CARNEGIE MELLON UNIVERSITY

# Modeling Organic Aerosol Formation from Alpha-Pinene Ozonolysis in the Volatility Basis Set Framework

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To my family and friends, who have supported me in all my endeavors. And to scientific skepticism and the pursuit of scientific knowledge, through which we understand the universe.

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## Abstract

Volatile organic compounds released by plants or through processes such as combustion reacts with oxidative species in the air, such as ozone or hydroxyl radicals. Smog chamber studies are conducted to determine the chemistry that these organic precursors undergo, and the products that are formed. These products span orders of magnitude in volatility, making the tracking of each individual species a difficult process. The volatility basis set (VBS), which separates species based on volatility, has been shown to be an effective framework to track the formation of aerosols from these products.

In the first part of this work, a 2-dimensional VBS model is used to investigate the introduction of NO<sub>x</sub> to  $\alpha$ -pinene aging. A new dimension is added to the VBS to track the formation and aging of organonitrates. The results show that higher volatility precursors produce less aerosol mass, while lower volatility precursors produce more, which is consistent with prior experiments of NO<sub>x</sub> effects. In addition, the model shows that the detection of small concentrations of nitrate ions can still indicate presence of substantial organonitrate mass.

The formation of aerosols from  $\alpha$ -pinene ozonolysis experiments at CLOUD are modeled in the next part of this work. CLOUD experiments show the production of low volatility organic compounds, or (E)LVOCs, from  $\alpha$ -pinene ozonolysis contribute to the growth of nucleated particles. The inclusion of a Kelvin effect is necessary to reproduce particle growth rates at small diameters (< 4 nm). Flux balance calculations from the dynamic VBS model show that the raw distribution of products seen by the nitrate-CIMS cannot fully explain the particle growth, and indicate that product masses must be higher. When the model accounts for the charging efficiency of LVOCs in the nitrate-CIMS, it is capable of reproducing the growth of particles from these experiments.

Lastly, the yields of E(LVOC)s required to reproduce the data in the previous chapter appear to contradict yields from prior  $\alpha$ -pinene experiments. We explore potential explanations for this disagreement. By treating the chamber model as a dynamical process, the model demonstrates that high yields will appear lower due to the delay between (E)LVOC formation and condensation. While the results still show an overprediction by the current model, it indicates that a dynamical treatment is indeed necessary to capture the condensation of vapors to particles.

## Contents

Contents							
Lis	List of Figures						
1	Intro	oduction	1				
2	Mod	leling Organonitrate Formation from $\alpha$ -pinene ozonolysis	10				
	2.1		11				
	2.2	Background	14				
		2.2.1 Volatility basis set	14				
		2.2.2 Mathematical overview	16				
		2.2.3 Treatment of organonitrates	19				
		2.2.4 Time evolution	21				
	2.3	Results and discussion	23				
	2.4	Conclusion	29				
3	Mod	leling the Growth of Freshly Nucleated Particles	40				
	3.1	Introduction	41				
	3.2	Aerosol Growth Model	42				
	3.3	Experimental Data	45				
	3.4	Model Results	49				
	3.5	Conclusion	55				
4	Whe	ere New Yields Lead Us	62				
	4.1	Introduction	63				
	4.2	The Dynamic Model	69				
		4.2.1 Mathematical background	69				
		4.2.2 (E)LVOC mass yield distribution	70				
		4.2.3 Polydispersity and the condensation sink diameter	73				
	4.3	Results and Discussion	74				
		4.3.1 Modeling organic aerosol production	76				

	4.4	4.3.2Oligomerization	81 85 89
5	Con	clusions and future work	97
	5.1	Conclusions	98
	5.2	Future Work	.00

# **List of Figures**

2.1	Atomic N: C ratio isopleths in the organonitrate layer of the 2D-VBS	20
2.2	Organic mass concentration over 2h of dark ozonolysis followed by 10h	
	of OH aging for low-NO <sub>x</sub> and high-NO <sub>x</sub> conditions	24
2.3	Mass of first-generation products for each cell in the 2D-VBS, from 100-	
	$\mu$ g m <sup>-3</sup> $\alpha$ -pinene + ozone at $\beta = 0.15$ .	25
2.4	The effect of peroxy-radical branching on the first-generation secondary	•
o -	organic aerosol concentration, C <sub>OM</sub> .	26
2.5	The effect of peroxy-radical branching on the aged secondary organic aer-	•
•	osol concentration, $C_{OM}$ , after 10 h of oxidation by 10' OH cm <sup>-3</sup>	28
2.6	The distribution of mass is plotted over the 2D-VBS space for multi-gen-	
	eration products, after 10 h of OH aging of $100 \mu g \mathrm{m}^{-3} \alpha$ -pinene + ozone	•
	at $\beta = 0.15$ .	29
3.1	Appearance times of clusters and aerosols as seen by APi-TOF, DEG, PSM,	
	nRDMA, NAIS, and Nano-SMPS.	46
3.2	Observed mass spectrum as seen by the nitrate-CI-APi-TOF at 278 K, 38%	
	relative humidity.	47
3.3	Possible structures of $\alpha$ -pinene oxidation products.	48
3.4	Estimation of <i>C</i> <sup>*</sup> for monomer and dimer molecules at 293 K.	49
3.5	Observed gas-phase HOMs and their volatility distribution.	50
3.6	Size dependent growth - a comparison between measurement and model.	51
3.7	HOM distribution binned to a volatility basis set.	52
3.8	Dynamic volatility-distribution modeling results with and without Kelvin	
	term and with original and modified HOM volatility distribution for the	
	case of constant HOMs.	53
3.9	Dynamic volatility-distribution model details.	54
4.1	Apparent contradiction between CIMS (E)LVOC measurements and cham-	
	ber SOA mass yields.	65
4.2	Distribution of HOMs at 278 K.	71
4.3	Distribution of HOMs at 293 K.	72

4.4	Comparison of organic mass produced between the monodisperse and	
	polydisperse models.	75
4.5	Odum plots from model runs of the experiments.	76
4.6	The reservoirs of organics at the beginning of an experimental run.	78
4.7	Comparison of organic mass between the model and the CMU chamber	
	experiments.	79
4.8	The vapor saturation ratios for the experiments.	80
4.9	Oligomerization model results for CLOUD experiments.	82
4.10	Comparison of organic mass produced between the oligomerization model	
	and the CMU chamber experiments.	83
4.11	Odum plot with the LVOC and oligomer models for Experiment 2	84
4.12	The effect of varying particle-to-wall condensation sink ratio.	86
4.13	Change in condensation sink ratio over time.	87
4.14	Location of organics under various ozone concentrations and condensa-	
	tion sinks.	88

Chapter 1

# Introduction

Aerosols, or particulate matter (PM), cause numerous cardiovascular and respiratory diseases, and chronic exposure to high concentrations can significantly reduce life expectancy (Dockery et al., 1993; Peng et al., 2005; Pope et al., 2009). Particles smaller than 2.5 micrometers (PM<sub>2.5</sub>) directly contribute to respiratory- and cardiovascular-related deaths. This is most concerning in major cities where air pollution can reach extremely hazardous levels. In addition, PM affects ecosystems and the atmosphere, exerting significant direct and indirect forces on climate. Direct forcing comes from the scattering or absorption of solar radiation by aerosols. Indirect forcing comes from the scattering of solar radiation by clouds, which is in turn controlled by hydrophilic particles known as cloud condensation nuclei (CCN) (Seinfeld and Pandis, 2006). In order to track the production of aerosols, models predict the interactions between emissions from various sources and their effects on the formation of PM.

 $PM_{2.5}$  consists of a rich mixture including both inorganic and organic compounds, commonly found within individual particles. Inorganics include sodium chloride (from sea spray); sulfate (mostly from coal combustion); nitrate (mostly from high-temperature combustion); ammonium (from animal husbandry); elemental carbon (from combustion of organic fuels); and trace metals such as nickel and manganese. Organics comprise 20–50 % of  $PM_{2.5}$  mass in the continental midlatitudes and as much as 90 % in tropical forests (Andreae and Crutzen, 1997; Kanakidou et al., 2005). The organics are called organic aerosol (OA), and, while the inorganics consist of a relatively small set of compounds, OA consists of a rich mixture containing many thousands of different individual organic compounds (Goldstein and Galbally, 2007; Kroll et al., 2011).

OA comes from biogenic (naturally occurring) and anthropogenic (human-related) sources. Biomass burning (BBOA) is the largest contributor to OA worldwide (Bond et al., 2004). Some BBOA comes from natural carbon (woodsmoke), but the combustion is largely associated with human activity, and so BBOA is classified as anthropogenic. Overall, OA comprises roughly 10% of the total flux of organic carbon into (or out of) the atmosphere (Goldstein and Galbally, 2007; Hallquist et al., 2009); thus only a fraction of organic compounds have the right properties to reside in the condensed phase. The requisite property is a low volatility (Pankow, 1994; Donahue et al., 2011; Donahue et al., 2014); to stay in the organic phase under typical conditions, an organic molecule must have a vapor pressure lower than roughly  $10^{-10}$  atm ( $10^{-5}$  Pa,  $C^* < 1 \ \mu \text{g m}^{-3}$ ) (Donahue et al., 2011).

OA is also classified as primary or secondary (Murphy et al., 2014; Cronn et al., 1977; Turpin and Huntzicker, 1995). Primary organic aerosols (POAs) are directly emitted into the atmosphere on particles and are largely from anthropogenic sources such as automobile exhaust and biomass burning. Secondary organic aerosols (SOAs) are formed when chemical reactions cause condensation of organic compounds from the gas phase. Oxidants include ozone, hydroxyl (OH•) radicals, and nitrate (NO<sub>3</sub>) radicals (Turpin et al., 2000), and oxidation can occur in the gas phase (Pandis et al., 1991) or in the aqueous phase (Turpin et al., 2000). Oxidation can add functional groups to an organic backbone (functionalization), forming products with a lowered volatility; however, oxidation can also lead to C–C bond cleavage (fragmentation), often forming products with an elevated volatility (Kroll et al., 2011; Chacon-Madrid et al., 2010). In addition, association reactions between relatively volatile reaction products can lead to higher-molecular-weight, lowervapor-pressure products (oligomers) (Kalberer et al., 2004).

Oxidation of an organic compound, even one generation, generally forms many products, each with a different volatility (Atkinson et al., 1997; Aumont et al., 2005; Lim and Ziemann, 2009). Thus SOA production has been described in terms of a volatility distribution of reaction products (Odum et al., 1996; Presto and Donahue, 2006; Donahue et al., 2012). However, this also means that the oxidation products (and thus volatility distribution and overall SOA mass yields) often depend strongly on ambient conditions. The dominant oxidant can have a large effect (OH vs. ozone during the day, NO<sub>3</sub> vs. ozone at night), but so can the organic radical chemistry following the initial oxidation step.

In the following chapters, the formation of organic aerosols from the aging of  $\alpha$ -pinene,

one of the more abundant organic vapors emitted, is modeled. The model is based on the volatility basis set (VBS) framework, which separates compounds by their vapor pressures. By tracking vapor pressure, the model can determine how much organic aerosol mass is formed, and the rate at which it forms.

In Chapter 2, a 2D-VBS framework is used to model the formation of organonitrates from  $\alpha$ -pinene ozonolysis in the presence of NO<sub>x</sub>. The 2D-VBS framework includes a second axis to track the atomic oxygen to atomic carbon ratio, a measure of the degree of chemical aging in the atmosphere. The addition of NO<sub>x</sub> are found to decrease the aerosol mass formed from  $\alpha$ -pinene ozonolysis, but would increase for lower volatility precursors, such as sesquiterpenes. As NO<sub>x</sub> is increased, this difference widens. As the products continue aging, all scenarios result in lower mass than the no NO<sub>x</sub> condition. In addition, we found that while an Aerosol Mass Spectrometer may detect low concentrations of nitrate ions, a signature of organonitrates, the actual mass of organonitrate compounds may be far higher.

In Chapter 3, we looked at the recently discovered formation of extremely low volatility compounds from  $\alpha$ -pinene ozonolysis. Recent experiments conducted at the CLOUD chamber in CERN characterized these compounds. Based on these experiments we obtained a volatility distribution of yields and used these yields to create a dynamic chamber model based on the 1D-VBS. By accounting for the Kelvin effect on small particles and correcting for instrumental charging efficiencies, we were able to reproduce the growth of particles in the CLOUD chamber. However, the quantification of the low volatility products presented a conundrum–if they exist, then they should have shown up in older experiments that looked at yields.

In Chapter 4, we attempt to reconcile the discrepancy in the supposed yields by taking the model developed in Chapter 3 and applying it to  $\alpha$ -pinene ozonolysis experiments conducted at CMU. While the yields produced from these experiments were higher than prior results, we show that by modeling the chamber dynamically, we can have a distribution of low volatility compounds and still show lower yields during an experiment. An alternate dynamic model exploring the possibility of oligomerization from semi-volatile organics finds that it can reproduce CLOUD measurements, though it still overestimates organic aerosol mass in CMU experiments. The model also tests hypothetical chamber studies, determining that capturing most of the condensable reaction products requires both a high condensation sink to the particles and a high oxidation rate.

Chapter 5 summarizes the modeling results and discusses the direction of future experimental and modeling studies.

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## Chapter 2

# Modeling Organonitrate Formation from $\alpha$ -pinene ozonolysis

When NO<sub>x</sub> is introduced to organic emissions, aerosol production is sometimes, but not always, reduced. Under certain conditions, these interactions will instead increase aerosol concentrations. We expanded the two-dimensional volatility basis set (2D-VBS) to include the effects of NO<sub>x</sub> on aerosol formation. This includes the formation of organonitrates, where the addition of a nitrate group contributes to a decrease of 2.5 orders of magnitude in volatility. With this refinement, we model outputs from experimental results, such as the atomic N:C ratio, organonitrate mass, and nitrate fragments in Aerosol Mass Spectrometer (AMS) measurements.

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### 2.1 Introduction

One notable source of variability in SOA mass yields is the NO<sub>x</sub> level (Presto and Donahue, 2006; Zhang et al., 2006; Ng et al., 2007; Logan et al., 1981; Thompson and Cicerone, 1982). NO<sub>x</sub> (NO and NO<sub>2</sub>) can react with organic radicals to change the product distribution from oxidation reactions (Atkinson et al., 1997). NO<sub>x</sub> is most commonly formed under high-temperature conditions such as combustion; NO<sub>x</sub> concentrations range from 10–1000 ppb in urban areas to 10 ppt in remote regions (Seinfeld and Pandis, 2006), and so NO<sub>x</sub> is one of the most highly variable reactive trace species in the atmosphere and also one of the most potent indications of human activity. Because NO<sub>x</sub> can alter the oxidation chemistry of organic compounds, even biogenic organic precursors (e.g., isoprene and terpenes) may in fact form "anthropogenically enhanced" SOA if the SOA mass yields are in some way enhanced by the presence of NO<sub>x</sub>.

