations.

2.2 Design of Flow Tube Techniques

TPOT version 1.0 was developed and previously used by Ingrid George at the University of Toronto to study OH-initiated heterogeneous oxidation of atmospheric organic
aerosol. However, several features of the existing technique (described in the following section) suggest that it may not be suitable to examine the SOA formation and gas-phase aging mechanism. TPOT version 2.0 was designed to address these limitations.

2.2.1 Toronto Photo-Oxidation Flow Tube (TPOT) version 1.0

![Figure 2.1](image)

Figure 2.1 Overall schematic of the Toronto Photo-Oxidation Tube version 1.0.

The main operation of the TPOT was to generate the oxidant in the confines of the reactor to initiate the chemical process of aerosol aging. In particular, oxidation due to OH is of interest as its relatively high ambient concentration, along with its high reactivity with other atmospheric constituents renders it the most important reactive species in the troposphere. In the reactor, OH production occurred as follows:

\[
\begin{align*}
\text{O}_3 & \xrightarrow{h\nu} \text{O}_2 + \text{O}^{(1\text{D})} & \quad \text{(R1)} \\
\text{H}_2\text{O} + \text{O}^{(1\text{D})} & \rightarrow 2 \text{OH} & \quad \text{(R2)}
\end{align*}
\]

For TPOT v1.0 (Figure 2.1), \( \text{O}_3 \) was generated by passing a gas flow of 500 sccm \( \text{N}_2 \) (BOC, 99.998%) and \( \text{O}_2 \) (5 - 22 sccm) (BOC, 99.994%) through an \( \text{O}_3 \) generator (Jelight model 1000). \( \text{O}_3 \) concentrations were monitored using an absorbance cell (\( l = 10\text{cm} \)) and photodiode setup (\( \lambda = 254\text{nm} \)). Following measurement, 200 sccm of this \( \text{O}_3/\text{O}_2/\text{N}_2 \) gas flow (remaining was removed) was further combined with 300 sccm of water vapour (\( \text{N}_2 \) gas through a water bubbler, 18Ω deionized water) and 1100 sccm of \( \text{N}_2 \) with the sample of
interest – to a total flow of 1600 sccm. To ensure proper mixing of the different gas species, this stream of gas flowed through a mixing tube (Pyrex®, volume: 0.5 L). After mixing, this flow was pulled through the oxidation tube (Pyrex®, volume: 1.0 L) and bypass tube (Pyrex®, volume: 0.9 L). The schematics of the mixing, oxidation, and bypass tubes are shown in Figure 2.2 A-C, with their specific dimensions. For the oxidation tube, an important parameter was its volume-to-surface area ratio, which indicates the impact wall effects may have on SOA formation and aging processes. For TPOT v1.0, the volume-to-surface-area ratio was approximately one, which suggested that wall effects may hinder the ability of the technique to investigate SOA formation and gas-phase aging processes.

Figure 2.2 Side view of the mixing tube (A), bypass tube (B), and oxidation tube (C). For the oxidation tube, the UV lamp is shown here in light blue, enclosed by the quartz housing. Directions of the gas flows through the flow tubes are indicated by the dotted arrows.

The humidified O₃ + sample flow introduced in the oxidation tube was then illuminated by a 22.9 cm Hg Pen-ray lamp (UVP) that was placed in the centre of the flow tube to generate OH. The UV lamp had a strong line at λ = 254 nm and was surrounded by a quartz tube that was purged with a flow of compressed air (13 slpm). The temperature inside the quartz housing was monitored using a thermocouple. OH concentrations were varied by changing the O₂ flow rate, consequently, the concentration of O₃. It is important to note that the outlet of the oxidation tube was orthogonal to the UV lamp.
Even though the total volume of the oxidation tube was 1.0L, the UV lamp did not illuminate the entire length of the tube, so of importance is the volume that is actually illuminated, where OH were generated (0.8 L). A manual 4-way valve (Swagelok) was placed downstream of the oxidation and bypass flow tube to allow rapid switching for the analysis of the OH-oxidized or O₃- oxidized flow. One of the flows was used for most measurements, in which the instrumentation was varied depending on the characterization experiment (to be discussed in Chapter 3). For the other flow, the relative humidity (RH%) was measured using a hygrometer (VWR) before removal.

2.2.2 Toronto Photo-Oxidation Flow Tube (TPOT) version 2.0

![Figure 2.3 Overall schematic of the Toronto Photo-Oxidation Tube version 2.0.](image)

TPOT v2.0 was developed to extend the TPOT's ability to study the OH-initiated SOA formation process, along with aging. Unless specified, the hardware components used for TPOT v2.0 were identical to those used in v1.0. The method of OH production for v2.0 is identical to v1.0, however, changes are made to allow the opportunity to easily conduct control experiments to examine other chemical processes that might be occurring in the reactor. A flow of 1250 sccm of N₂ and O₂ (≤ 2 sccm) was divided into two flows – one bypassing and the other passing through the O₃ generator. Two automated three-way valves (Swagelok), acting as a four-way valve, were used to alternate between the introduction of the O₃ flow to the flow tubes or O₃ monitor. The three-ways valves were controlled...
externally via a National Instrument USB-6229 DAQ device (using a Labview program written by Joel C. Corbin, based on an earlier version developed by the author). It is important to note that this program allowed the user to pre-define the period of time the valves spend in each duty cycle - an useful feature for remote field measurements.

880 sccm of the N₂/O₂ flow was sampled by the O₃ monitor (2B Technologies, Inc., Model 202) and the remainder was further combined with a flow of water vapour (600 - 850 sccm) and N₂ with the sample of interest (780-1030 sccm) – to a total flow of 2000 sccm. All the flows were controlled using Mass Flo® Controllers (MFC; MKS Instrument, Inc.), except for O₂, in which the flow was controlled using a needle valve, and monitored using a Mass Flo® Meter (MFM; MKS Instrument, Inc.).

To ensure proper mixing of the different gas species, this stream of gas flowed through a mixing tube (Pyrex®, volume: 0.9 L). After mixing, this flow was pulled through the oxidation tube (stainless steel, volume: 3.2 L) and bypass tube (stainless steel; volume: 3.2 L). The schematics of the mixing, oxidation, and bypass tubes are shown in Figure 2.3 A-C, with their specific dimensions. The volume-to-surface area ratio of the oxidation tube was increased from approximately one for v1.0 to approximately three for v2.0 – in order to minimize wall effects on SOA formation and aging processes. Even though the total volume of the oxidation tube was 3.2L, the UV lamp did not illuminate the entire length of the tube, so of importance was the volume that was actually illuminated, where OH were generated (2.6 L). To eliminate the need for compressed air to cool the UV lamp, a pump (23 slpm) was used to pull room air through the quartz housing (open on both ends). Along with the temperature measurement of the UV lamp, a photodiode (max responsivity at λ = 254 nm) was placed near one end of the quartz housing to monitor the UV output.
Figure 2.4 Side view of the mixing tube (A), bypass tube (B), and oxidation tube (C). For each of the bypass and oxidation tubes, a quartz tube that extends the entire length of the flow tube resided in the centre. The UV lamp is shown here in light blue, enclosed by the quartz housing for the oxidation tube only. The direction of gas flows are indicated by the dotted arrows.