There is evidence that a large source of SOA associated with CO emissions (and thus presumably anthropogenic activity) is required to explain global surface OA observations (Gouw and Jimenez, 2009; Spracklen et al., 2011). At the same time, a large fraction of OA appears to consist of modern carbon (containing <sup>14</sup>C) (Weber et al., 2007; Aiken et al., 2010; Minguillón et al., 2011; Zhang et al., 2012). This has led to speculation that interactions between biogenic precursors and urban plumes – possibly NO<sub>x</sub> – may be responsible for the anthropogenic enhancement (Shilling et al., 2013). If so, the dramatic decline in NO<sub>x</sub> levels in the southeast United States over the past decade (Russell et al., 2012) might be associated with a corresponding decrease in anthropogenically enhanced SOA.

Tracking any  $NO_x$  effect is thus extremely important. If changed product distributions (and thus SOA mass yields) were the sole effect of increased  $NO_x$ , then the  $NO_x$  influence could be dealt with easily by adjusting SOA mass yields based on  $NO_x$  levels (Presto and Donahue, 2006; Lane et al., 2008b). However, if there is a reason to track specific products, or if the subsequent, later-generation chemistry of the reaction products also differs substantially under high- and low- $NO_x$  conditions, then simply adjusting mass yields will

not suffice. In the case of  $NO_x$ , both of these conditions apply: there is strong evidence that the aging chemistry of SOA depends on its composition (Zhang et al., 2006; Henry and Donahue, 2012) and also that organonitrates produced under high- $NO_x$  conditions are independently measured as a diagnostic of ambient aging conditions.

High organonitrate concentrations are typically found in areas with high NO<sub>x</sub> levels (Garnes and Allen, 2002; Mylonas et al., 1991). The addition of a nitrate functional group to a carbon backbone reduces volatility by ~ 2.5 orders of magnitude (Pankow and Asher, 2008), potentially contributing to SOA formation as a result. Organonitrates can be identified on filter samples by characteristic absorption features using Fourier transform infrared spectroscopy (FTIR; Russell et al., 2011) and also in bulk mass spectra from the Aerosol Mass Spectrometer (AMS, Aerodyne Inc.) (Zhang et al., 2006; Farmer et al., 2010). Detection in the AMS is challenging because organonitrates fragment almost completely to give NO<sup>+</sup> (m/z = 30) and NO<sup>+</sup><sub>2</sub> (m/z = 46). The same fragments arise from (often much more abundant) inorganic nitrate; however, the fragment signal ratio (30:46) can be indicative of organonitrates and is quite distinct from ammonium nitrate (Farmer et al., 2010).

Depending on the carbon chain length, organonitrates can have a gas-phase atmospheric lifetime ranging from days to months, and thus drive long-range NO<sub>x</sub> transport into remote marine regions (Atherton, 1989). Higher-carbon-number organonitrates will partition to the condensed phase (Ziemann and Atkinson, 2012). Organonitrates have been found in aerosol samples at numerous sites across North America (Russell et al., 2011). In particular, high concentrations of organonitrates have been observed in California and Texas (Garnes and Allen, 2002; Day et al., 2010). AMS data from photooxidation of  $\alpha$ -pinene, limonene, and longifolene under high-NO<sub>x</sub> conditions show mass fragments corresponding to the formation of organonitrates (Zhang et al., 2006; Ng et al., 2007). In some field observations, roughly 10–20 % of the organic aerosol mass is comprised of organonitrates; however, organonitrates are not always found in urban areas even in high-NO<sub>x</sub> conditions. Field data from Pittsburgh and the US east coast revealed low concentrations

Chapter 2. Modeling Organonitrate Formation from  $\alpha$ -pinene ozonolysis

of aerosol organonitrates (Wittig et al., 2004; Russell et al., 2011). This may be due to the hydrolysis of organonitrates, where water reacts in the condensed phase with the nitrate group to form an alcohol and nitric acid (inorganic nitrate) (Liu et al., 2012). The change in the functional group likely has little effect on the volatility of the compound; the -OH functional group replacing the -ONO<sub>2</sub> group has about the same effect on volatility (Pankow and Asher, 2008).

During daytime, organonitrates are formed through reactions of NO with organic peroxy radicals ( $RO_2$ •). As  $NO_x$  concentrations rise, progressively more  $RO_2$ • react with NO instead of  $RO_2$ • or  $HO_2$ •. The reaction with NO produces an intermediate product, ROONO, that can either decompose into an alkoxy radical (RO• and  $NO_2$ ) or isomerize to form an organonitrate ( $RONO_2$ ) (Atkinson et al., 1997; Zhang et al., 2004). The alkoxy radicals will further react, either forming stable organics that are more functionalized or fragmenting to produce lower carbon-number products. Organonitrate yields from ROONO rise with carbon number and decreasing temperature and vary somewhat with structure, reaching an asymptotic limit of roughly 0.3 at 300 K for most compounds relevant to SOA formation (Atkinson and Arey, 2003; Ziemann and Atkinson, 2012). Alkyl nitrates for species with > 20 carbons are predominantly in the particle phase (Lim and Ziemann, 2009). High-NO<sub>x</sub> products differ from low-NO<sub>x</sub> products; this can lead to comparatively higher or lower SOA concentrations (Presto et al., 2005; Kroll et al., 2006; Ng et al., 2007).

During nighttime, organonitrates are formed through reactions of NO<sub>3</sub> with unsaturated organic precursors (Crowley et al., 2011; Rollins et al., 2009). This reaction can produce organonitrates on the same magnitude as daytime organonitrate formation (Fry et al., 2013). However, the concentration profile of NO<sub>3</sub> is not well understood and can vary widely depending on boundary layer conditions (He et al., 2014; Fry et al., 2013). Daytime NO<sub>3</sub> rapidly undergoes photolysis or reacts with NO to form NO<sub>2</sub> and is thus typically unable to form organonitrates in the presence of light. Product distributions for NO<sub>3</sub> + VOC reactions have not been developed for the 2D-VBS, but its contribution to organonitrate production can eventually be incorporated within the current framework.

## 2.2 Background

#### 2.2.1 Volatility basis set

The complexity of OA partitioning and the vast number of reaction products motivated the volatility basis set (VBS). The original (one-dimensional) VBS was designed to represent partitioning and aging by lumping organic molecules only by volatility, in bins separated by an order of magnitude (at 300 K) in a logarithmic volatility space (Donahue et al., 2006). In principle the 1D-VBS can be implemented with as few as four transportable species (a single four-bin VBS with  $C^* = [1, 10, 100, 1000] \,\mu \text{g m}^{-3}$ ) at the cost of losing all information about the source of the SOA. SOA models that retain information (e.g., biogenic vs. anthropogenic SOA) have correspondingly more transportable species; Lane et al., (2008b) retained four VBS bins for each SOA precursor source. Other 1D-VBS implementations have used a wider volatility range, for example transporting seven species with  $0.01 \le C^* \le 10\,000$  for SOA formed via oxidation of evaporated primary emissions (Shrivastava et al., 2008).

Aging schemes within the 1D-VBS employ a single coupling matrix (Donahue et al., 2006) that can vary with ambient conditions to represent changes in chemistry (Lane et al., 2008b). However, individual VBS bins can include such different species as  $C_{23}H_{48}$  (tricosane) and  $C_6H_{10}O_5$  (levoglucosan). There is good reason to believe that the chemistry of these species is quite different – most notably, fragmentation is likely to become more important with increasing oxygenation (Kroll et al., 2009; Kroll et al., 2011). Furthermore, the degree of oxidation is an important diagnostic of ambient (Zhang et al., 2007; Jimenez et al., 2009) and chamber (Shilling et al., 2009; Chen et al., 2011) OA measurements. While fragmentation is described in the original 1D-VBS implementation (Donahue et al., 2006), the oxygen content is not tracked, cannot be used as a diagnostic, and cannot inform the

Chapter 2. Modeling Organonitrate Formation from  $\alpha$ -pinene ozonolysis

aging chemistry.

The 2D-VBS adds a second dimension of oxygenation (O : C) or average carbon oxidation state ( $\overline{OS}_C = 2O : C - H : C$ ) (Donahue et al., 2011; Donahue et al., 2012a). It was developed to capture these important defining properties of OA and track and predict changes over time.

The volatility and  $\overline{OS}_{C}$  of organic material are represented explicitly and evolve with aging chemistry, enabling explicit description of the production and evolution of SOA over time. In addition, rate constants for reactions with OH radicals are assigned based on typical chemical structures throughout the two-dimensional space (Donahue et al., 2013). While adding complexity, this expanded representation enables much more systematic exploration of different aging mechanisms in both box models (Donahue et al., 2012a) and Lagrangian chemical transport models (Murphy et al., 2012). It does not, however, enable explicit tracking of product categories such as organonitrates.

Here we describe a refinement to the 2D-VBS by introducing layers to hold key product classes – organonitrates in this case. This allows us to more accurately account for the effect of NO<sub>x</sub> on the production and evolution of SOA and to capture a more complete picture of organic aging by incorporating the production and removal of organonitrates. The model replicates experimental data on the effect of NO<sub>x</sub>, where high-NO<sub>x</sub> conditions increase SOA formation for certain precursors (longifolene) and decrease in others ( $\alpha$ -pinene) (Presto et al., 2005; Pathak et al., 2007; Kroll et al., 2006; Ng et al., 2007).

Mathematically, all implementations of the VBS are formally one-dimensional: an array of species is connected via a chemical coupling matrix that describes transformations due to aging reactions. However, the physical properties represented by that array of species can be cast into multiple dimensions – volatility, oxidation state, and now levels of key molecular classes. As part of the Supplement for this paper we have released a full implementation of the VBS, coded in MATLAB, providing full graphical diagnostics, access to the different levels of complexity (1-D, 2-D, layered), and instructions for alteration and

expansion (e.g. changing volatility or oxidation state ranges, adding layers).

### 2.2.2 Mathematical overview

The 2D-VBS follows the movement of carbon mass throughout the volatility and  $OS_C$  space by modeling the basic aging processes of functionalization and fragmentation. Functionalization adds functional groups, producing more oxidized organics that have lower volatility than the parent compound. Fragmentation splits the carbon backbone of an oxidized compound, producing two smaller compounds of higher volatility and generally higher  $\overline{OS}_C$  (Donahue et al., 2012a). The 2D-VBS implements these aging processes as a series of matrix manipulations.

While the 2D-VBS is typically presented as a two-dimensional space, it is implemented as a one-dimensional concentration vector in the code.

The mass of carbon  $(C_{v,o})$  per cubic meter  $(\mu g m^{-3})$  is described in each cell (v, o), where v is the volatility (x) index and o is the oxidation (y) index. This can be transformed into a single row vector  $\vec{C}$  with n elements, or cells,  $n = v \times o$ . The transformation method concatenates the rows (the volatilities of each O : C) together:

$$\begin{bmatrix} C_{1,1} & \dots & C_{x,1} \\ \vdots & \ddots & \vdots \\ C_{1,y} & \dots & C_{x,y} \end{bmatrix}$$

$$\rightarrow \begin{bmatrix} C_{1,1} \dots C_{x,1} C_{1,2} \dots C_{x,2} \dots C_{1,y} \dots C_{x,y} \end{bmatrix}.$$
(2.1)

The addition of dimensions, such as organonitrates, is implemented the same way by extending the one-dimensional array to track these compounds.

Chemical reactions can then be represented as transformations from an initial cell *i* to all potential final cells *f*; each transformation  $\vec{T}$  is a column vector of length *n*, with  $\sum_f T_f = 1$  (the transformations conserve carbon). The *n* transformation vectors for each initial cell *i* can then be concatenated to form an  $n \times n$  transformation matrix,  $\mathbf{T} = [\vec{T}_1 \dots \vec{T}_n]$ . The

overall chemical transformation is then given by  $\vec{C} \mathbf{T}$ .

The rate at which components react with OH (or any other oxidant) depends on their composition. Molecules with more carbons typically have more hydrogens available for abstraction reactions. Additionally, the more oxygens a molecule has, the more it is destabilized, and the more likely it will react (Kwok and Atkinson, 1995). However, when enough functional groups become attached to the carbon backbone, the remaining hydrogen atoms are typically less reactive, and so reactivity decreases. A composition–activity relationship from Donahue et al., (2013) accounts for these factors and is used to approximate rate constants gas-phase reactivity for each cell in the VBS. These values form a gas-phase reactivity vector,  $\vec{k}^{vap}$ :

$$\vec{k}^{\mathrm{vap}} \simeq -1.2 \times 10^{-12} (n_{\mathrm{C}} + 9n_{\mathrm{O}} - 10(\mathrm{O} \, : \, \mathrm{C})^2) \, \mathrm{cm}^3 \, \mathrm{molec}^{-1} \, \mathrm{s}^{-1},$$

where  $n_{\rm C}$  and  $n_{\rm O}$  correspond to the number of carbon and oxygen atoms, respectively.

We also parametrize the chemistry following the initial reaction with OH. The probabilities of fragmentation and functionalization are represented by vectors  $\vec{f}^{\text{frag}}$  and  $\vec{f}^{\text{func}}$ , respectively, where  $\vec{f}^{\text{frag}} = (O : C)^n$  and  $\vec{f}^{\text{func}} = 1 - \vec{f}^{\text{frag}}$ . The formula for the potential for fragmentation is determined by the higher likelihood of fragmentation when a molecule is highly oxidized, because of the destabilizing effect of functional groups on the carbon backbone. The exponent, n, expresses the strength of fragmentation reactions, and is currently estimated to be 1/4 (Donahue et al., 2012b).

Functionalization kernels are created using a distribution based on the degree of oxidation of the compound. The kernel is defined in terms of a probability distribution for added oxygen and decreased volatility (Donahue et al., 2012b). That distribution is then mapped onto the  $C^{\circ}$ , O:C space to form a functionalization transformation array. For each volatility cell *i*, functionalization ( $\vec{T}_i^{\text{func}}$ ) distributes carbon mass throughout the *n* VBS cells.