Gas flows were introduced into the bypass and oxidation tube via four inlet/outlet ports (shown in Figure 2.4). This ensured the gas flows evenly around the quartz housing, and minimized dead volumes within the flow tubes. Restek Siltek®-treated electropolished tubing was used for the inlet/outlet sample lines (Chromatographic Specialties, Inc.). The inner diameter of this stainless steel tubing was chemically deactivated by a 100-250 nm coating of hydrogenated amorphous silicon material with bonded ethyl groups. Similarly, the inner walls of the bypass and oxidation flow tubes, as well as the fittings used for the injection ports, were coated with an identical material (SilcoTek™Corp.). This coating prevents the reaction of the walls with reactive gas-phase species that would otherwise participate in SOA formation and aging processes.
A manual 4-way valve (Swagelok) was placed downstream of the oxidation and bypass flow tube to allow rapid switching for the analysis of the sample subjected to different conditions. The resulting chemistry that occurs in the oxidation and bypass flow tubes was controlled by the following: the addition of O$_3$ into the flow tubes by the automatic 4-way valve (Table 2.1).

**Table 2.1** Oxidation conditions in each flow tube was dependent on the direction of the O$_3$ flow.

<table>
<thead>
<tr>
<th>Direction of O$_3$ Flow</th>
<th>Oxidation Tube</th>
<th>Bypass Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Tubes</td>
<td>OH</td>
<td>O$_3$</td>
</tr>
<tr>
<td>O$_3$ Monitor</td>
<td>$hv$ (photolysis)</td>
<td>null</td>
</tr>
</tbody>
</table>

One of the flows from either the bypass tube or the oxidation tube was used for analysis and the instrumentation was varied depending on the characterization experiment (discussed in Chapter 3), however, relative humidity was always measured (Vaisala HMP50).

**Figure 2.5** A) Front view of the end caps of both the bypass and oxidation flow tubes. The UV lamp quartz housing was inserted in the center hole, and the other four holes were the inlet/outlet ports of the flow tubes. B) Photo of an end cap with injection ports installed. One flow was divided into four flows for the inlets (shown in red), similarly, the four outlet flows were recombined to one flow for measurement using an end cap of the same geometry.
To allow the continuous recording of the various measurements made (e.g. RH%, O₃ mixing ratio, and UV lamp output) by the NI-DAQ device, a Labview program was written to record and monitor these parameters online.

2.2.3 Portable Photo-Oxidation Technique

For field deployment of this technique, both versions of TPOT along with all essential electronics, flow control boxes, power supplies, and data acquisition board (DAQ) were mounted on a 1.0 m x 0.62 m x 0.57 m steel frame with three levels (Figure 2.5). The entire system weights approximately 100kg, and can be easily packed for shipment for field measurements.

**Figure 2.6** A) Schematic of the steel frame; B to D) top views of each level of the frame, with the electronic and accessory components of the TPOT v2.0.
2.3 References


CHAPTER THREE: CHARACTERIZATION EXPERIMENTS

3 Performance Evaluation of the TPOT Flow Tube Reactors

Characterization experiments were conducted on the TPOT reactors (v1.0 and v2.0) to understand the different performance features that may affect SOA measurements, including their oxidative capacity, particle transmission efficiency, and the flow dynamics of particles and gases in the reactors. In addition, to evaluate the potential of the technique to examine SOA formation processes, the ability of the technique to generate secondary aerosol under ambient conditions was measured. The following is a detailed summary of these experiments.

Note: For TPOT v1.0, the characterization experiments were conducted as part of an Intercomparison study between two flow reactors (TPOT and the Potential Aerosol Mass, PAM reactor) over the course of two weeks during March 2010. For TPOT v2.0, the experiments were conducted at the University of Toronto during the fall of 2010. The main experimental procedure and method of analysis were identical for both sets of experiments. However, specific instrumentation and source of materials used were different at the two locations; for brevity and because the TPOT v2.0 design was implemented by the author, only the detailed experimental methods used for TPOT v2.0 will be discussed as follows. For TPOT v1.0, the specific information was discussed by Lambe et al. 2010.1

3.1 OH Quantification

Given the high reactivity of OH with most atmospheric constituents and its relative abundance, OH is the main oxidant in the atmosphere.2,3 In order to mechanistically study
the effects OH oxidation have on SOA formation and aging processes, the range of OH concentrations the TPOT technique can generate needs to be measured and parameterized. In particular, the OH exposure, which is the amount of time a sample is subjected to a specific steady state concentration of OH, is of interest. For the TPOT reactor, the OH exposure is the product of the steady state concentration of OH and the residence time of the oxidation flow tube. The oxidative capacity of the technique was measured by monitoring the decay of two different chemical species, sulfur dioxide (SO$_2$) and methyl-ethyl-ketone (MEK), due to OH oxidation.

### 3.1.1 Sulfur Dioxide (SO$_2$) Oxidation by OH

The reaction of SO$_2$ with OH has been studied extensively since the 1980’s due to its importance in the formation of acid rain where SO$_2$ reacts with OH to ultimately form H$_2$SO$_4$:

$$\text{SO}_2(g) + \text{OH} \rightarrow \ldots \rightarrow \text{H}_2\text{SO}_4(g)$$

(R1)

The OH exposure ([OH]t) can be calculated from the integrated rate equation (Equation 3.0) for R1 by monitoring the fraction of SO$_2$ reacted with OH:

$$[OH]t = (\ln \frac{[\text{SO}_2]_0}{[\text{SO}_2]_t}) / k$$

(3.0)

where the second-order rate constant ($k_{\text{SO}_2+\text{OH}}$) for R1 at 298K and 1 atm was $9.59 \times 10^{-13}$ molec$^{-1}$ cm$^3$ s$^{-1}$.

#### 3.1.1.1 Experimental Methods

A SO$_2$ gas bulb was made by delivering a small amount (approx. 7 torr) of anhydrous SO$_2$ gas (Matheson Gas Products, Inc.) into a 3435 cm$^3$ glass bulb under vacuum. This volume of SO$_2$ was diluted with N$_2$ gas until the fraction of SO$_2$ in the glass bulb was...
approximately 1.0 x 10^{-3} and the final pressure was above 1000 torr. The mixing ratio of the SO_2 (C_{SO_2}) delivered into the TPOT was calculated as follows (Eq. 3.2 and 3.3):\(^6\)

\[ \phi_{SO_2} = \frac{273 \ K}{T} \times \frac{V_{manifold}}{760 \ \text{torr}} \times \frac{\Delta P}{\Delta t} \times f \quad (3.2) \]

\[ C_{SO_2} = \frac{\phi_{SO_2}}{\phi_{total}} \quad (3.3) \]

where \( V_{manifold} \) was the volume of the manifold used to control gas delivery; \( \Delta P/\Delta t \) was the pressure drop in the manifold (torr per minute), \( f \) was the fraction of SO_2 in the bulb, \( \phi_{SO_2} \) was the flow rate of SO_2, and \( \phi_{total} \) was the total flow rate in the reactor. The SO_2 flow was combined with a dry N_2 flow of 800 sccm, a water-saturated N_2 flow of 800 sccm, and a N_2 flow containing O_3 of 400 sccm, to a total flow of 2000 sccm in the mixing tube. At a \( \Delta P/\Delta t \) of 1 torr/min, the final mixing ratio of SO_2 calculated using Eq. 3.2 and 3.3 was 14.2 ppb. The mixing ratio of SO_2 was changed by varying the \( \Delta P/\Delta t \) value (1.7 – 9.4 torr per min; 24 - 133 ppb).

The entire reactor system was passivated with SO_2 until a stable concentration was measured using a SO_2 monitor (Thermo Scientific, Model 43C). Control experiments were conducted to determine and account for: interferences with the SO_2 measurements due to O_3, H_2O; differences in the calculated and measured SO_2 concentrations; and differences in the SO_2 conditioning of the bypass and oxidation tube.

OH was generated using the same method as described in Chapter 2, section 2.2.2 for TPOT v2.0. OH exposure was calculated using Eq. 3.2 and 3.3 where the SO_2 concentration measured from the bypass tube was taken as \([SO_2]_0\) and measurement made from the oxidation tube as \([SO_2]_t\). An OH exposure calibration was conducted by varying the O_3 concentration from 206 – 1075 ppb (by varying O_2 flow into the O_3 generator) in the oxidation tube, hence the concentration of OH generated. Due to the dependence of OH
exposure on O₃ concentration, the resulting range of OH exposure was plotted as a function of the O₃ concentration.

3.1.1.2 Results and Discussion

The average OH exposure calibrations obtained from the reaction of SO₂ with OH for TPOT v1.0 and v2.0 are shown in Figure 3.1. It can be seen that both versions of TPOT were capable of attaining a similar range of OH exposures (approx. 3.0 x 10¹¹ – 1.4 x 10¹² molec cm⁻³ s). Assuming an average atmospheric OH concentration of 1.5 x 10⁶ molec cm⁻³, this range of OH exposures in the reactors was equivalent to 2.3 to 10.8 days of atmospheric OH oxidation.³ The typical atmospheric lifetime of particles is from several days to a week; therefore, these experimental OH exposures were atmospherically relevant.⁷

![Figure 3.1 OH exposure calibrations obtained from the oxidation of SO₂ with OH.](image)

**Figure 3.1** OH exposure calibrations obtained from the oxidation of SO₂ with OH. The average relative humidity in the reactors was: 28 ± 3 % (TPOT v1.0); 44 ± 2.3 % (TPOT v2.0). Error bars represent ± 1σ of the measured values.

The concentration of O₃ used in TPOT v1.0 was an order of magnitude higher compared to v2.0. This was due in part to the differences in residence time between the two reactors. Since v1.0 had a shorter residence time compared to v2.0, a higher steady state concentration of OH was required to attain similar levels of OH exposure. Other effects may
include a higher UV flux given that the inner walls of the v2.0 design were shiny metal, perhaps allowing for some reflection of light whereas the v1.0 had glass walls which allow for UV transmission. This was achieved by using a higher concentration of O$_3$ (the photolysis of O$_3$ generates O($^1$D), which reacts with water vapour to generate OH). O$_3$ was not only the source of OH, but it was also a sink – at high concentrations of O$_3$, it reacts with OH to form water vapour and O$_2$. This was observed in Figure 3.1 where the OH exposures reached a plateau at approximately 1.4 x 10$^{12}$ molec cm$^{-3}$ s.$^{-1}$

3.1.2 Methyl-Ethyl-Ketone (MEK) Oxidation by OH

An OH exposure calibration needs to be conducted routinely in order to accurately quantify the oxidative capacity of the reactor over a period of time. It is advantageous for a field technique, such as TPOT v2.0, to have the flexibility to conduct the OH exposure calibration in more than one manner. This was achieved by monitoring the decay of methyl-ethyl-ketone (MEK; C$_4$H$_8$O) due to reaction with OH using an Ionicon Proton-Transfer-Reaction Mass Spectrometry (PTR-MS), which is an online technique used to monitor volatile organic compounds.$^8$

3.1.2.1 Experimental Methods

The experimental conditions and methods used for the oxidation of MEK with OH were identical to the methods used for SO$_2$ oxidation (discussed in section 3.1.1.1). Instead, MEK was used instead of SO$_2$. MEK was supplied from a cylinder that was custom-ordered (Scott Specialty Gases) consisting of a 10 ppm concentration of MEK in N$_2$; the flow of MEK/N$_2$ was constant at 7.5 sccm (final mixing ratio of 100 ppb). The concentration of MEK was monitored using a PTR-MS (Ionicon), with a quadrupole mass analyzer. For the OH oxidation of MEK, a rate constant of ($k_{MEK+OH}$) = 1.2 x 10$^{-12}$ molec$^{-1}$ cm$^3$ s$^{-1}$ was used to calculate the OH exposure.$^9$
3.1.2.2 Results and Discussion

The average OH exposure calibration obtained from the reaction of MEK with OH for TPOT v2.0 is shown in Figure 3.2. The average OH exposure calibration obtained from the OH oxidation of SO$_2$ was included in the figure for comparison. The OH exposures calculated from the oxidation of MEK were in good agreement to those calculated using SO$_2$. This indicates that two different methods, using different instrumentation (SO$_2$ monitor and PTR-MS) can be performed to obtain an OH exposure calibration.

Figure 3.2 OH exposure calibration obtained from the oxidation of MEK with OH. The OH exposure calibration from the oxidation of SO$_2$ is included for comparison. The average relative humidity in the reactor was 42 ± 1.3 %. Error bars represent ± 1σ of the measured values.

3.1.3 Conclusions

By monitoring the decay of SO$_2$ due to its reaction with OH, it can be seen that the oxidative capacities of both versions of TPOT were similar. The range of OH exposures in the TPOT reactors was atmospherically relevant and specific OH exposure was easily selected for by changing the O$_3$ concentration. In addition, it was shown that the OH exposure calibration can be conducted using a two different chemical species (SO$_2$, MEK)
and measurement technique (SO$_2$ monitor, PTR-MS). Overall, this provides the flexibility to use either MEK or SO$_2$ (or both) to carry out an OH exposure calibration during field measurements, depending on instrumentation availability.