Fragmentation kernels describe the distribution of organic material throughout (mostly)

higher-volatility bins and O:C following cleavage of the carbon backbone. Some fragmentation products are molecules and some are radicals, which in turn are rapidly functionalized; the fragmentation kernel describes the ultimate distribution of stable products from this process and thus distributes carbon over a much wider range of the VBS than functionalization (Donahue et al., 2012b). The overall transformation vector  $\vec{T}_i$  is found for functionalization and fragmentation by combining the two processes together:  $\vec{T}_i = \vec{f}_i^{\text{frag}} \cdot \vec{T}_i^{\text{frag}} + \vec{f}_i^{\text{func}} \cdot \vec{T}_i^{\text{func}}$ . Also,  $\sum_{f=1}^n T_{i,f} = 1$ , meaning carbon mass is conserved. Concatenated over all columns, i = 1...n, the transformations form the transformation matrix **T**. The aging process is then expressed as

$$\frac{\partial \vec{C}}{\partial t} = \vec{k}^{\text{vap}} \cdot [\text{OH}] \cdot \vec{C} \left(\mathbf{T} - \mathbf{I}\right).$$
(2.2)

This can be modeled with differential solvers in MATLAB.

The transformations just described apply to species in the vapor phase. The VBS separately tracks vapor ( $\vec{C}^{\text{vap}}$ ) and condensed ( $\vec{C}^{\text{cond}}$ ) phase concentrations. For the condensed phase, the OH rate constant is specified as an effective gas-phase rate constant,  $k_i^{\text{eff}}$ , which is determined by the diffusion-limited uptake of gas-phase OH by particles, based on the Fuchs corrected surface area of a given particle size distribution (Donahue et al., 2013). We generally assume this is independent of composition and that OH reacts with unit efficiency once it reaches the surface of a particle. Lacking other constraints, we assume that  $\vec{f}^{\text{func}}$  and  $\vec{f}^{\text{frag}}$  are the same in the gas and condensed phases, so  $\vec{T}^{\text{vap}} = \vec{T}^{\text{cond}}$ ; however, it is likely that even the functionalization and fragmentation kernels differ in the gas and condensed phases, so we anticipate that future refinements will remove this assumption.

Additional details on the distribution of material throughout the VBS may be found in Donahue et al., (2012b) and Murphy et al., (2012).

### 2.2.3 Treatment of organonitrates

The introduction of NO<sub>x</sub> to the system brings additional chemical reactions and the potential to form organonitrates through the functionalization process. Organonitrates are accounted for in a separate layer of the 2D-VBS, called the "N<sub>1</sub>" layer for the inclusion of an atomic nitrogen. The addition of a nitrate group decreases the volatility by ~2.5 orders of magnitude (Pankow and Asher, 2008) and increases the number of oxygens attached to the carbon backbone by 1 (the other oxygen atoms and the nitrogen constitute an NO<sub>2</sub> group).

This has the potential to produce high concentrations of organonitrates in the condensed phase because of the large decrease in the volatility of the product compared to the reactant.

The formation of an organonitrate involves two branch points. The first is the probability  $(1 - \beta)$  that RO<sub>2</sub> will react with NO; the second is the yield,  $\eta$ , of organonitrates from RO<sub>2</sub> + NO. The nitrate yield  $\eta$  rises with increasing carbon number (Arey et al., 2001; Yeh and Ziemann, 2014) and depends on the functionality of the RO<sub>2</sub> (Lim and Ziemann, 2009; Elrod, 2011); however, for organics large enough to partition to the condensed phase,  $\eta$  is at an asymptotic limit, and we assume a homogeneous distribution of RO<sub>2</sub> structures within any given VBS cell. We thus assume that  $\eta = 0.30$  in all cases. Various ways of estimating  $\beta$  are possible, such as from the VOC : NO<sub>x</sub> ratios obtainable in experimental data (Presto et al., 2005) to the comparison of the rates of reaction between RO<sub>2</sub> + NO and RO<sub>2</sub> + HO<sub>2</sub> (Lane et al., 2008a). In this work, we will simply vary  $\beta$  parametrically.

There are now three different transformation pathways for organics in the  $N_0$  (nonorganonitrate) layer: they can fragment, functionalize without forming organonitrates, or form organonitrates. As a simplification, we assume that there are two pathways for organonitrates in the  $N_1$  layer: they can fragment by eliminating the NO<sub>2</sub> group and return to the  $N_0$  layer, or they can functionalize and remain in the  $N_1$  layer. Also as a simplification we assume that dinitrates with 2-ONO<sub>2</sub> functional groups are minor products, and so



Figure 2.1: Atomic N:C ratio isopleths in the organonitrate layer of the 2D-VBS. The volatility space is divided into regions of organic compounds: extremely low volatility (ELVOC), low volatility (LVOC), semi-volatile (SVOC), intermediate volatility (IVOC), and volatile (VOC). Most organonitrate aerosols will have an N:C ratio lower than 0.2. The green line represents the single oxygen isopleth under which no organonitrate exists, because organonitrates themselves contribute an oxygen to the O:C ratio.

we do not add an N<sub>2</sub> layer. The transformations for the organonitrate case are analogous to the non-organonitrate case, but with expansions to accommodate the production and loss of organonitrates. The concentration array doubles in size:  $\vec{C} = [\vec{C}_{N_0}\vec{C}_{N_1}]$ , where  $\vec{C}_{N_0}$ represents all the cells in the N<sub>0</sub> layer and  $\vec{C}_{N_1}$  represents the cells in the N<sub>1</sub> layer. More complex is the transformation matrix, which is now

$$\mathbf{\Gamma} = \begin{bmatrix} \mathbf{T}_{N_0 \to N_0} & \mathbf{T}_{N_0 \to N_1} \\ \mathbf{T}_{N_1 \to N_0} & \mathbf{T}_{N_1 \to N_1} \end{bmatrix},$$
(2.3)

where  $\mathbf{T}_{N_0 \to N_0}$  represents the original functionalization and fragmentation of the nonorganonitrate layer.  $\mathbf{T}_{N_0 \to N_1}$  is the formation of an organonitrate through functionalization.  $\mathbf{T}_{N_1 \to N_0}$  is the fragmentation of an organonitrate.  $\mathbf{T}_{N_1 \to N_1}$  is the functionalization of an organonitrate. The organonitrate (N<sub>1</sub>) layer of the 2D-VBS contains only one nitrate group, and thus each species contains a single nitrogen atom. Because  $n_N$  is constant, N : C drops as volatility decreases and the chemical species become larger. In addition, the oxy-

Chapter 2. Modeling Organonitrate Formation from  $\alpha$ -pinene ozonolysis

gen attached to the carbon from the nitrate group contributes to the O:C of the overall compound. Therefore, the O:C of an organonitrate can never be 0. Figure 2.1 shows N:C for the nitrate layer (N<sub>1</sub>) of the 2D-VBS. In the regime where aerosols tend to form under atmospheric conditions, N:C ranges from 0.04 to 0.3. Semi-volatile organonitrates have N:C from around 0.05 to 0.3; extremely low volatility compounds have an N:C lower than 0.2.

N:C for ambient aerosols are experimentally obtainable through atomic mass spectroscopy. Rollins et al., (2010) tested compounds that act as aerosol precursors in the atmosphere using the AMS, and the data from elemental analyses of these organic hydroxynitrates showed N:C ranging from 0.02 to 0.1. Other experiments of SOA production from isoprene, toluene, and naphthalene in high-NO<sub>x</sub> conditions show N:C ranging from 0.04 to 0.08, indicating the existence of low-volatility compounds with moderate levels of oxygenation (Chhabra et al., 2010). In addition to providing a sense of the range of N:C expected in aerosols, Fig. 2.1 also reveals the relationship between N:C and the size of the molecule itself. Molecules with very small N:C actually indicate high carbon content, meaning these organonitrates are, on a per-molecule basis, contributing significant mass to the overall organic aerosol.

#### 2.2.4 Time evolution

Once the transformation matrix **T** has been specified for any VBS configuration, the time evolution is trivially specified. A final detail is that we separate vapor-phase and particle-phase processes to treat the very different kinetics of homogeneous and heterogeneous oxidation (Donahue et al., 2013). This also facilitates dynamical treatments of aerosol processes (Trump et al., 2014; Trump and Donahue, 2014). We can also treat oligomerization within the condensed phase (Trump and Donahue, 2014), though we shall not address that here. Formally, this again requires that we double the concentration array to distinguish vapor- and condensed-phase concentrations:  $\vec{C} = [\vec{C}^{\text{vap}} \vec{C}^{\text{cond}}]$ . The transformation matrix

becomes

$$\mathbf{T} = \begin{bmatrix} \mathbf{T}^{\text{vap}} & 0\\ 0 & \mathbf{T}^{\text{cond}} \end{bmatrix}.$$
 (2.4)

This is block diagonal because we do not treat particle microphysics – condensation and evaporation – at this stage. That is left to a later step via operator splitting, whether we assume equilibrium partitioning or specifically treat the dynamics.

The change in the mass within each cell is described by n differential equations. For each cell *i* out of a total of n cells in the VBS,

$$\frac{\mathrm{d}\vec{C}}{\mathrm{d}t} = C_{\mathrm{OH}}\left[\left(\vec{k}\cdot\vec{C}\right)\mathbf{T} - \left(\vec{k}\cdot\vec{C}\right)\right] = C_{\mathrm{OH}}\left(\vec{k}\cdot\vec{C}\right)\left[\mathbf{T}-\mathbf{I}\right],\tag{2.5}$$

where the first term is the amount of mass that is reacted into the cell from all other cells, and the second term is the loss from reactions out of the cell.

Any differential equation solver can be employed to solve Eq. (2.5). We currently use the approximation  $\exp(-k\Delta t) \approx 1 - k\Delta t$  for small  $\Delta t$ .

As functionalized products shift into lower-volatility cells, they can condense into the aerosol phase. At equilibrium this is given by

$$\xi_i = (1 + \frac{C_i^*}{C_{\text{OA}}})^{-1} ; \ C_{\text{OA}} = \sum_i C_i^* \xi_i,$$
(2.6)

where  $C^*$  is the volatility (in  $\mu$ g m<sup>-3</sup>) of the compound,  $\xi$  is the fraction of organics in the condensed phase, and  $C_{OA}$  is the total organic aerosol mass. This is a constant balancing act – if more functionalized material with lower volatility forms and more mass condenses, some higher-volatility products will also condense. The reverse is also true – if fragmentation becomes dominant and higher-volatility products form, lower-volatility products may enter the vapor phase.

## 2.3 Results and discussion

Prior VBS model implementations have treated ozonolysis and subsequent OH multigenerational aging of  $\alpha$ -pinene in chamber studies. A 2D-VBS model reproduced aerosol mass well throughout the course of the Multiple Chamber Aerosol Chemical Aging Study (MUCHACHAS) experiments, which studied SOA aging under similar conditions in four different chambers (Donahue et al., 2012b). Building upon this, the current version (v1.0 in Bitbucket) of the 2D-VBS model can also model  $\alpha$ -pinene aging under high-NO<sub>x</sub> conditions with both ozonolysis aging and OH aging periods. While there are currently few high-NO<sub>x</sub> experimental data addressing multi-generational aging, mass yields of firstgeneration products from ozonolysis of  $\alpha$ -pinene are available (Pathak et al., 2007; Presto et al., 2005). Simulations for high-NO<sub>x</sub> cases are run based on these data.

In the examples shown, we run the model under ideal chamber conditions, where there are no wall losses. A concentration of  $100 \,\mu g \,\mathrm{m}^{-3}$  of  $\alpha$ -pinene is introduced into the chamber. For the first 2 h, we model dark conditions with a constant ozone level of 300 ppbv. The ozone reacts with the unsaturated carbon bonds to form first-generation products. At the end of 2 h, after all of the precursor material has been reacted to form first-generation products, OH is introduced into the chamber at a constant rate of  $10^7$  molecules cm<sup>-3</sup> for 10 h. This is the equivalent of turning on the UV lights in a chamber with a strong OH precursor such as HONO. The continued reaction of organic compounds creates multigenerational products, many of which are low volatility and condense into the aerosol phase. We have taken a low- and high-NO<sub>x</sub> case, where  $\beta = 1$  and  $\beta = 0.15$ , respectively, and examined the differences in aerosol production during first-generation chemistry and subsequent multi-generation chemistry.

Figure 2.2 shows the differences in concentration of aerosol mass produced under lowand high-NO<sub>x</sub> conditions throughout the course of the chamber model run. During firstgeneration chemistry, high-NO<sub>x</sub> conditions form very little aerosol mass, while low-NO<sub>x</sub> conditions produce high SOA mass. This is due to higher-volatility compounds that are generated because of the presence of  $NO_x$ , instead of the semi-volatile compounds in the absence of  $NO_x$ . When OH aging begins at low  $NO_x$ , the aerosol mass more than doubles as volatile compounds react to form highly functionalized, low-volatility species. An even more dramatic effect is seen in the OH aging of high- $NO_x$  first-generation compounds. While most first-generation products were too volatile to condense, subsequent aging pushed a significant portion of these organics into the aerosol phase. Under these model conditions, even with the dramatic increase in concentration, the high- $NO_x$  condition produces less overall mass during OH aging. This alternate pathway results in



Figure 2.2: Organic mass concentration over 2 h of dark ozonolysis followed by 10 h of OH aging for low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions. The OM for non-nitrates and organonitrates plots is under high-NO<sub>x</sub> conditions. High-NO<sub>x</sub> conditions decrease the overall organic aerosol mass produced throughout the course of a model run. At  $\beta = 0.15$  (85 % RO<sub>2</sub> + NO), the mass concentration of organonitrates is roughly equivalent to the mass concentration of non-organonitrates. While the contribution of the -NO<sub>2</sub> group itself is small, the organonitrate compounds can comprise a significant portion of the overall mass.



Figure 2.3: Mass of first-generation products for each cell in the 2D-VBS, from 100- $\mu$ g m<sup>-3</sup>  $\alpha$ -pinene + ozone at  $\beta = 0.15$ . (a) Total mass of all (organonitrate and non-nitrate) organics in both the suspended and vapor phases. (b) Total mass of all organics in only the suspended phase. The suspended phase concentration axis is 2 orders of magnitude smaller than the vapor phase; most of the first-generation mass remains in the vapor phase.

a significant contribution by organonitrates to the overall aerosol mass – organonitrates comprised nearly half of the total organic mass at one point during OH aging. While the mass of organonitrates is significant, if the AMS were to test this sample, it would measure only a small concentration of N-containing mass fragments (indicated with the dashed blue curve in the figure). In essence, these are very large organonitrate molecules that have significant impact on overall aerosol mass.