### 3.2 Behavior of Particles and Gases

Previously discussed in Chapter 1, section 1.4.2, laboratory studies on SOA formation are often reported as a SOA yield, which is the fraction of SOA produced divided by the amount of precursor gas reacted (Eq. 1.1). Experimental artifacts can affect the SOA yield measured such as size dependent particle transmission efficiency. Correction factors were determined in order to account for these artifacts.

For an ideal reactor (as mentioned in Chapter 2, section 2.1), all volume elements should have the same residence time distribution. In order to understand the SOA formation and aging processes in the TPOT reactor, it is critical to quantify the range of oxidation the gas and particle phase is subjected to. This range of oxidation was interpreted by obtaining the residence time distribution curves of SO$_2$ and BES particles, which were reflective of the distributions of OH exposure times they experienced.

#### 3.2.1 Bis(2-Ethylhexyl) Sebacate (BES) Particle Transmission

In any reactor (smog chambers and flow tubes), the mass of the aerosol measured may not be the actual mass formed in the chamber/flow tube since particle loss can occur following formation. There are four particle loss mechanisms: gravitational, electrostatic, diffusion, and thermophoretic losses. Each of these mechanisms will be discussed briefly below.

Particle deposition due to gravity is related to the terminal settling velocity, which is the net particle velocity when the drag force of air on the particle is exactly equal and
opposite to the force of gravity acting on the particle. The terminal settling velocity is proportional to the square of particle diameter.\textsuperscript{11}

All particles carry some net charge and can be acted upon by an electrostatic force near charged surfaces, which cause them to deposit onto the surface itself. The surfaces of reactors made out of insulating material, such as Teflon\textsuperscript{®} and Pyrex\textsuperscript{®}, allow charge build-up, leading to electrostatic wall losses of particles. On the other hand, reactors made out of conductive materials, such as stainless steel, have minimal electrostatic wall losses. For ambient particles, the average number of charges increases with particle size.\textsuperscript{11}

Particle diffusion is the net motion of particles down a concentration gradient, and it is proportional to particle size (Table 3.1). The smaller the particle, the closer its diffusion coefficient is to the gas diffusion coefficient of air (2.0 x 10\textsuperscript{-5} cm\textsuperscript{2}/s), indicating that these particles are more likely to follow the motion of air compared to larger molecules.\textsuperscript{11} Hence, small particles have a greater likelihood to diffuse close to a reactor’s wall and collide with the surface – leading to irreversible loss.

\textbf{Table 3.1} Effect of Particle Size on Diffusion Coefficient at 293K (adapted from Hinds 1999\textsuperscript{11})

<table>
<thead>
<tr>
<th>Particle Diameter (nm)</th>
<th>Diffusion Coefficient (cm\textsuperscript{2}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.4 x 10\textsuperscript{8}</td>
</tr>
<tr>
<td>100</td>
<td>6.9 x 10\textsuperscript{-10}</td>
</tr>
<tr>
<td>1000</td>
<td>2.7 x 10\textsuperscript{-11}</td>
</tr>
</tbody>
</table>

Due to the presence of an UV lamp in the TPOT reactor, a temperature gradient is established inside the oxidation tube, with the highest temperatures immediately next to the lamp, and lowest near the reactors’ walls. Thermophoretic force occurs due to a greater transfer of momentum from gas molecules on the side of the particles with higher temperatures, compared to the colder side. This results in particle movement in the
direction of decreasing temperature and this leads to thermophoretic deposition onto the walls of the reactors. For particles ≤100 nm, thermophoretic deposition is independent of particle size and directly proportional to the temperature gradient. However, for particles > 100 nm, a temperature gradient is established in the particle as well, which in return, affects the temperature gradient of the gas surrounding the particle. Therefore, thermophoretic deposition was influenced by the temperature gradients inside the particle, and of its surroundings, thus larger particles experience greater thermophoretic losses.¹¹

Characterization of the particle transmission efficiency of the TPOT reactors is necessary for studying SOA formation processes. The overall particle transmission efficiency was investigated using bis(2-ethylhexyl) sebacate (C₂₆H₅₀O₄, BES), a model organic aerosol (Figure 3.3).

![Figure 3.3 Chemical structure of bis(2-ethylhexyl) sebacate (BES).](image)

### 3.2.1.1 Experimental Methods

A N₂ flow of 40 sccm carried the BES particles that were generated by homogeneous nucleation by heating liquid BES (Fluka, >97%) in a Pyrex® tube to approximately 115°C. This flow was further combined with 760 sccm of N₂ before passing through a neutralizer (TSI model 3077) and then size-selected by a differential mobility analyzer (DMA, TSI model 3081) with a mode mobility diameter (Dₘ) ranging from 50 to 300 nm. The ratio of sheath to sample flow rates in the DMA was held constant at a value of 10. The monodisperse aerosol flow was further combined with 800 sccm of water vapour/N₂ and 400 sccm of O₃/N₂ flow – to a total flow of 2000 sccm, into the mixing tube. Following this mixing volume, 1000 sccm of this aerosol flow was used to measure the number concentration.
using a condensation particle counter (CPC, TSI model 3010). The remainder of this flow passed through the oxidation tube (UV lamp on), followed by measurement of the number concentration using another CPC (TSI, model 3010). The particle transmission efficiency was calculated as the fraction of particle number concentration measured by the CPC before, and after the oxidation tube. Control experiments showed no changes in particle transmission efficiency due to OH oxidation.

3.2.1.2 Results and Discussion

![Graph](image)

**Figure 3.4** BES particle transmission efficiency as a function of mean mobility diameter (nm). The grey dashed line represents 100% particle efficiency, where no particle losses occur. Error bars represent ± 1σ of the measured values.

The particle transmission efficiencies of TPOT v1.0 and v2.0 are shown in Figure 3.4. Particles with $D_m < 150$ nm experienced significant losses in the oxidation tube of v1.0, whereas for all sizes measured, no significant particle loss was observed for TPOT v2.0.

There were two main differences in the design for the oxidation tubes for the two reactors: the material of the tube and the volume-to-surface-area ratio. The material of the tube affects electrostatic losses – for v1.0, the oxidation tube was made of Pyrex®, an
insulating material that will lead to particle loss due to electrostatic forces. This was
minimized in TPOT v2.0 with the use of a stainless steel tube. As mentioned previously,
electrostatic losses increases with particle size, however, the trend observed experimentally
for TPOT v1.0 was in fact, opposite (particle loss increases with decreasing size). This
suggests that electrostatic loss was unlikely the major particle loss mechanism in TPOT
v1.0.

Of the four particle loss mechanisms discussed, only diffusion loss increases with
decreasing particle size, therefore in good agreement with the experimental observations.
In addition, given the smaller volume-to-surface-area ratio of TPOT v1.0 compared to v2.0,
small particles have a higher probability to diffuse close to and then collide with a surface,
thereby leading to irreversible loss in v1.0. Taken together, it was likely that diffusion loss
was the main particle loss mechanism in v1.0.