The distribution of mass under high-NO<sub>x</sub> conditions offers insight into the low mass production during first-generation aging. Figure 2.3 shows the first-generation distribution (at t = 0 of Fig. 2.2) of organics when  $\beta = 0.15$ . This distribution is based on chamber experiments by Pathak et al., (2007) and Presto et al., (2005) of  $\alpha$ -pinene ozonolysis under high-NO<sub>x</sub> concentrations. Figure 2.3a shows the distribution of all organics (both aerosol and vapor phase). The majority of the organics reside in the IVOC range, which is too volatile to condense in the typical mass loadings of the atmosphere. Figure 2.3b shows the distribution of total suspended material, comprised of both organonitrates and nonnitrates. This mass contains more oxidized material than those in the vapor phase and


Figure 2.4: The effect of peroxy-radical branching on the first-generation secondary organic aerosol concentration,  $C_{OM}$ . The *x* axis is the branching ratio for RO<sub>2</sub> reaction ( $\beta$ ), where  $\beta = 1$  corresponds to low-NO<sub>x</sub> conditions dominated by RO<sub>2</sub> + HO<sub>2</sub> and  $\beta = 0$  corresponds to high-NO<sub>x</sub> conditions dominated by RO<sub>2</sub> + NO. The *y* axis is the ratio of  $C_{OM}$  at a given value of  $\beta$  to the low-NO<sub>x</sub> value. Each curve represents a different amount of oxidized precursor, spanning 5 orders of magnitude from 10<sup>2</sup> to 10<sup>6</sup> µg m<sup>-3</sup>.

ranges from LVOC to SVOC. Compared to the first-generation distribution in low- $NO_x$  conditions shown in Fig. 2.2, the high- $NO_x$  condition produces less aerosol mass because of the overall higher volatilities of resulting compounds.

The previous figures have shown that the presence of NO<sub>x</sub> decreases aerosol mass production for  $\alpha$ -pinene under moderate loadings. Less volatile precursors like sesquiterpenes are affected differently by NO<sub>x</sub>. A precursor with a lower volatility than  $\alpha$ -pinene, such as longifolene, produces products with correspondingly lower volatility (Ng et al., 2007). While first-generation distributions for these precursors are currently lacking, we can emulate this effect by increasing the mass loading of  $\alpha$ -pinene instead. A precursor compound that is an order of magnitude less volatile than  $\alpha$ -pinene can be modeled by an order-of-magnitude increase in mass loading. Figure 2.4 shows a comparison of firstgeneration aerosol concentration under various  $\beta$  and mass loadings to the mass concentration produced under low NO<sub>x</sub>. This shows that, for lower mass loadings of  $\alpha$ -pinene such as 100  $\mu$ g m<sup>-3</sup>, increasing NO<sub>x</sub> levels decreases resultant mass. As the loadings increase in magnitude, the aerosol suppression effect of NO<sub>x</sub> decreases. When loadings reach 10<sup>5</sup>  $\mu$ g m<sup>-3</sup>, the effect is reversed, instead producing more mass as NO<sub>x</sub> levels increase. This has been shown in experimental data from Ng et al., (2007), where longifolene exhibits higher yields under high-NO<sub>x</sub> conditions than low-NO<sub>x</sub> conditions. Even though the presence of NO<sub>x</sub> produces first-generation compounds from longifolene that are higher in volatility than first-generation compounds produced under low NO<sub>x</sub>, these compounds are still LVOCs and SVOCs, and they partition into the aerosol phase. In addition, the organonitrate group contributes significant mass to the aerosol phase, resulting in the >1 high-NO<sub>x</sub> to low-NO<sub>x</sub> organic mass ratio. Depending on the volatility of the organic precursor, it is therefore possible for the presence of NO<sub>x</sub> to increase the total first-generation aerosol mass.

As these first-generation products undergo multi-generational chemistry, becoming a more complex mix of organics, the stark differences between the mass loadings under first-generation chemistry are dampened. Figure 2.5 shows the comparison between different  $\beta$  and different initial mass loadings with respect to the low-NO<sub>x</sub> ( $\beta = 1$ ) case, after 10 h of OH aging. This corresponds to the end of the time period in Fig. 2.2. While higher loadings continue to produce more aerosol mass, an increase in NO<sub>x</sub> now consistently produces lower mass. This comes from the tendency to cleave the nitrate group during fragmentation, decreasing the effect of the nitrate group on overall mass. In addition, the probability of fragmentation increases as functionalization continues throughout the course of aging, contributing to the loss of organonitrates and the loss of aerosol mass to the vapor phase.

The distribution of suspended mass throughout the VBS also changes over the course of OH aging. Figure 2.6 shows the distribution of mass in the 2D-VBS for the organonitrate



Figure 2.5: The effect of peroxy-radical branching on the aged secondary organic aerosol concentration,  $C_{OM}$ , after 10 h of oxidation by  $10^7$  OH cm<sup>-3</sup>. As in Fig. 4 the *x* axis is the branching ratio for RO<sub>2</sub> reaction ( $\beta$ ), where  $\beta = 1$  corresponds to the low-NO<sub>x</sub> conditions dominated by RO<sub>2</sub> + HO<sub>2</sub> and  $\beta = 0$  corresponds to high-NO<sub>x</sub> conditions dominated by RO<sub>2</sub> + NO. The *y* axis is the ratio of  $C_{OM}$  at a given value of  $\beta$  to the low-NO<sub>x</sub> value. Each curve represents a different amount of oxidized precursor, spanning 5 orders of magnitude from  $10^2$  to  $10^6 \,\mu \text{g m}^{-3}$ .

layer (Fig. 2.6a) and the non-nitrate (Fig. 2.6b) after 10 h of OH aging. This corresponds to the end points of the "OM of organonitrates" and "OM of non-nitrates" lines in Fig. 2.2. The organonitrate concentration is fairly small, and they are only moderately oxidized, while the non-nitrate organics are highly oxidized. Each cell of the organonitrate layer, with higher mass yet lower carbon numbers, is slower to react compared to the corresponding cell in the non-nitrate layer. However, as the organonitrates undergo repeated functionalization, fragmentation of the products becomes more preferable, leaving behind less oxidized material in the organonitrate layer. Fragmentation of these highly functionalized organonitrates cleaves the nitrate group, resulting in highly oxidized non-nitrate organics. As a result, the organonitrate layer tends to be less oxidized and semi-volatile, while non-nitrates are highly oxidized.

#### 2.4 CONCLUSION



Figure 2.6: The distribution of mass is plotted over the 2D-VBS space for multi-generation products, after 10 h of OH aging of 100  $\mu$ g m<sup>-3</sup>  $\alpha$ -pinene + ozone at  $\beta = 0.15$ . (a) The 1N layer, where the mass of products is highest in the moderately oxidized and semi-volatile ranges. (b) The 0N layer, where the mass is highly oxidized and lower in volatility.

#### 2.4 Conclusion

We have added a layer to the 2D-VBS to account for organonitrates. In addition, we have developed a module to treat the formation and aging of organonitrates under high-NO<sub>x</sub> conditions, and we released a complete implementation of this code in MATLAB.

There are relatively few experimental constraints on the behavior of organonitrates in SOA, especially for multi-generational aging. Unknowns include differences between homogeneous and heterogeneous oxidation and the fate of nitrates after fragmentation. As a simplification we have assumed that homogeneous and heterogeneous product distributions are the same and that fragmentation breaks the weakest bond in the organonitrate, assumed to be the O–NO<sub>2</sub> bond. However, it is certain that semi-volatile products (nitrates and non-nitrates alike) will react relatively rapidly in the gas phase and consequently that any first-generation semi-volatile products will not be long lived in the atmosphere.

We explored the aging chemistry of SOA under conditions typical of chamber experiments. During multi-generational aging under high- $NO_x$  conditions, the contribution of organonitrates to organic mass is similar to non-nitrate organics. This contribution of organonitrates to aerosol mass can be large even though the actual nitrate (- $ONO_2$ ) mass is low, because the N : C of condensed-phase organonitrates can be low. We also reproduced the enhancement of aerosol production in the presence of  $NO_x$ , under conditions such as high mass loadings or low-volatility precursors. This showed that the VBS is capable of accounting for these effects on extensive organic chemistry and emphasized the important role that  $NO_x$  plays as part of the aging process.

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## **Chapter 3**

# Modeling the Growth of Freshly Nucleated Particles

This chapter is a distillation of a paper published in *Nature* in 2016, as "Tröstl, Chuang et al.: The role of low-volatility organic compounds in initial particle growth in the atmosphere, Nature, 533, 527-531, doi:10.1038/nature18271, 2016. That paper describes experiments conducted in the CLOUD chamber at CERN on the growth of freshly nucleated particles formed (and grown) purely from products of  $\alpha$ -pinene ozonolysis. As the second author on the paper, I focused creating a dynamic chamber model for the experimental data using the volatility basis set framework. Much of the text of this chapter is taken from material in the main body and supplemental material of that paper, but the presentation here emphasizes my own contributions to the research.

#### 3.1 Introduction

About half of present-day cloud condensation nuclei (CCN) originate from atmospheric nucleation, frequently appearing as a burst of new particles near midday (Merikanto et al., 2009). Atmospheric observations show that the growth rate of new particles often accelerates between 1 and 10 nm (Kulmala et al., 2013; Kuang et al., 2012). In this critical size range new particles are most likely to be lost by coagulation with pre-existing particles (Lehtinen et al., 2007), thereby failing to form new CCN at sizes around 50-100 nm. Sulphuric acid vapour is often involved in nucleation but is too scarce to explain most subsequent growth (Nieminen et al., 2010; Riccobono et al., 2012), leaving organic vapours as the most plausible alternative, at least in the planetary boundary layer (Riipinen et al., 2012; Smith et al., 2008; Laaksonen and Kulmala, 2008; Donahue et al., 2013). While recent studies (Zhao et al., 2013; Donahue et al., 2011; Pierce et al., 2011) predict that low-volatility organic vapours contribute during initial growth, direct evidence has been lacking. The accelerating growth may result from increased photolytic production of condensible organic species in the afternoon (Kulmala et al., 2013) and the presence of a possible Kelvin (curvature) effect, which inhibits organic vapour condensation on the smallest particles (Nano-Köhler theory) (Kulmala et al., 2013; Kulmala, 2004), has so far remained ambiguous. Experiments performed in the CERN CLOUD chamber under atmospheric conditions investigated the role of organic vapours in the initial growth of nucleated organic particles in the absence of inorganic acids and bases such as sulphuric acid or ammonia and amines, respectively. Using data from the same set of experiments, Kirkby et al., (2016) show that organic vapours alone can drive nucleation. We focus on the growth of nucleated particles and find that the organic vapours that drive initial growth have extremely low volatilities (saturation concentration  $C^* < 10^{-4.5} \,\mu \text{g m}^{-3}$ ). As the particles increase in size and the Kelvin barrier falls, subsequent growth is primarily due to more abundant organic vapours of slightly higher volatility ( $10^{-4.5} \le C^* \le 10^{-0.5} \,\mu \text{g m}^{-3}$ ). We present here a particle growth model that quantitatively reproduces our measurements.

#### 3.2 Aerosol Growth Model

The net condensation flux is defined as Seinfeld and Pandis, 2006:

$$\phi_{i,p}^{c} = N_p \underbrace{\left( \frac{\pi}{4} \left( D_p + D_i \right)^2 \right)}_{\substack{\text{particle-vapour collision cross section \\ \sigma_{i,p}}} \underbrace{\left( \frac{\pi}{4} \left( D_p + D_i \right)^2 \right)}_{\substack{\text{particle-vapour collision cross section \\ \sigma_{i,p}}} \underbrace{\left( \frac{C_i^v - a'_{i,p} C_i^0}{\alpha_{i,p} v_{i,p} \beta_{i,p}} \right)}_{\substack{\text{driving force of condensation \\ F_{i,p}}} = \alpha'_{i,p} \nu_{i,p}^c C_i^0 \left[ S_i - a'_{i,p} \right]$$
(3.1)

with  $N_p$  the particle number concentration,  $D_p$  the particle diameter,  $D_i$  the vapour diameter,  $\alpha_{i,p}$  the accommodation coefficient, the vapour concentration  $C_i^v$  and the saturation vapour concentration of  $C_i^o$ . In the following the indicated terms of eq. 3.1 will be further explained.

**Deposition rate coefficient:** In the molecular regime the collision cross section is the appropriate metric of a collision probability. Here we assume a hard-sphere limit, neglecting charge interactions. The deposition rate coefficient is corrected for the transition regime using the  $\beta_{i,p}$  correction factor (Fuchs and Sutugin, 1965).

$$\beta_{i,p} = \frac{Kn(1+Kn)}{Kn^2 + Kn + 0.283 Kn \alpha_{i,p} + 0.75 \alpha_{i,p}}; \qquad Kn = \frac{2\lambda}{D_p}$$
(3.2)

The  $\beta_{i,p}$  correction term and the mass accommodation coefficient  $\alpha_{i,p}$  are connected, as the correction term considers the onset of the gas-phase concentration gradients near the particle. For very small particles (Knudsen number,  $Kn \gg 1$ ), no gradients exist. However, for very large particles ( $Kn \ll 1$ ), the gas concentration at the particle surface can be near zero even with  $\alpha_{i,p} < 1$ . The effective mass accommodation coefficient,  $\alpha'_{i,p'}$  is therefore introduced as well.

For the collision between vapours and ultrafine particles, the reduced mass  $\mu_{i,p}$  needs to be considered;  $v_{i,p}$  is then the center of mass velocity:

$$v_{i,p} = \sqrt{8RT/(\pi\mu_{i,p})}; \quad \mu_{i,p} = M_i M_p / (M_i + M_p)$$
 (3.3)

The two first terms - collision cross section and the deposition rate - can be combined. Instead of using the cross section, the suspended surface area  $(N_p \pi D_p^2)$  can be used. The modified deposition rate coefficient is then given by:

$$s_{i,p} = \frac{(D_p + D_i)^2}{D_p^2} \frac{v_i}{4} \alpha_{i,p} \beta_{i,p}$$
(3.4)

**Condensation sink:** Combining the surface area and the deposition rate coefficient we can calculate the collision frequency, which is the frequency with which species *i* collides with the particle surface:

$$\nu_{i,p}^{c} = v_{i}\beta(D_{p}, \alpha_{i} = 1)(\pi D_{p}^{2}N_{p})$$
(3.5)

The condensation sink,  $k_c = \sum_p \alpha'_p \nu^c_p$ , gives the actual time constant for interaction of vapours with particles. The condensation sink is also the fundamental equilibration time-scale between the gas and particle phases when condensation is the main loss of vapours.

**Driving force of condensation:** The driving force of condensation  $F_{i,p}$  and excess saturation ratio  $S_{i,p}^{XS}$  are:

$$F_{i,p} = \left[C_i^v - a'_{i,p}C_i^0\right] = C_i^0 \underbrace{\left[S_i - a'_{i,p}\right]}_{S_i^{XS}}$$
(3.6)

The saturation ratio (gas-phase activity) is  $S_i = C_i^v/C_i^0$ . The term  $a_{i,p}$  is the activity of the species *i* at the condensed-phase surface of the particle ( $a_{i,p} = X_{i,p}\gamma_{i,p}$ , Raoult term), where  $X_{i,p} = C_{i,p}^s/C_p^s$  is the mass fraction, and  $\gamma_{i,p}$  the mass based activity coefficient in the organic condensed phase. Due to their curved surfaces, the activity of a small particle  $-a'_{i,p} = a_{i,p}K_{i,p}$  - includes the Kelvin term  $K_{i,p}$ . The Kelvin term is defined as (Seinfeld and Pandis, 2006):

$$K_{i,p} = 10^{D_{K10}/D_p} = exp\left(\frac{4\sigma_i M_i}{RT\rho_i D_p}\right)$$
(3.7)

$$D_{K10} = \log_{10}(e) \cdot \frac{4\sigma_i M_i}{RT\rho_i}$$
(3.8)

with the surface tension  $\sigma$ , the molar weight M and the density  $\rho$ . For very small particles a large supersaturation is needed to allow for condensation. For  $\sigma = 0.023 \,\mathrm{Nm^{-1}}$ , a molar weight of 300 g/mol at 300 K,  $D_K = 3.75 \,\mathrm{nm}$ . Any charge effect on the growth rate would appear in either an enhancement to the collision cross section,  $\sigma_{i,p}$ , due to charge-dipole interactions, or a change in the effective Kelvin diameter reflecting enhanced stability of small clusters. Further investigation of a possible enhancement in the growth rate caused by ions requires dedicated experiments.

**Equilibrium solution:** At equilibrium,  $F_{i,p}$  is zero. In this case, equilibrium partitioning is the basis for organic aerosol calculations. Aerosol partitioning theory describes the condensation and evaporation of gas phase species on or from an aerosol surface (Pankow, 1994). The fraction of the condensed phase (*s*) of a species *i* in the suspended aerosol particle within the partitioning frame work is defined as

$$f_i^s = \frac{1}{1 + C_i^* / C_{OA}^s} \tag{3.9}$$

 $C_i^*$  is the effective saturation concentration of the vapour and  $C_{OA}^s$  the concentration of species k in the particle phase.

Steady-state solution: Organic aerosol production,  $P_i$ , (or loss) is inherently not an equilibrium process, but many terms will reach a steady state in different situations. There are two relevant limits: one where condensation to suspended particles controls the vapour concentrations on a timescale given by the condensation sink ( $\alpha'\nu_p^c$ ), and one where losses,  $k_i$  (i.e. wall losses), control those vapour concentrations. We are interested in the steadystate saturation ratios  $S_i^{ss}$  and excess saturation ratio  $S_i^{xs,ss}$ .

When losses control the steady-state,  $S_i^{ss} = (P_i/C_i^o)/k_i$ . If the suspended particles con-

trol the steady-state, the excess saturation ratio will be in steady state. A fraction of  $P_i$  will go to vapours and a fraction to the particles. The latter fraction will be approximately  $f_i^s$ .

$$\phi_i^{xs} = f_i^s P_i = \alpha' k^c C_i^o [S_i - a_i'] = \alpha' k^c C_i^o S_i^{xs,ss}; \quad S_i^{xs,ss} = f_i^s \frac{P_i / C_i^o}{\alpha' k^c}$$
(3.10)

 $S_i^{xs,ss}$  is a key diagnostic for organic condensation. If  $S_i^{xs,ss} \gg 1$ , the condensation will be essentially "non-volatile" ( $a'_{i,p}$  will have no influence on the condensation), while if  $S_i^{xs,ss} \leq 1$  then the condensation will be "semi-volatile". Finally, if  $S_i^{xs,ss} \ll 1$ , species *i* cannot be an important driver of the condensation, as  $a'_{i,p}$  cannot grow larger than  $S_i$ during net gas-phase production.

#### 3.3 Experimental Data

Two measurement campaigns at the CERN CLOUD chamber focused on aerosol growth with different levels of sulphuric acid and  $\alpha$ -pinene oxidation products. With the chamber at 278 K and 38% relative humidity, tropospheric concentrations of  $\alpha$ -pinene, ozone and SO<sub>2</sub> were introduced. Using various instruments (Figure 3.1) we measured the behaviour of freshly nucleated 1-2 nm diameter particles and their subsequent growth up to 80 nm. Two chemical ionisation mass spectrometers using nitrate as the reagent ion (nitrate-CI-APi-TOF) measured the concentrations of sulphuric acid and highly oxygenated organic compounds (Jokinen et al., 2015; Ehn et al., 2014). Nitrate anions tend to cluster with highly oxygenated molecules (HOMs), and the measured HOMs fall broadly into two product ranges based on carbon number (Figure 3.2): monomers,  $C_xH_yO_z$  with x=8-10, y=12-16 and z=6-12, and dimers with x=17-20, y=26-32 and z=8-18.

Here we refer to these measured compounds as HOMs rather than Extremely Low-Volatility Organic Compounds (ELVOCs), as previously reported (Ehn et al., 2014). As we shall show, the HOM volatility spans a wide range (although it is always very low), and we shall separate HOMs into volatility bins using the volatility basis set (VBS) (Donahue



Figure 3.1: Appearance times of clusters and aerosols as seen by APi-TOF, DEG, PSM, nRDMA, NAIS, and Nano-SMPS.

et al., 2012).

To explore the potential role of HOM volatility, we use the SIMPOL model (Pankow and Asher, 2008) to estimate the saturation mass concentration ( $C^*$ ,  $\mu g m^{-3}$ ) and saturation molecular concentration ( $N^*$ , cm<sup>-3</sup>) of each HOM using its measured atomic composition together with an estimation of its likely chemical structure (see 3.3).

We grouped the HOMs in volatility bins (separated by factors of ten) and assigned them to several volatility classes (see Figure 3.4).

The HOMs span a wide range from extremely low-volatility (ELVOC,  $C^* < 10^{-4.5} \,\mu \text{g m}^{-3}$ ;  $N^* < 5 \cdot 10^4 \text{ cm}^{-3}$  assuming a molecular mass of 300 Da) to low-volatility (LVOC,  $10^{-4.5} \leq C^* \leq 10^{-0.5} \,\mu \text{g m}^{-3}$ ;  $5 \cdot 10^4 \leq N^* \leq 5 \cdot 10^8 \text{ cm}^{-3}$ ) to some semi-volatile (SVOC,  $10^{-0.5} \leq C^* \leq 10^{2.5} \,\mu \text{g m}^{-3}$ ;  $5 \cdot 10^8 \leq N^* \leq 5 \cdot 10^{11} \text{ cm}^{-3}$ ) organic compounds. In Figure 3.5a we show a mass defect plot of the observed compounds during a representative run, and in Figure 3.5b we show the corresponding volatility distribution (colours based on Donahue et al., (2012)). The binned volatility distribution of measured gas-phase organic



Figure 3.2: **Observed mass spectrum as seen by the nitrate-CI-APi-TOF at 278 K, 38% relative humidity.** A steady state mixing ratio of approximately 250 pptv of  $\alpha$ -pinene was established in the chamber in the presence of 35 ppbv ozone and no injection of SO<sub>2</sub>. Black bars indicate all identified monomers and dimers, with the red bars indicating the corresponding m/Q range. Intermediate molecules or clusters (with carbon atoms between 11 and 17) that cannot be explained by the formation mechanism shown in Kirkby et al., (2016), are indicated by the cyan bars.

species (Figure 3.5b) shows a substantial fraction of ELVOCs, maximal contribution in the LVOC range and even low levels of SVOCs. Because the LVOCs and SVOCs do not build up a sufficient saturation ratio to overcome the Kelvin barrier, they should not be able to condense onto the smallest particles, so that only the ELVOCs should contribute to the initial growth. While nitrate ions cluster efficiently with ELVOCs and calibration based on sulphuric acid should be fairly accurate, the concentration of LVOCs and SVOCs is likely to be underestimated because of inefficient clustering (Hyttinen et al., 2015). Indeed, SVOCs are formed with high yield in  $\alpha$ -pinene oxidation (Presto and Donahue, 2006) but most of them evidently are not detected by the nitrate-CI-APi-TOF. The fact that even the non-volatile model based on measured HOMs underestimates the observed growth rates for particles >5 nm by a factor of three strongly indicates that the concentration of condensing organic vapours is significantly higher than measured, at least after the Kelvin



Figure 3.3: **Possible structures of**  $\alpha$ **-pinene oxidation products.** (a) Possible structures of HOM monomer molecules.  $C^*$  was estimated using the SIMPOL method (at 293 K). Note that the volatility is less once the ring structure is open. The volatility generally decreases with increasing oxidation and decreasing temperature. (b) Possible structures of HOM dimer molecules.  $C^*$  was estimated using the SIMPOL method (at 293 K). Structures with \* and \*\* were confirmed by or taken from Kurtén et al., (2015), respectively.

barrier has diminished.

We further consider two very different experiments. During the first experiment, the HOM concentration increased non-linearly with time, which replicates the diurnal variation of biogenic emissions and oxidants in the ambient for the morning and early afternoon



Figure 3.4: Estimation of  $C^*$  for monomer and dimer molecules at 293 K. Colours indicate the volatility class based on Donahue et al., (2012). A linear fit was applied to the  $C^*$  estimates (dashed lines). This fit was then applied to all compounds using their O:C ratio to estimate  $C^*$  for all observed compounds.

(Figure 3.6a). This situation leads to a non-linear increase in the growth rate. During the second experiment, the HOM concentration remained at a constant steady state (production balanced by wall loss). This allowed us to test whether the accelerating growth seen in the first experiment was due to the diminishing Kelvin effect or the increasing HOM concentration. The constant HOM concentration led to a nearly constant growth rate, except for the smallest particles below  $\sim$ 5 nm (Figure 3.6d).

#### 3.4 Model Results

In order to quantify the importance of the Kelvin effect and HOM measurement biases, we analysed the contribution of HOMs to early growth and assessed the dependence on HOM volatility by using a dynamic volatility-distribution model (Trump and Donahue, 2014) for these two cases. The HOM volatility-distribution model comprises 9  $C^*$  bins ranging from  $10^{-8}$  to 1 µg m<sup>-3</sup> ( $10^1$  to  $10^9$  cm<sup>-3</sup>), split into three ranges (see Figure 3.5



Figure 3.5: **Observed gas-phase HOMs and their volatility distribution.** (a) Mass defect plot of all HOMs including the estimated volatility distribution based on the proposed structures (3.3). The marker size is proportional to the logarithm of the counting rate. White circles are  $C_5$ - $C_7$  compounds, which were not included in the volatility analysis. (b) HOMs binned to a volatility distribution showing the measured relative counting rates in per cent, with ELVOCs comprising ~ 36%.

and 3.7): ELVOC (grey), LVOC (pink) and SVOC (light green). When we run the HOM volatility-distribution model using the directly measured volatility-binned HOM concentrations as input, the simulated growth rates for particles >2 nm are underestimated by a large factor (see 3.8, blue dashed line). This is consistent with the expectation that the detection efficiency of LVOCs in the nitrate-CI-APi-TOF is lower as discussed above.



Figure 3.6: **Comparison of the growth rates in two experiments with a dynamic volatility basis set (VBS) model.** Panel (a) shows the temporal evolution of the particle size and the modelled particle size for an experiment with increasing HOM concentration, and panel (b) for constant HOM concentration. Panel (c) shows the size-dependent modelled and measured growth rate for the increasing HOM concentration, and panel (d) for the constant HOM concentration. Colours indicate the contribution of different volatility bins to the condensational growth. Error bars indicate the error of the fit alone, whiskers  $1\sigma$  total errors of the measured growth rates.

We tuned the LVOCs on the basis that the charging efficiency is lower for less oxidized compounds. From Figure 3.5a, the less oxidized LVOCs are also higher in volatility. Therefore, we scale the higher volatility LVOCs by a larger factor, and the lower volatility LVOCs by a smaller factor. Our best result was achieved with values of [0.5, 0.4, 0.3, 0.1] for the VBS bins from  $10^{-4}$  to  $10^{-1}$  µg m<sup>-3</sup>, meaning that we increased the raw measured values by [2, 2.5, 3.3, and 10].

An attempt to adjust the HOM volatility-distribution by increasing the LVOCs to repro-

duce the observed growth rates was not successful (see 3.8, blue solid line). The model can be brought into agreement with observations by increasing the LVOC concentrations and introducing a Kelvin effect (Figure 3.6 and 3.8 grey line). This tuned model, adjusting for inefficient LVOC measurement in the nitrate-CI-APi-TOF and considering the Kelvin effect (see 3.7b and 3.9 for details), captures the observed particle growth in both example cases with high fidelity (Figure 3.6). While the agreement at 10 nm diameter is ensured by our LVOC correction, the Kelvin term is essential to reproduce the observed growth rate over the full size range for these two quite different cases, although the strong size dependence in Figure 3.6a is primarily due to the increasing HOM concentration. This is evidence that the Kelvin term (along with abundant LVOCs) is responsible for the acceleration in growth observed in field experiments in the afternoon, and that only ELVOCs have a sufficiently



Figure 3.7: **HOM distribution binned to a volatility basis set.** (a) Measured HOM distribution (green) binned to a volatility basis set. As the nitrate-CI-APi-TOF is expected to underestimate SVOC, which are often observed during secondary aerosol aerosol formation in smog chamber studies, we added a representative SOA bin at  $\log C^* = 0$  (light green). (b) Modified HOM distribution after scaling for the weaker charging efficiency for LVOC (light green). The ELVOC:LVOC:SVOC ratios are **a**, 20:34:46 and **b**, 7:77:16.

high saturation ratio to overcome the Kelvin barrier at the smallest sizes.