3.2.2 Residence Time Distribution of BES and SO₂

Residence time distributions (RTDs) illustrate the range of time a volume element
spends in a reactor. For an ideal reactor, the RTDs should be reflective of a plug flow, where
the volume element is well-mixed radially, but no mixing occurs with the adjacent volume
element axially. In other words, the lifetime of a pulsed element in a plug flow reactor is
the average residence time of the flow in the reactor, plus the length of the pulse (see Figure
3.6A-B). However, all real reactors do not generally behave as a plug flow reactor because
the volume element close to the walls of a reactor will always experience friction – thereby
slowing the velocity of this volume. This results in a distribution of velocities radically and
axially, termed laminar flow (see Figure 3.6C-D). If radial diffusion is sufficiently fast,
laminar flow reactors can approach a plug-flow limit.
Due to the multiphase nature of the SOA formation and aging processes (discussed in Chapter 1), the range of oxidation exposure in the gas phase should be identical to that of the particle phase. To characterize these parameters, the residence time distributions of 10s pulses of BES particles and SO$_2$ (gas) were obtained and compared.

![Diagram](image1)

**Figure 3.5** Side view of a plug flow reactor (A), where a pulse travels down the length of the reactor at a constant radial velocity. The corresponding RTD (B) will be narrow and well defined. The beginning of the pulse arrives at the outlet at the reactor’s residence time ($t_R$), and the end of the pulse arrives at $t_R + x$, where $x$ is the length of the pulse. Side view of a laminar flow reactor (C) with little to no radial diffusion, where a pulse travels down the length of the reactor at different velocities radially, with the highest velocity of the pulse at the center. The corresponding RTD (D) will correspond to the velocity distribution of the pulse. The beginning of the pulse arrives at the outlet at half of the reactor’s residence time ($0.5t_R$) (adapted from Levernspiel 1999$^{12}$ and Davis 2003$^{13}$).

### 3.2.2.1 Experimental Methods

The experimental conditions to deliver SO$_2$ and BES pulses were identical to those discussed in sections 3.1.1.1 and 3.2.1.1. However, instead of a continuous flow of BES particles or SO$_2$ gas, they were introduced for 10s into the TPOT reactors separately. In addition, O$_3$ was not introduced into the reactors so no OH oxidation can occurred. For SO$_2$,
the reactors were passivated by flowing SO₂ prior to the pulse inputs until a stable concentration was measured, at which point SO₂ flow was removed to re-establish background concentrations. SO₂ pulses were introduced by opening and closing a two-way valve (Swagelok) and the concentration was measured downstream of the oxidation tube using a SO₂ monitor (Thermo Scientific Inc. Model 43C). For the particle pulses, 10s of 145 nm BES particles (size selected using a DMA, TSI model 3081) were introduced by switching a three-way valve (Swagelok), which directs the particle flow to either pass through, or bypass a HEPA filter, which removes particles in the gas flow. Following the oxidation tube, the particle concentration was measured with a CPC (TSI, model 3010).

3.2.2.2 Results and Discussion

![Figure 3.6 RTDs plot for a representative 10s SO₂ pulse. The corresponding plug flow RTDs are plotted for each reactor for comparison.](image)

Figure 3.6 RTDs plot for a representative 10s SO₂ pulse. The corresponding plug flow RTDs are plotted for each reactor for comparison.
The residence time distributions (RTDs) of TPOT v1.0 and v2.0 were characterized with a gas (SO$_2$) and a model OA particle (BES). The RTDs for SO$_2$ and BES particles, along with the theoretical plug flow RTDs for each reactor, are plotted on Figure 3.6 (SO$_2$) and Figure 3.7 (BES). The overall shape of the RTDs were similar to laminar flow predictions (Figure 3.5D), and not of plug flow predictions (Figure 3.5B). This indicates that there was a wide range of OH exposure for both gases and particles in the two versions of TPOT. However, the main objective of this experiment was to determine if the range of OH exposures for gases and particle was identical in the reactors. This can be estimated by examining the times at which a certain fraction of the total gas/particle input has been transmitted. This was conducted by integrating the RTD curves for SO$_2$ and BES pulses. For this thesis, the point in time at which 50% and 95% of the total input has been transmitted will be denoted as $t_{50}$ and $t_{95}$. Differences in the $t_{50}$ and $t_{95}$ values for SO$_2$ and BES particles will provide insight on the variability of OH exposures for the two species at two different times during a pulse (Table 3.2).
Table 3.2 Differences in the range of OH exposure for a gas and particles, indicated by the $t_{50}$ and $t_{95}$ values.

<table>
<thead>
<tr>
<th></th>
<th>$t_{50}$ (min)</th>
<th>$t_{95}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TPOT v1.0</td>
<td>TPOT v2.0</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>2.3</td>
<td>5.0</td>
</tr>
<tr>
<td>BES</td>
<td>1.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 3.8 RTDs plot for the 10s SO$_2$ (dotted distribution curves) and BES (solid distribution curves) pulses for TPOT A) v1.0 and B) v2.0.
By comparing the RTDs and the $t_{50}$ and $t_{95}$ values, it can be seen that BES particles were transmitted through both reactors at least twice as quickly as SO$_2$. In addition, shown in Figure 3.8, the RTDs of BES particles were narrower than the corresponding RTDs for SO$_2$. However, SO$_2$ was a wall-adhering species where the delay observed in the RTDs compared to BES RTDs may be due to incomplete passivation. RTDs should be obtained using a wall-inert gaseous species, such as CO$_2$, in order to accurately characterize the OH exposure of a gas.

Nonetheless, by comparing the RTDs of SO$_2$ and BES particles, it suggests that the particle OH exposure is approximately half of the gas OH exposure, so the level of oxidation for a gas and particle is different in the TPOT reactor. This is an important parameter to determine in order to accurately interpret changes in SOA “age” due to changes in OH exposure. For example, if only heterogeneous oxidation occurs in the TPOT reactor, the OH exposure can be estimated from the BES RTDs. On the other hand, if gas-phase oxidation is the major aging mechanism in the reactor, the OH exposure can be estimated from the SO$_2$ RTDs. To reduce the complexity and uncertainties in interpolating an OH exposure, it is ideal to match the RTDs of both gases and particles.