ELVOCs govern the contribution to growth up to  $\sim$ 2 nm; beyond this, LVOCs take over in sequence as the Kelvin effect becomes progressively weaker with increasing size. Thus, while growth rates in the non-volatile HOM model decrease by a factor of  $\sim$ 3 between 1 and 5 nm, in the volatility-distribution HOM model they increase by a factor of  $\sim$ 3 over this



Figure 3.8: Dynamic volatility-distribution modeling results with and without Kelvin term and with original and modified HOM volatility distribution for the case of constant HOMs. (a) Different model approaches compared to the measured diameter evolution. (b) Enlargement of the first 30 minutes of the experiment and first 5 nm of the diameter evolution. (c) Size dependent growth rate for different model approaches. The Kelvin effect is essential to describe the measured diameter behaviour. Using the original volatility distribution (blue dashed line), the model slightly overestimates the initial growth but strongly underestimates it at larger sizes. Although considering a Kelvin effect fits the initial growth well, growth at larger sizes is underestimated even more (pink dashed line). By adjusting the HOM volatility distribution in the model with no Kelvin effect, the best fit (blue solid curve) still fails to reproduce the observations, substantially overpredicting growth at small sizes and then underpredicting growth at larger sizes. However, adjusting the volatility distribution and treating the Kelvin effect captures the growth well over the full size range (grey solid line). Error bars indicate  $1\sigma$  systematic scale uncertainty of the determined growth rates.



Figure 3.9: **Dynamic volatility-distribution model details.** (a) Vapour and condensedphase activities during a simulated particle growth event in CLOUD (Figure 3.6b, d). Vapours are in steady-state with respect to production and wall loss, with the saturation ratio increasing monotonically with decreasing volatility. (b) Excess saturation ratios (left) and particle composition (mass fractions; right) during simulated particle growth event in CLOUD. (c) Driving force of condensation (left)and equilibrium concentrations of vapours over particles (right) during simulated particle growth event in CLOUD. Volatility is indicated by brightness, with darkest grey corresponding to  $C^* = 10^{-8} \,\mu \mathrm{g \, m^{-3}}$ .

range, consistent with observations. This volatility distribution growth model is a version of "nano-Köhler theory", in which the effects of condensed-phase mixing (Raoult's law) and particle curvature (the Kelvin term) combine for miscible organics. The Kelvin effect dominates because curvature enhances particle-phase activities by orders of magnitude for the smallest particles, regardless of their particle composition, and the critical issue is whether the saturation ratio of an LVOC volatility bin exceeds this threshold (see 3.9 for detailed model results). Finally, the volatility-distribution model shows that, in the experiments, SVOCs cannot contribute to the observed growth via non-reactive uptake as their gas-phase saturation ratio never rises high enough for them to contribute (Figure 3.9).

### 3.5 Conclusion

The  $\alpha$ -pinene + ozone system explored here is among the most efficient sources of ELVOCs yet observed (Ehn et al., 2014; Jokinen et al., 2015), but it is likely that many sources of LVOCs may be important in the atmosphere. The latter include the first-generation compounds described here but also later-generation "aging" products by OH radicals (Schobesberger et al., 2013; Riccobono et al., 2014; Donahue et al., 2013). Different sources are almost certain to produce LVOCs with differing volatility distributions and chemical properties, which also might influence their reactivity in the condensed phase, including oligomerisation (Trump and Donahue, 2014) and reactive uptake (Wang et al., 2010), resulting in different growth patterns compared to those in Figure 3.6. These growth patterns thus constitute a critical and variable link between new particle formation and CCN formation.

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## Chapter 4

## Where New Yields Lead Us

The growth-rate measurements and calculations presented in the previous chapter represent a conundrum. The growth rate can only be explained by condensation resulting in organic compounds of very low volatility (ELVOCs and LVOCs in Volatility Basis Set parlance); otherwise the compounds would simply evaporate back off the very small particles. The model presented in that work for formation of highly oxidized multifunctional compounds from  $\alpha$ -pinene ozonolysis successfully described the observed growth rates under different conditions, but with an embedded assumption that the sensitivity of the nitrate chemical ionization mass spectrometer was less sensitive to the LVOCs than the ELVOCs and thus that there were actually more LVOCs than suggested by the raw signals. The actual mass yield of ELVOC and LVOC products required from  $\alpha$ -pinene ozonolysis is very high — of order 37% — and this is the conundrum. The very large yields would seem to be in sharp disagreement of more traditional smog-chamber experiments (including those conducted at CMU) that suggest quite low (< 1%) mass yields of very low vapor pressure compounds. This chapter explores possible answers to that problem.

### 4.1 Introduction

The mass yields of Secondary Organic Aerosols (SOA) under ambient conditions are a central issue in atmospheric chemistry. SOA production from biogenic compounds, especially monoterpenes such as  $\alpha$ -pinene, has been studied for decades because of its contribution to "blue haze" (Haagen- Smit, 1952) and its potentially large contribution to background aerosol concentrations both in the pre-industrial and present-day atmosphere (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Traditional smog-chamber experiments have been interpreted since Odum et al., (1996) in the context of equilibrium partitioning theory (Pankow, 1994). Specifically, the mass yield of SOA in smog-chamber experiments is defined as the mass of SOA formed ( $C_{OA}$ ) divided by the amount of precursor consumed ( $\Delta C_{prec}$ ), measured in  $\mu g m^{-3}$ . SOA mass yields characteristically increase with increasing  $C_{OA}$ , and Odum's key insight was to realize that this was consistent with equilibrium partitioning theory (Pankow, 1994) and furthermore that "Odum plots" of mass yield vs  $C_{OA}$ organized seemingly scattered experimental data and could be interpreted via the now widely used "two-product" equilibrium partitioning model (Odum et al., 1996).

Ozonolysis of  $\alpha$ -pinene has been extensively studied, and the equilibrium partitioning analysis of Odum et al., (1996) to constrain the volatility of reaction products shows a dramatic increase as the SOA loading increases. Because aerosol loading (and product volatility) can span a wide range, the SOA loading axis of the Odum plot is best expressed along a log scale (Donahue et al., 2006). Smog-chamber experiments have typically covered a mass concentration range of  $1 \leq C_{OA} \leq 1000 \,\mu \text{g m}^{-3}$ , with and without inorganic seeds to promote condensation of vapors (Odum et al., 1996; Griffin et al., 1999; Cocker et al., 2001; Presto et al., 2005; Presto and Donahue, 2006; Pathak et al., 2007a; Shilling et al., 2008; Shilling et al., 2009; Song et al., 2007). These data show little to no mass yield for  $C_{OA} \leq$  $1 \,\mu \text{g m}^{-3}$ , but for  $1 \leq C_{OA} \leq 1000 \,\mu \text{g m}^{-3}$ , the mass yield increases dramatically. Even studies with high seed surface area (Pathak et al., 2007b; Song et al., 2007) and continuousflow chambers that should encourage equilibration (Shilling et al., 2009) show mass yields below 10% at low  $C_{\text{OA}}$ , though the results of Song et al., (2007) and Shilling et al., (2009) approach 10%. The equilibrium partitioning analysis relates the volatility of an organic species to determine at which loading ( $C_{\text{OA}}$ ) a compound would contribute significantly to the SOA mass yield (Presto and Donahue, 2006). For instance, for an aerosol loading of  $C_{\text{OA}} = 10 \,\mu\text{g} \,\text{m}^{-3}$ , an organic species with a volatility of  $C^* = 10 \,\mu\text{g} \,\text{m}^{-3}$  will partition 50% into the gas phase and 50% into the (organic) particle phase. If the loading were 10 times lower, at  $C_{\text{OA}} = 1 \,\mu\text{g} \,\text{m}^{-3}$ , the species would partition 90% into the gas phase and 10% into the particle phase. This equilibrium behavior motivates the volatility basis set, which separates compounds into volatility bins, each an order of magnitude apart (Donahue et al., 2006). In this way, an equilibrium partitioning analysis of smog-chamber data for  $\alpha$ -pinene SOA parses the yield data to form a distribution of compounds by their volatilities, with few to no compounds with low volatilities,  $C^* \leq 1 \,\mu\text{g} \,\text{m}^{-3}$ , and most of the mass with volatilities  $1 < C^* < 10^6 \,\mu\text{g} \,\text{m}^{-3}$  (Presto and Donahue, 2006).

Recent experiments using nitrate-ion clustering chemical ionization mass spectrometry (nitrate CIMS) have revealed the presence of "highly oxidized multifunctional organics" (HOMs) that have been interpreted as Extremely Low Volatility Organic Compounds (ELVOCs) and Low Volatility Organic Compounds (LVOCs, collectively (E)LVOCs) in the VBS nomenclature (Ehn et al., 2014). The molar yield of HOMs was initially estimated to be  $7 \pm 3.5\%$  (Ehn et al., 2014), and their volatilities are thought to be much lower than  $10^{-1} \ \mu g \ m^{-3}$  based on their molecular formulas and assumed structures. Recent experiments conducted in the CLOUD chamber at CERN confirmed a wide distribution of HOMs from oxidation of  $\alpha$ -pinene, especially by ozone, with the estimated volatility ranging from  $10^{-20} \leq C^* \leq 10^{-2} \ \mu g \ m^{-3}$  (Tröstl et al., 2016; Kirkby et al., 2016). The raw molar yields from the CLOUD nitrate-CIMS measurements were at the low end of prior measurements, near 3.5% (Kirkby et al., 2016), but flux-balance calculations based on the observed particle growth rates require more than three times the mass flux that can be explained by those measurements. Because the nitrate-CIMS relies on clustering between polar functional groups and the nitrate anion, which broadly corresponds with what makes the compounds have a low vapor pressure and stick to small particles, and because more volatile species that dominate (> 90%) the molar product distribution are invisible to the nitrate-CIMS, Tröstl et al., (2016) proposed that the clustering efficiency of the nitrate-CIMS scales with  $C^*$  and that the efficiency drops off in the LVOC volatility range. The empirically derived clustering efficiency quantitatively explained the observed particle growth rates for  $1 \le d_p \le 30$  nm, both at constant measured HOM concentrations and when the HOM concentrations were rising steadily. However, with molar yields well over 10% the derived mass yields of these highly functionalized ELVOC and LVOC products exceeds 30%.

The high mass yields of (E)LVOC products based on direct CIMS measurements from Ehn et al., (2014) and both CIMS measurements and dynamic flux balances based on growth rates from Tröstl et al., (2016) appear to contradict the earlier smog-chamber studies



Figure 4.1: A VBS equilibrium partitioning analysis for  $\alpha$ -pinene ozonolysis SOA compared with equilibrium partitioning expected from CIMS observations showing high yields of extremely low volatility (E)LVOC products.

CHAPTER 4. WHERE NEW YIELDS LEAD US

of  $\alpha$ -pinene ozonolysis SOA mass yields. We illustrate this in Figure 4.1, where we contrast the VBS equilibrium partitioning analysis carried out by Presto and Donahue, (2006) with the equilibrium expectations of the nitrate-CIMS (E)LVOC observations. In the equilibrium analysis we expect rising mass yields where  $C^* \simeq C_{OA}$ , indicated by the stacked histogram showing 50% partitioning for bins with  $C^* = C_{OA}$  and the black equilibrium partitioning curve. In contrast, if the mass yield of (E)LVOCs is of order 30% and even if they are at the extreme high end of the LVOC range suitable for condensation in Tröstl et al., (2016) with  $C^* \simeq 10^{-2} \,\mu \text{g m}^{-3}$ , we would expect the observed mass yields to rise to 30% by the time  $C_{OA} \ge 10^{-1} \,\mu \text{g m}^{-3}$  in an ideal, loss-free chamber, as shown by the solid green curve. There is a vast difference between the two curves. If these (E)LVOC products exist at such high mass yields, the simple question is thus: why do they not appear as high mass yields at low  $C_{OA}$  in the Odum plots? There are several possibilities:

- 1. Dynamical effects could delay condensation and thus bias the observed mass yields low for a given amount of precursor loss,
- Condensible vapor loss to the chamber walls could bias the observed mass yields low,
- Oligomerization and not direct condensation of (E)LVOCs could explain some of the CLOUD growth-rate observations, with uncertain effects on the SOA chamber mass yields,
- 4. High oxidation rates in the SOA chambers could interfere with HOM formation via the peroxy-radical auto-oxidation mechanism.

In the equilibrium partitioning interpretation, HOMs would instantly condense into the particle phase and show a high mass yield at low aerosol loading. However, barriers to condensation such as the Kelvin effect, a low mass accommodation coefficient, or simply a low aerosol surface area, can delay the effects enough that this mass does not appear until more  $\alpha$ -pinene has reacted, thus lowering the observed mass yield. Further, if condensation to suspended particles is low, vapor wall losses may be high (Matsunaga and

Ziemann, 2010; Ye et al., 2016a; Trump et al., 2016). While the growth-rate data demand that the eventual reaction products have a very low volatility, it is possible that condensed-phase chemistry ("oligomerization") (Kalberer et al., 2004) could produce ELVOC products in the CLOUD chamber on a timescale of several hours, driving the 2-6 nm hr<sup>-1</sup> growth rates, but be less evident in chamber SOA experiments where typical conditions involve  $\alpha$ -pinene oxidation in well under an hour and growth rates above 100 nm hr<sup>-1</sup>. Finally, those high oxidation rates in the chamber experiments could interfere with the RO<sub>2</sub> auto-oxidation chemistry (Ehn et al., 2014; Rissanen et al., 2014) by shortening the RO<sub>2</sub> bimolecular lifetime, thus sharply reducing the (E)LVOC mass yields in the SOA chamber experiments.

In this study, we begin by modeling aerosol growth dynamically within a VBS framework. Our objective is to explore whether the mass yields required to explain the growth rates observed in CLOUD do indeed over-predict the SOA chamber observations, as suggested by Figure 4.1, or whether some combination of dynamics, wall losses, and condensedphase chemistry may reconcile this apparent contradiction. Because of this, we shall consider only condensible products required to explain the CLOUD growth-rate observations (consisting broadly of products with  $C^* \leq 10^{-2} \,\mu \text{g m}^{-3}$ , whether formed in the gas or the condensed phase). We shall correct for the temperature difference, as the CLOUD experiments were conducted at 278 K and typical chamber SOA experiments have been conducted almost 20 K higher in temperature (corresponding to approximately a one-decade shift in volatility toward higher values in the SOA chamber experiments). Besides that, however, we shall not model production or condensation of any SVOC products (other than reactive monomers that ultimately oligomerize). The question is whether this reduced set of (E)LVOC products over-predicts SOA chamber mass yield experiments; any under-prediction would presumably be due to condensation of SVOCs in those experiments.

Recent studies imply that a dynamic approach is necessary to capture the interactions

#### 4.1 INTRODUCTION

between the organics in the vapor phase and the suspended phase (Mcvay et al., 2014; McVay et al., 2016), and the loss of vapors and particles to the chamber walls (Zhang et al., 2014). Because condensation is not instantaneous, some condensible vapors are lost to the walls instead of settling onto particles. The dynamic model accounts for the time it takes for vapors to interact with particles and condense, or hit the chamber wall and become absorbed by the Teflon.

We can use the model to explore how changes in chamber experiment parameters can change the production (mass yields) of organic aerosols. The production of particle mass depends on the ratio of the particle condensation sink to the wall loss sink. The particle condensation sink scales approximately proportionally with particle surface area. Therefore, to decrease the wall loss of condensible vapors, chamber experiments often use ammonium sulfate seeds to encourage condensation as opposed to relying on nucleation, which can result in high wall loss of condensible vapors early in experiments when the nucleated particle condensation sink is very low. However, the polydisperse seeds generated often span a wide size range, over an order of magnitude or more. At any point in time, each particle size has a different condensation sink, which affects the growth rate of the particle. This complicates calculations, as each particle would have a different growth rate and also (transiently) a different composition due to different surface-area to volume ratios. The polydispersity may also have implications in particle-phase chemistry (Shiraiwa et al., 2013), though that is not explored here. Saleh et al., (2013) showed that it is possible to use a monodisperse population with the size of a condensation sink diameter to approximate the dynamical behavior of a polydisperse aerosol suspension. We utilize a condensation sink diameter to compare the polydisperse and monodisperse versions of the model, and confirm that the condensation sink diameter provides a good approximation. We also look at how changes in the ratio between the particle condensation sink and the vapor wall loss affects production of suspended organic aerosol.

### 4.2 The Dynamic Model

#### 4.2.1 Mathematical background

We modeled the production of  $\alpha$ -pinene SOA using a dynamic 1-dimensional VBS. This was previously discussed in the supplemental material for Tröstl et al., (2016), but here we summarize the essential features. The VBS product distribution spans a volatility range  $10^{-8} \leq C^* \leq 10^{-1} \,\mu \text{g m}^{-3}$ , covering extremely-low-volatile to semi-volatile organic compounds (ELVOCs and LVOCs).

Interactions between the bulk vapors and suspended particles, and between chamber walls, are described by a set of ODEs for each volatility bin *i*:

$$\frac{dC_i^v}{dt} = P_i^{\text{prec}} - \phi_i^{v,s} - \phi_i^{v,t}$$
(4.1)

$$\frac{dC_i^s}{dt} = \phi_i^{v,s} - \phi_i^{s,d} \tag{4.2}$$

$$\frac{dC_i^t}{dt} = \phi_i^{v,t} \tag{4.3}$$

$$\frac{dC_i^d}{dt} = \phi_i^{s,d} \tag{4.4}$$

where superscripts identify reservoirs: v is vapor; s, suspended particles; t, teflon(wall)absorbed vapors; and d, wall-deposited particles. The superscript order is a transfer of mass from the first to the second reservoir.  $P_i^{\text{prec}}$  is the production of vapors through  $\alpha$ pinene ozonolysis, and is distributed according to the mass yield for each bin. Vapor phase HOMs generated through oxidation of  $\alpha$ -pinene either condense onto suspended particles  $(\phi_i^{v,s})$  or are irreversibly lost to the walls  $(\phi_i^{v,t})$ . Vapor wall loss is a first-order loss rate  $\phi_i^{v,t} = k^{v,t} C_i^v$  with a timescale of 10 minutes (Ye et al., 2016a; Krechmer et al., 2016; Trump et al., 2016). This is currently assumed to be irreversible, due to the low volatility of the HOMs and the high effective saturation concentration of the walls (McVay et al., 2016). A major difference between the CLOUD experiment and SOA production experiments in teflon chambers is that in CLOUD the collision frequency (condensation sink) of vapors to the walls typically exceeds the suspended condensation sink, whereas in most chamber SOA experiments the suspended condensation sink exceeds the wall collision frequency. Also, CLOUD is stainless steel whereas most SOA smog chambers are Teflon; especially on the metal surfaces, it is possible that reactive uptake (i.e. decarboxylation) is important. However, in each case we model the vapor wall loss as irreversible. Organics in the suspended phase can evaporate into the bulk vapor  $(-\phi_i^{v,s})$ ; alternatively, the particle itself with its mix of organics and seed can be irreversibly lost to the walls. This is determined by data on the first order loss rate of SOA in the chamber  $(\phi_i^{s,d} = k^{s,d} C_i^s)$ .

In a typical experiment, ammonium-sulfate seeds are first injected into a cleaned empty chamber to provide a condensation sink and also to constrain the particle wall loss rate constant. Then  $\alpha$ -pinene and ozone are added, producing HOMs that condense to the walls or seeds. For the experiments we explicitly model here, the suspended particle evolution was monitored with a Scanning Mobility Particle Sizer (SMPS), which measures particle volume but does not differentiate between organics and seeds. In order to separate the two, we rely on the seed loss rate measured prior to the injection of  $\alpha$ -pinene and extrapolate the seed concentration subsequent to the injection. This results in minor discrepancies between the data and the model concerning the mass of seeds in the chamber, but does not have a major effect on our overall conclusions. Because of the many time-dependent influences, such as wall losses and delays to condensation, we shall focus on directly comparing measured to modeled suspended-particle mass (i.e. without any wall loss corrections) to determine whether the CLOUD constrained products over- or underpredict the chamber SOA results.

#### 4.2.2 (E)LVOC mass yield distribution

Based on experiments conducted at CLOUD, we obtained a mass yield distribution for  $\alpha$ -pinene ozonolysis, shown in Figure 4.2 (Tröstl et al., 2016). The dark green section is the mass of organics detected by the nitrate-CIMS. Those yields were insufficient to reproduce



Figure 4.2: **Distribution of HOMs at 278 K.** Mass yields consistent with product and growthrate observations from CLOUD. The dark green bars are the mass yields detected by the nitrate-CIMS. The light green bars show additional mass required to reproduce growth rates, assuming that the nitrate clustering efficiency in the CIMS declines with increasing product volatility.

the observed particle growth rates, and so we used the observed growth rate at  $d_p = 10$  nm to constrain the LVOC mass yields, assuming that clustering and detection inefficiencies in the CIMS led to under-estimation of the LVOC concentrations. These (large) corrections are shown as light-green bars in Figure 4.2. This resulting distribution reproduced the particle growth rates for two different experimental conditions in CLOUD, as discussed in Chapter 3.

The CLOUD chamber experiments were conducted at 278 K, and we wish to apply those results to CMU smog- chamber data collected near room temperature. Product volatility depends on temperature. By applying the Clausius-Clapeyron equation and assuming an enthalpy of vaporization of 110 kJ mol<sup>-1</sup> (Bilde and Pandis, 2001; Sheehan and Bowman, 2001), we estimate that an increase of 15 K results in approximately one order of magnitude increase in volatility. The resulting distribution, shown in Figure 4.3, is [.011 .0060 .0043 .0044 .0075 .075 .12 .15] for volatility bins ranging from  $10^{-8}$  to  $10^{-1} \mu g/m^3$ . This

#### 4.2 The Dynamic Model

distribution does *not* conserve mass. The total mass yields are roughly 0.38, but the molar yields are 0.23. The remaining 0.77 molar yields are presumably more volatile products, including SVOC products that may well condense in chamber experiments. There is compelling evidence that between 30% and 60% of the SOA from  $\alpha$ -pinene ozonolysis behaves like SVOCs, either evaporating during dilution (Grieshop et al., 2007; Vaden et al., 2011) or transferring between different suspended populations when they are mixed (Robinson et al., 2013; Ye et al., 2016b). However, our objective is to test whether the (E)LVOC products alone pose a mass-balance problem for the chamber SOA experiments, and so in the following simulations we shall completely neglect any SVOC production, instead leaving any potential gaps between the (E)LVOC condensation and the total observed SOA to be explained by SVOCs.



Figure 4.3: **Distribution of HOMs at 293 K.** This is the distribution from Figure 4.2 adjusted by shifting the yields up by one volatility bin due to a higher temperature.

#### 4.2.3 Polydispersity and the condensation sink diameter

The condensation sink of vapors to particles is dependent on total available surface area, and thus the size and number concentration of the seed particles. As shown previously in Tröstl et al., (2016), the condensation flux is defined as:

$$\phi_{i,p}^{v,s} = N_p \underbrace{(\pi/4(d_p + d_i)^2)}_{\substack{\text{particle-vapor}\\\text{collision cross-section,}\\\sigma_{v,p}}} \underbrace{\alpha_{i,p}v_{i,p}B_{i,p}}_{\alpha_{i,p}v_{i,p}B_{i,p}} \underbrace{[C_i^v - a'_{i,p}C_i^0]}_{\substack{\text{driving force of}\\\text{condensation,}\\F_{i,p}}}$$
(4.5)

where  $N_p$  is the particle number concentration of a specific particle type (size or composition),  $d_p$  is the particle diameter,  $d_i$  is the effective spherical diameter of molecule i in the vapor phase,  $\alpha_{i,p}$  is the accommodation coefficient,  $C_i^{v}$  is the vapor concentration,  $a'_{i,p}$  is the activity of the organics in the particle phase, and  $C_i^{\circ}$  is the saturation vapor concentration over a pure, flat, sub-cooled liquid surface. The total condensation flux is the sum over all particle sizes and types:  $\phi_i^{v,s} = \sum_p \phi_{i,p}^{v,s}$ .

However, particles in chamber studies are rarely monodisperse–they often range in size up to an order of magnitude. Yet modeling a polydisperse population with time- and size-dependent organic composition requires far more computational power, making application into other models difficult. A polydisperse model can be approximated by a monodisperse model using a condensation sink-weighted average diameter to represent the total particle population with the appropriate vapor-particle equilibration timescales. The condensation sink diameter is the diameter that monodisperse particles would have to preserve the condensation sink and the total number concentration of a polydisperse population. This does *not* conserve mass, so the seed mass concentrations in these simulations does not match observations. We determine the condensation-sink diameter by summing the contribution to the condensation sink from each size bin, and calculating the diameter of a monodisperse seed that would produce the same condensation sink. In other words, we find a monodisperse seed of size  $d_p^{\text{CS}}$  such that:

$$k_c(d_p^{\text{CS}}, \sum_p^n N_p) = \sum_j^n k_{c,j}(d_p, N_p)$$
 (4.6)

where

$$k_c(d_p, N_p) = N_p(\pi/4(d_p + d_i)^2)\alpha_{i,p}v_{i,p}B_{i,p}$$
(4.7)

In the following simulations we compare simplified cases with a monodisperse seed population set initially at the seed condensation sink diameter with a polydisperse simulation in which we initialize the simulation using the seed size distribution spread over 108 distinct particle sizes, and then allow the diameter of each seed bin to evolve as net condensation dictates. We simulate data from two experiments described by Pathak et al., (2007b), both of which had relatively high initial seed surface area and thus should have had relatively low (E)LVOC particle wall loss and relatively rapid equilibration. In addition, they were conducted near room temperature, common in many other smog chamber experiments. Lastly, the SMPS data for these experiments show clear peaks and particle wall losses that are essential to obtaining parameters for the model. The first was conducted with 17 ppb  $\alpha$ -pinene, a constant 250 ppb O<sub>3</sub>, and 12000 cm<sup>-3</sup> ammonium sulfate seeds (Experiment 1); the second was conducted with 38.3 ppb  $\alpha$ -pinene, a constant 250 ppb O<sub>3</sub>, and 6000 cm<sup>-3</sup> ammonium sulfate seeds (Experiment 2).

#### 4.3 **Results and Discussion**

Figure 4.4 shows simulations of the two experiments. In the first experiment the  $\alpha$ -pinene oxidation produces a total of about 36 µg m<sup>-3</sup> of (E)LVOC products, while in the second experiment the oxidation produces about 81 µg m<sup>-3</sup> of (E)LVOC products. Because the products are effectively non volatile and the seed concentrations were similar, aside from scaled y axes the simulations look very similar. Figure 4.4a and Figure 4.4c are results from

the monodisperse model using the weighted condensation-sink diameter, and Figure 4.4b and Figure 4.4d are the polydisperse model results. The different colors denote different reservoirs of organics. The light blue is the concentration of organics that have not yet been formed by ozonolysis–essentially a proxy for the  $\alpha$ -pinene remaining. The grey, which will be shown more prominently later, is the oxidized products that are in the vapor phase,  $C^v$  – these are products that have yet to condense. The red is vapors that have been absorbed into the Teflon walls of the chamber,  $C^t$ . The dark blue is organics condensed onto particles that subsequently were deposited to the chamber walls,  $C^d$ . The green is organics that have condensed but remain suspended in the bulk of the chamber,  $C^s$ . A quick look at the monodisperse and its corresponding polydisperse models show that the two models agree



Figure 4.4: **Comparison of organic mass produced between the monodisperse and polydisperse models.** (a) and (b) show the monodisperse and polydisperse model results for Experiment 1, respectively. (c) and (d) show the monodisperse and polydisperse model results for Experiment 2, respectively. The monodisperse model uses a "condensation sink diameter" to approximate the rate that organics condense onto particles. This serves as a good proxy for a polydisperse model that accounts for the different condensation sinks for a polydisperse seed distribution.

well.



#### 4.3.1 Modeling organic aerosol production

Figure 4.5: Odum plots from model runs of the experiments. (a) and (b) show the model results Experiment 1 and Experiment 2, respectively, compared to prior data from Presto and Donahue, (2006) in grey, Shilling et al., (2008) in blue, Pathak et al., (2007a) in red, and Song et al., (2007) in cyan. The Odum plots show the model predicting higher yields than prior experiments. The dotted green line is the equilibrium partitioning yield at a certain total organic aerosol mass. The model demonstrates that there is a significant time delay to condensation, as the solid line is far below the equilibrium line. Thus, it is possible to have substantial production of low volatility products from  $\alpha$ -pinene ozonolysis that results in the experimental data shown in this plot.