3.2.3 Conclusions

The particle transmission efficiency was improved for TPOT v2.0 compared to v1.0 as losses due to diffusion were minimized due to the increase in volume-to-surface-area ratio for v2.0. Even though TPOT v1.0 was used to investigate heterogeneous oxidation of organic aerosol, the ability for TPOT v2.0 to study this process has been improved for particles smaller than 150 nm because of fewer particle losses (heterogeneous oxidation is dependent on particle surface area).
By obtaining the RTDs of a gas (SO₂) and particle (BES), it can be seen that gases and particle experience different levels of OH exposure in both versions of TPOT. Particles are subjected to approximately half of the OH exposure compared to gases. Neither versions of the TPOT reactor behaved ideally on this regard.¹

3.3 Formation of Secondary Aerosol

Following the parameterization of the TPOT reactors, the capacity of the technique to generate secondary aerosol (including SOA) under ambient conditions needs to be determined and evaluated. This was first explored by examining the ability of the TPOT technique to generate H₂SO₄ particles, a well-studied, simple system. This was followed by the formation of α-pinene SOA, a commonly studied SOA system in smog chambers. The measured α-pinene SOA yield was used to place the performance of the TPOT technique in the context of other reactors used to examine SOA formation processes.

3.3.1 Formation of Secondary Aerosol: Sulfuric Acid Particle Yield

Sulfuric acid particles are formed from sulfuric acid vapour generated by the OH oxidation of SO₂:⁴

\[
\begin{align*}
SO₂ + OH & \rightarrow HSO₃ \quad (R2) \\
HSO₃ + O₂ & \rightarrow SO₃ + HO₂ \quad (R3) \\
SO₃ + H₂O & \rightarrow H₂SO₄ \quad (R4)
\end{align*}
\]

In the presence of water vapour, the first reaction is the rate-limiting step, with a known rate constant. In addition, the thermodynamics of this simple binary system (H₂SO₄-H₂O)

¹ Ingrid George used TPOT v1.0 in a different geometry (discussed in Chapter 2, section 2.2.1); therefore the RTDs and its implications discussed in this thesis do not apply to her work.
were extensively studied and characterized. The oxidation of SO\textsubscript{2} generates only one product that readily nucleates to form sulfuric acid particles. Therefore, a sulfuric acid particle yield of one is expected. Deviation from this value of unity indicates that the oxidation products were subjected to significant wall effects (wall deposition). By determining the sulfuric acid yield, the impact wall effects have on secondary aerosol formation was investigated.

3.3.1.1 Experimental Methods

The experimental conditions and methods used for the formation of sulfuric acid particles were identical to the OH exposure calibration experiments using SO\textsubscript{2}. However, in addition to the measurement of SO\textsubscript{2} concentration, the volume concentration of the polydisperse sulfuric acid particles were measured using a scanning-mobility particle sizer (SMPS), including a DMA (TSI, model 3081) and a CPC (TSI, model 3010).

Due to the high hygroscopicity of sulfuric acid particles, the volume concentration measured by the SMPS included the amount of water absorbed. To calculate the dry H\textsubscript{2}SO\textsubscript{4} mass yield, the mass of H\textsubscript{2}SO\textsubscript{4} measured was calculated as follows (Eq. 3.4):

\[
\text{mass of } H_2SO_4 \text{ (measured)} = X_{H_2SO_4} \times V_{H_2SO_4 \cdot H_2O} \times \rho_{H_2SO_4 \cdot H_2O} \quad (3.4)
\]

where \( X_{H_2SO_4} \) was the mass fraction of H\textsubscript{2}SO\textsubscript{4} in solution, \( V_{H_2SO_4 \cdot H_2O} \) was the volume of H\textsubscript{2}SO\textsubscript{4} measured from the SMPS (nm\textsuperscript{3} cm\textsuperscript{-3}), and \( \rho_{H_2SO_4 \cdot H_2O} \) is the solution density (g cm\textsuperscript{-3}). The values for \( X_{H_2SO_4} \) and \( \rho_{H_2SO_4 \cdot H_2O} \) were specific for the relative humidity measured in the SMPS sheath flow and were taken from Seinfeld and Pandis 2006.\textsuperscript{14} The mass of H\textsubscript{2}SO\textsubscript{4} measured was also corrected for the size-dependent particle transmission efficiency (section 3.2.1.2). The H\textsubscript{2}SO\textsubscript{4} dry yield, \( Y_{H_2SO_4,dry} \) from OH oxidation was calculated in a similar fashion as a SOA yield (Eq. 3.5):
The mass of \( H_2SO_4 \) (measured) was calculated using Eq. 3.4, and the mass of \( H_2SO_4 \) (predicted) was calculated by the mass of the \( H_2SO_4 \) formed per ppb of \( SO_2 \) reacted. The amount of \( SO_2 \) reacted was taken as the difference in \( SO_2 \) concentration measured in the bypass and oxidation tube (with and without OH oxidation).

\[ Y_{H_2SO_4\text{dry}} = \frac{\text{mass of } H_2SO_4 \text{ (measured)}}{\text{mass of } H_2SO_4 \text{ (predicted)}} \] (3.5)

3.3.1.2 Results and Discussion

The \( H_2SO_4 \) dry yields measured from TPOT v1.0 and v2.0 are shown in Figure 3.8. The yields observed for v1.0 were significantly lower than unity, indicating there was substantial wall loss of \( SO_2 \) oxidation products, reducing the amount of aerosol formed. To compensate for wall loss, a higher concentration of \( SO_2 \) (from 40 to 65 ppb) was used to assist aerosol the formation, improving the yield from 0.2 to 0.44. For v2.0, the \( H_2SO_4 \) dry yields measured were drastically improved upon compared to v1.0. Upon closer examination of Figure 3.8, two groups of \( H_2SO_4 \) yields can be identified for v2.0. The average yield calculated from cluster of data at lower concentration of reacted \( SO_2 \) was 0.89 ± 0.14 and the average yield was 0.99 ± 0.17 for the cluster of data obtained at high \( SO_2 \) concentration reacted. This suggests that there was some dependence of \( H_2SO_4 \) yield with the \( SO_2 \) reacted for v2.0. Wall losses were reduced since the volume-to-surface-area ratio was increased for v2.0 compared to v1.0. It is important to emphasize that the \( H_2SO_4 \) is an ideal secondary aerosol system due to the fact that the only oxidation product readily nucleates; therefore, the \( H_2SO_4 \) yields presented are reflective of the upper limit of the reactors' ability to generate secondary aerosol.
Figure 3.9 $\text{H}_2\text{SO}_4$ dry yield as a function of concentration of $\text{SO}_2$ reacted (ppb). The dotted grey line indicates a aerosol yield of 1.0. Error bars represent ± 1σ of the measured values.

3.3.2 Formation of SOA: $\alpha$-Pinene

The capacity of the TPOT reactors to generate secondary aerosol was evaluated in the previous section, however, the $\text{H}_2\text{SO}_4$ system used was not representative of a SOA system as the number of oxidation products and their wall loss behaviours are different ($\text{H}_2\text{SO}_3$ and semi-volatile organic compounds). Also, since the vapour pressure of semi-volatile organic compounds are higher than that of sulfuric acid vapor, nucleation proceeds correspondingly more slowly. This leads to a higher potential impact from wall loss. Since the technique was developed to study SOA formation, the characterization of the reactors’ capacity to generate SOA is the ultimate test of their performance.

$\alpha$-Pinene ($\text{C}_{10}\text{H}_{16}$), a monoterpenone, is a commonly used SOA precursor in laboratory studies because it constitutes a large fraction of global non-isoprene biogenic VOC emission (12-58%) and it is believed that monoterpenes dominate global SOA formation.\textsuperscript{7,15} To test the feasibility of the TPOT reactors to generate SOA \textit{in-situ}, $\alpha$-pinene SOA yield was measured under conditions that are atmospherically relevant.
3.3.2.1 Experimental Methods

An α-pinene gas bulb was made in a similar manner as the SO$_2$ gas bulb described in section 3.1.1.1. However, pure α-pinene vapour was prepared by a “freeze-pump-thaw” method, where a drop of liquid α-pinene (Fluka, 99.0%) in a glass bulb, was frozen using liquid nitrogen, and the air inside the bulb was removed to create a vacuum. As the solid α-pinene thaws, the glass bulb comprises only of pure α-pinene vapour. A small amount (approx. 1 torr) of this pure α-pinene vapour was delivered into a 3113 cm$^3$ glass bulb under vacuum. This glass bulb was filled with N$_2$ gas until the fraction of α-pinene in the glass bulb was approximately 1.0 x 10$^{-3}$ and the final pressure was above 1000 torr. The mixing ratio of the α-pinene ($C_{\alpha\text{-pinene}}$) delivered into the TPOT was calculated using Eq. 3.2 and 3.3. To minimize the ozonolysis of α-pinene prior to the bypass/oxidation tube, the α-pinene flow (in 10 sccm of dry N$_2$) was combined with a dry N$_2$ flow of 790 sccm, a water-saturated flow of 800 sccm, and a N$_2$ flow containing O$_3$ of 400 sccm after the mixing flow tube (total flow of 2000 sccm). At a ΔP/Δt of 1 torr/min, the final mixing ratio of α-pinene calculated using Eq. 3.2 and 3.3 was 19.5 ppb. The mixing ratio of α-pinene was changed by varying the ΔP/Δt value (0.56 – 4.7 torr per min; 11 – 92 ppb).

Prior to each SOA formation experiment, OH was generated in the absence of α-pinene until background particle volume concentration was measured using a SMPS, which includes a DMA (TSI, model 3081) and a CPC (TSI, model 3010). Subsequently, the entire reactor system was passivated with α-pinene until a stable signal was measured using a PTR-MS (Ionicon), with a quadrupole mass analyzer. For particle generation, a constant OH exposure of 8.33 x 10$^{11}$ molec cm$^{-3}$ s was used while the concentration of α-pinene was varied, as noted above. Water uptake by α-pinene SOA was accounted for by the hygroscopic growth factor (HGF), given by Eq. 3.6:
where RH is the relative humidity measured and \( A, B, \) and \( C \) were empirical parameters, specific for \( \alpha \)-pinene SOA, as measured by Varutbangkul \textit{et al.} 2006.  

The resulting mass of dry \( \alpha \)-pinene SOA was given by Eq. 3.7:

\[
\text{mass of } \alpha - \text{pinene SOA (measured)} = \text{HGF}_{\alpha - \text{pinene SOA}} \times V_{\alpha - \text{pinene SOA}} \times HGF \times \rho_{\alpha - \text{pinene SOA}} 
\]

where \( \text{HGF}_{\alpha - \text{pinene SOA}} \) was calculated using Eq. 3.6 (% RH: 45, HGF: 1.012), \( V_{\alpha - \text{pinene SOA}} \) was the volume of \( \alpha \)-pinene SOA measured from the SMPS (nm\(^3\) cm\(^{-3}\)), and \( \rho_{\alpha - \text{pinene SOA}} \) was the density of \( \alpha \)-pinene SOA (1.4 g cm\(^{-3}\)).  

The mass of \( \alpha \)-pinene measured was also corrected for the size-dependent particle transmission efficiency (section 3.2.1.2). Lastly, the \( \alpha \)-pinene dry yield, \( Y_{\alpha - \text{pinene SOA}} \) from OH oxidation was calculated using Eq. 3.8:

\[
Y_{\alpha - \text{pinene, dry}} = \frac{\text{mass of } \alpha - \text{pinene (measured)}}{\text{mass of } \alpha - \text{pinene (predicted)}} 
\]

where the mass of \( \alpha - \text{pinene SOA (measured)} \) was given by Eq. 3.7, and the mass of \( \alpha - \text{pinene (predicted)} \) was calculated by the mass of the SOA formed per ppb of \( \alpha \)-pinene reacted.  

The lifetime of \( \alpha \)-pinene against OH oxidation was 3.2 s (\( \alpha \)-pinene concentration = 92 ppb, OH concentration of 5.87 \times 10^9 molec cm\(^{-3}\), \( k_{\alpha - \text{pinene} + \text{OH}} = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)), which was shorter than the residence time of the oxidation tube (142 s). In addition, the lifetime of \( \alpha \)-pinene against O\(_3\) oxidation was 2108 s (O\(_3\) concentration of 5.27 \times 10^{12} \text{ molec cm}^{-3}, k_{\alpha - \text{pinene} + \text{O}_3} = 9.0 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)), thus, all the \( \alpha \)-pinene would have reacted with OH.  

Therefore, the amount of \( \alpha \)-pinene reacted was taken as the amount introduced into the reactor.
3.3.2.2 Results and Discussion

The α-pinene SOA yields measured from TPOT v1.0 and v2.0 are shown in Figure 3.9. As discussed in Chapter 1, section 1.4.2, two factors can increase SOA yield: an increasing amount of particles and increasing amount of semi-volatile compounds of sufficiently low vapour pressure. For each reactor, the OH exposure was held constant so differences in the yields observed can only be attributed to differences in the amount of α-pinene reacted - therefore, differences in the amount of semi-volatile oxidation products generated.

In the TPOT reactors, following the formation of the semi-volatile oxidation products, two competing processes occur: nucleation or condensation of these products onto existing particles, or the condensation onto the reactors’ walls. For TPOT v1.0, no particle formation was observed from the oxidation of α-pinene at concentrations less than 71 ppb. Following the oxidation of 71 ppb of α-pinene, minimal particle formation was observed, resulting in a low yield of 0.02, suggesting significant wall loss of the oxidation products. The concentration of α-pinene was increased to 263 ppb to increase the SOA yield to 0.073. A much lower α-pinene concentration (11 ppb) was required to observe a comparable low SOA yield of 0.01 for TPOT v2.0, which indicates that the wall loss of the oxidation products was not as significant as v1.0. However, since ambient concentration of α-pinene is only several ppb above a boreal forest, these laboratory results indicate that neither versions of TPOT have the capacity to generate α-pinene SOA in-situ. Even in the laboratory setting, the TPOT reactors obtained very low SOA yields compared to a typical smog chamber technique, where α-pinene SOA yields of 0.4 were normally observed for the oxidation of 10 to 100’s ppb of α-pinene. However, compared to smog chambers and the atmosphere, in the TPOT reactors, the rate of gas-phase OH oxidation was much faster compared to nucleation, due to the high concentrations of OH.
substantial fragmentation can occur, which results in compounds with high vapour pressures, therefore less likely to participate in SOA formation. This may have resulted in the low α-pinene SOA yield observed in the TPOT compared to smog chamber techniques.

![Graph showing SOA mass yield as a function of α-pinene reacted (ppb).](image)

**Figure 3.10** α-Pinene SOA yield as a function of α-pinene reacted (ppb). The OH exposure in TPOT v1.0 was approx. $10^{11}$ molec cm$^{-3}$ s and for TPOT v2.0, it was $8.33 \times 10^{11}$ molec cm$^{-3}$ s. Error bars represent ± 1σ of the measured values.

### 3.3.3 Conclusions

The feasibility of the TPOT system to examine secondary aerosol and ambient SOA formation processes was evaluated by the measuring the aerosol yields of H$_2$SO$_4$ and α-pinene SOA. For a simple aerosol system, such as H$_2$SO$_4$, significantly higher aerosol yields were observed for TPOT v2.0 compared to v1.0 due to less wall losses. In fact, the aerosol yield was close to the theoretical value. However, for α-pinene SOA, where a range of oxidation products were generated, low SOA yields were observed in both versions of TPOT. Nevertheless, the ability of v2.0 to generate SOA was improved compared to v1.0.
3.4 References


3593-3624.


CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

4 Overall Conclusions and Future Work

4.1 Summary and Conclusions

Despite the importance secondary organic aerosol has on climate forcing and air quality, the formation and transformation processes of these particles, along with their chemical composition and properties remain poorly understood. Most of our current understanding has resulted from laboratory studies using smog chambers; however, the chemical composition of laboratory SOA is different than that measured in the atmosphere.\textsuperscript{1-3} Despite this discrepancy, there is still paucity in research results connecting laboratory studies and ambient measurements. The main objective of this thesis was to further develop and characterize a portable flow tube technique that was originally designed to study the OH-initiated heterogeneous oxidation of organic aerosol in order to better study SOA formation processes and aerosol aging processes both in the field and the laboratory.

Firstly, the research in this thesis investigated the different parameters of the Toronto Photo-Oxidation Tube (TPOT) v1.0 and v2.0, including their oxidation capacity, particle transmission efficiency, and the flow dynamics of particles and gases. The two versions of the TPOT technique generated a similar range of OH exposure, from approx. $3.0 \times 10^{11} - 1.4 \times 10^{12}$ molec cm$^{-3}$ s, which were equivalent to ambient exposures from 2.3 to 10.8 days. Given a typical ambient aerosol lifetime of several days to a week, these were atmospherically relevant oxidizing conditions.\textsuperscript{4} In addition, two different methods of OH exposure calibration have been employed and validated, providing flexibility to conduct this characterization experiment during future field measurements. The particle transmission
efficiency of both reactors was evaluated using BES particles. Due to an increase in volume-to-surface-area ratio for v2.0, the particle transmission efficiency of particles smaller than 150 nm was improved as diffusion losses were minimized. The flow dynamics of BES particles and SO$_2$ gas was the final performance feature characterized by obtaining the residence time distributions of these species in the two reactors. Most importantly, the residence time distributions were reflective of the OH exposures particles and gases were subjected to in both reactors. The main result is that this work illustrates that the particles’ OH exposure was approximately half of the gas OH exposure.

The second study evaluated the ability of the TPOT technique to generate secondary aerosol under ambient conditions by measuring the H$_2$SO$_4$ aerosol and $\alpha$-pinene SOA yields. For both model secondary aerosol systems, TPOT v2.0 obtained higher yields compared to v1.0, reflective of a reduction in wall losses of the oxidation products, due to an increase in volume-to-surface-area ratio. However, low SOA yields were still observed for TPOT v2.0 under atmospherically relevant conditions, suggestive of an inability to generate SOA by homogeneous nucleation during field deployment. As such, the technique requires further modifications in order to fully realize its capacity to generate and monitor SOA formation processes \textit{in-situ}. Nonetheless, the development and characterization of the TPOT technique offers the possibility to control and monitor the SOA formation and aging processes in real-time, under atmospherically-relevant conditions.

4.2 Future Work

Over the past 10 years, immense progress has been made in our understanding of SOA formation and aging processes. However, the discrepancy in the chemical composition of laboratory generated SOA and field measurements illustrates a gap in our knowledge and inability to represent the conditions and complexity of the real atmosphere.$^{1,5}$
As suggested by the research summarized in this thesis, further development of the TPOT system is critical to explore its potential to control and monitor the OH-initiated formation and chemical aging of SOA in-situ. Firstly, the RTDs of a wall-inert species, such as CO$_2$, should be obtained and compared to the corresponding RTDs of a wall-adhering species, SO$_2$. This will provide a more complete understanding of the flow dynamics of a gas in the TPOT reactors, and to accurately quantify the range of OH exposures gaseous species are objected to in the oxidation tube. In addition, the current characterization experiments indicate that particles reside in the oxidation tube for half the amount of time as gases, therefore particle OH exposure is half of the gas OH exposure. Due to the multiphase nature of the formation and aging processes of SOA, the oxidizing environment for both gases and particles should be identical. For example, the OH exposures for both phases can be matched by increasing the trajectory of particles passing through the TPOT oxidation tube with the use of a showerhead disk that will add the particles at a range of radial positions across the flow tube. This development is underway in the laboratory.

The SOA formation experiments in this study examined the ability of the technique to generate $\alpha$-pinene SOA by homogeneous nucleation. However, in the atmosphere, SOA can be formed either by nucleation, or the condensation of semi-volatile organic compounds onto existing particles. To fully explore the potential of the technique to generate SOA, the second mechanism of SOA formation needs to be investigated as well. This process can be studied with the addition of inorganic particles (commonly known as a “seed” for SOA), such as ammonium sulfate, into the reactor. Thus, the need for nucleation to occur is removed. By monitoring the changes in SOA yield as a function of seed concentration, the loss of semi-volatile oxidation products to the reactor’s walls can be quantified.
Following the optimization of the TPOT technique in the laboratory, measurement of ambient samples should be conducted in order to connect previous laboratory observations to ambient measurements. This can be achieved by conducting process-oriented field studies, where the oxidation environment can be varied in the TPOT to mimic conditions that approximate to those in the atmosphere, or to the extreme conditions often employed in laboratories. Field work should also be performed at various locations to understand the SOA formation and aging processes of different types of aerosol.

Studies are planned for this coming summer using urban air in Toronto where we plan to employ seed aerosol and to have the residence time distributions equal for gases and particles. Our goal is to perform the first simultaneous oxidative aging study of urban gas and particle constituents.

4.3 References


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