Figure 4.5 shows the Odum plots – the mass yield of the SOA versus the total organic mass produced – for both simulations, plotted along with the SOA mass yields presented in Presto and Donahue, (2006), which include chamber results from Odum et al., (1996), Griffin et al., (1999), and Cocker et al., (2001). SOA mass yields from Shilling et al., (2008), Pathak et al., (2007a), and Song et al., (2007) are also presented. In this case we assume a perfect correction for the deposited particle mass, and so the total SOA concentration at any given time is  $C_{\text{OA}} = C^{s} + C^{d}$ . However, the mass yield is given by  $\Delta \alpha$ -pinene/ $C_{\text{OA}}$  and so excludes any vapors yet to condense as well as any vapors lost to the teflon walls. The dashed green equilibrium partitioning curve shows the expected mass yield if the system were to reach equilibrium without any vapor wall losses. As hypothesized in Figure 4.1, this greatly exceeds the observations. However, while the dynamical simulations show overall higher yields than the literature experimental results, the discrepancy is far less dramatic than the pure equilibrium simulation would suggest. This curve shows that the condensation delay, along with some vapor wall loss, may explain some of the apparent conflict between the CLOUD results and traditional SOA chamber experiments.

The simulation also lies below the equilibrium result for the entirety of the run, showing that the chamber system is always out of equilibrium (and that vapor wall losses are important). Equilibrium partitioning therefore cannot be assumed when determining yields. The model demonstrates that when smog chambers are treated dynamically, it is possible to miss substantial yields of low volatility organic compounds if the data are interpreted assuming equilibrium behavior. However, the simulations still predict substantially more SOA at any given  $C_{OA}$  than we have reported previously.

Part of the dynamical effect is the delay between the production and condensation of (E)LVOCs. We show this delay more clearly in Figure 4.6a by focusing on the first few minutes of Experiment 1, shown in Figure 4.4a. As the experiment starts, the amount of oxidized  $\alpha$ -pinene increases nearly linearly, but the bulk vapor concentration (grey) grows substantially before condensation to the bulk suspended particles begins to be significant. In addition, this reservoir remains as the experiment progresses because there is always a steady-state concentration of condensible vapors driving particle growth, indicating that the delay occurs throughout the experiment and emphasizing the importance of having a dynamic model. In Figure 4.6b we show the fractional product distribution for this same experiment over the first 90 minutes of the experiment by normalizing each product reservoir by the total concentration of condensible products  $C^{\text{tot}} = C^v + C^t + C^d + C^s$ . This confirms that the dynamical effect is greatest early in the experiment but also that a combination of steady-state condensation delay and vapor wall losses contribute at all times.

In Figure 4.7 we compare the observations and the model results for both suspended seed and suspended organic aerosol concentration over the duration of each experiments. In both scenarios, the model substantially over-predicts the observed organic mass con-

CHAPTER 4. WHERE NEW YIELDS LEAD US



Figure 4.6: The reservoirs of organics at the beginning of an experimental run. By zooming into the first few minutes of aging from 4.4a, we can clearly see the different reservoirs of organic mass in (a). The buildup of the bulk vapor (grey section) demonstrates that there is a significant delay between the formation of low volatility compounds and the condensation of these compounds onto particles. This results in lower detected yields during chamber experiments and the loss of vapors to the walls. (b) shows the fraction of organics that are in each of the reservoirs over the first 90 minutes. At the beginning, all of the organics are in the bulk vapor reservoir. The bulk vapor fraction decreases as vapors condense or are lost to the walls and claim a larger fraction of total organic mass.

centrations at all times. Delayed condensation and wall losses of (E)LVOC vapors are thus likely not a sufficient explanation for the disagreement, as both are treated in the model. One potential explanation is the different experimental conditions between the CLOUD and CMU chambers. Specifically, the CMU experiments have reaction rates almost 3 orders of magnitude higher than the CLOUD experiments (19 pptv s<sup>-1</sup> vs 0.03 pptv s<sup>-1</sup>). As reaction rates increase, the higher frequency of collisions of products with each other may terminate the auto-oxidation reactions that create the HOMs, producing higher volatility yields than those seen at CLOUD. This may be especially important for termination reactions between peroxy radicals (RO<sub>2</sub>), which are second order and will increase in importance for higher overall reaction rates. While we can not rule this out as a cause of the apparent discrepancy, we do not yet have sufficient data for the smog-chamber experiments to test whether the apparent yield of HOMs is lower under the high-concentration conditions of the SOA formation experiments than under the more atmospherically representative experiments conducted at CLOUD. Conducting SOA formation experiments at very low oxidation rates is not an obvious solution, as the resulting mismatch between ambient and chamber SOA concentrations and also the very small growth rates compared to the relatively large particle wall loss rates would make data interpretation extremely difficult; the experiments have been carried out rapidly at ambient SOA concentrations for a reason.



Figure 4.7: **Comparison of organic mass between the model and the CMU chamber experiments.** (a) and (b) show the data and the model results of seed mass and organic mass over the course of an experiment for Experiment 1 and Experiment 2, respectively. Given the initial conditions of these experiments, we find that our model overestimates the mass produced from ozonolysis. This may be due to CMU conditions that differ from CLOUD conditions, primarily the higher rate of ozonolysis. This raises the possibility that auto-oxidation of peroxy radicals produced by ozonolysis is being terminated by reactions of  $RO_2$  with other products, such as  $HO_2$  and other  $RO_2$  molecules.

Under the higher concentration of HOMs in the CMU chamber, there is a possibility of nucleation from ELVOCs. Figure 4.8a and 4.8b show the vapor supersaturation ratios from each volatility bin for Experiment 1 and Experiment 2, respectively. The ELVOC saturation ratio is an order of magnitude higher than the saturation ratio in CLOUD (see 3.9), indicating that nucleation is likely to occur. We take a lower-bounded model where new particle formation occurs only from the mass in the  $C^* = 10^{-8} \ \mu \text{g m}^{-3}$  bin, which comprises ~ 10% of the total detected HOMs (Figure 3.7a or ED Figure 5 in Tröstl et al., (2016)). Figure 3 in Kirkby et al., (2016) relates the nucleation rate to the detected HOM concentration. The fit in the log-log plot has a slope of 2, indicating that the nucleation rate is a second order reaction with respect to the HOM concentration. Thus, we draw a



Figure 4.8: Vapor saturation ratios for the experiments. (a) and (b) show the model results of the vapor saturation ratio for Experiment 1 and Experiment 2, respectively. The color of the line indicates the volatility bin, with the ELVOCs in shades of grey and LVOCs in shades of pink, and darker shades indicate lower volatility within the category. If the concentration of ELVOCs from CLOUD are present in the same concentrations in the CMU chamber, then we expect a high nucleation rate ((c) and (d))due to the higher saturation ratio of ELVOCs. However, this is not seen in the data for these experiments. RO<sub>2</sub> auto-oxidation reactions that produce ELVOCs may be terminated under the higher  $\alpha$ -pinene concentrations used in the CMU chambers.

relation between the nucleation rate and the concentration of nucleating HOMs (10% of the measured HOMs) to calculate a nucleation rate constant of  $\sim 4 \times 10^{-14}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. Using the nucleation rate constant, we calculate the nucleation rate for each experiment (Figures 4.8c and 4.8d). By integrating the nucleation rate over time, we find that the concentration of nucleated particles that would have formed is on the order of  $10^5$  to  $10^6$  cm<sup>-3</sup>. We also find that the growth rate of these particles are on the order of hundreds of nm per hour, indicating fast growth into larger sizes that are easily detected in the SMPS. However, this was not observed in the data. This is consistent with the hypothesis that the production of ELVOCs is interrupted under higher  $\alpha$ -pinene concentrations, possibly

through the termination of RO<sub>2</sub> auto-oxidation reactions.

#### 4.3.2 Oligomerization

Oligomerization has been shown in modeling to be a plausible aging mechanism (Kalberer et al., 2004; Trump and Donahue, 2014), and we explore that possibility here. Semi-volatile organics in the condensed phase may interact with particle phase HOMs, creating a dimer. This sequesters SVOC compounds that would otherwise easily evaporate off of a particle. Furthermore, because the growth rates observed in CLOUD are small and the time constants are long (many hours), it is possible that this slow chemistry might not be evident on the shorter timescales of the SOA formation chamber experiments we are modeling here.

As in our previous simulations we start by creating a model that matches the growthrate results from CLOUD. There is little information on the actual yield of semi-volatile organics; thus we are merely looking to show that there is a reasonable hypothetical yield that can reproduce the CLOUD data. In this model, we start with the unscaled yields from CLOUD (the dark green in Figure 4.2) and add in an SVOC mass yield of 0.20 in the C\* =  $10^1 \ \mu g \ m^{-3}$  volatility bin. We assume that this compound is a reactive monomer that will react with *any* condensed-phase organic species to form an ELVOC product. This is an overly simplistic model that serves as a proof of concept. As described by Trump and Donahue, (2014), the rate of dimerization is described by

$$R_{\rm dimer} = C_{OA}(k_f w_m w_{\rm org} - k_r w_d), \tag{4.8}$$

where  $C_{OA}$  is the organic aerosol concentration,  $k_f$  is the forward rate constant of dimerization,  $w_m$  is the mass fraction of monomers,  $w_{org}$  is the mass fraction of other organics in the particle phase (we assume the monomer reacts with all organics, so  $w_{org} = 1$ ),  $k_r$  is the dissociation rate, and  $w_d$  is the mass fraction of dimers. For the purpose of this simple model, we assume that there is no dimer dissociation ( $k_r = 0$ ). The CLOUD chamber operated at low  $\alpha$ -pinene concentrations. Thus, when we use the original, lower yield dis-



Figure 4.9: **Oligomerization model results for CLOUD experiments.** We can create an oligomerization model that can reproduce the CLOUD experiments. Figures 4.9a and 4.9c show the oligomerization model reproducing the particle diameter data over the course of the experiment. Figures 4.9b and 4.9d show the contribution to particle growth from each of the volatility bins, as shown in Figure 4.2. The dark blue is the contribution to growth from dimers. While the growth rate curves look different than the model shown in the previous chapter, the most important point is the growth rate at 10 nm, which was experimentally determined, and that our model matches.

tribution, the dimerization rate must be high ( $k_f = 20000 \text{ min}^{-1}$ ) in order to produce the detected growth rate.

Figure 4.9 shows the model results of the CLOUD experiments. Figures 4.9a and 4.9b show the results of the constant HOM experiment, and Figures 4.9c and 4.9d show the increasing HOM experiment. In both cases, the oligomerization model reproduces the particle size and growth rate reasonably over the course of the experiments. Figures 4.9b and 4.9d show the contributions from each of the volatility bins to the growth rate. The colors indicate the volatility of the compound, as shown in 4.2, with the dimers shown as dark blue following Trump and Donahue, (2014). The ELVOC and LVOC compounds contribute very little to the overall particle growth after the very early stages of growth.



Figure 4.10: Comparison of organic mass produced between the oligomerization model and the CMU chamber experiments. (a) and (b) show the model and data results for organic and seed mass over time for Experiment 1 and Experiment 2, respectively. The oligomer model still overpredicts Experiment 1, though not as much as the LVOC boosted model, and reasonably matches Experiment 2.

Because of the high condensed-phase rate constant, nearly all of the SVOCs that condense are immediately converted to ELVOC dimers; simulations including a slower forward reaction simply required much higher monomer yields, which we rejected as unrealistic. While the growth-rate plot differs somewhat from the model constrained entirely by (E)LVOCs (Tröstl et al., 2016), the experimentally determined growth rate at 10 nm matches the model. Therefore, for the purposes of this exercise, this is a second product model consistent with the CLOUD observations.

We can now take this oligomerization model and apply it to the SOA formation experiments from the CMU chamber. Figure 4.10 shows simulation results for the two CMU experiments we have considered here in detail, with the oligomerization case represented in dark green and the (extra mass from) the (E)LVOC simulation shown in light green. The oligomerization model results in a better fit to the data, though for Experiment 1 the model continues to over-predict the observations. In Figure 4.11 we show an Odum plot for Experiment 2, including the corrected mass yield data from that experiment, for this oligomerization simulation.

In this simulation, to reproduce the particle growth rates without excessive monomer concentrations we had to assume effectively irreversible condensation of monomers and

CHAPTER 4. WHERE NEW YIELDS LEAD US



Figure 4.11: Odum plot with the LVOC and oligomer models for Experiment 2 The figure shows the LVOC model and oligomer model results from Experiment 2, compared to prior data from Presto and Donahue, (2006) in grey, Shilling et al., (2008) in blue triangles, Pathak et al., (2007a) in red circles, and Song et al., (2007) in cyan. The Odum plot shows the oligomer model consistent with some prior experiments. The dashed green line is the equilibrium partitioning yield at a certain total organic aerosol mass. The solid green line is the scaled LVOC model. The dot-dashed green line is the oligomer model. The oligomer model appears to fit better with prior experiments.

rapid oligomerization. On its face, this case is not qualitatively different from effectively non-volatile condensation, though it does reproduce the slow growth rate at very low particle diameters observed in the CLOUD experiment. It is thus somewhat surprising that the mass yields in the oligomerization simulations are significantly lower than the (E)LVOC case. Most of this difference is because a flux balance differs from a mass balance. The SVOC monomers are relatively light, with  $M_i = 175$  g mole<sup>-1</sup> as compared to (E)LVOCs with  $M_i \simeq 350$  g mole<sup>-1</sup>. This means that for the same vapor mass concentration, the SVOC monomers have a 44% higher condensation rate, simply because they have a higher velocity.

#### 4.3.3 The condensation sink and reaction rates

At this point we have a dynamical model that can reproduce the growth-rate observations from CLOUD while not grossly over-predicting the SOA mass production rate observed in at least some SOA formation chamber experiments. However, the model still leaves no room for true SVOC condensation (save for effectively irreversible conversion to oligomers), and so it is not yet fully consistent with observations strongly suggesting that 30-60% of the SOA in chambers is semi volatile. We thus can not rule out possible changes to the gas-phase chemistry (and the volatility distribution of the products); this is difficult without corresponding measurements of gas-phase HOMs via nitrate-CIMS in the chamber experiments.

Other dynamical effects also remain possible. One possibility is that the mass accommodation coefficients differ in the high-mass SOA formation experiments and in the low-mass CLOUD experiments. However the flux-balance constraints for CLOUD strongly suggest a mass accommodation coefficient near unity. Specifically, the total mass yields required to explain the growth rates already stretch plausibility, and  $\alpha < 1$  would only require higher vapor concentrations (and thus higher yields) to compensate for the lower specific condensation rate. However, if larger particles had a lower effective mass accommodation coefficient, that might direct more vapors to the walls and lower the overall observed SOA production. We explore this by varying the particle condensation sink in our simulations, using the (E)LVOC simulations as our base case.

The particle condensation sink is key to condensing organic vapors, and in chamber studies, this process is in competition with the loss of vapors to chamber walls. The key to capturing oxidation products is therefore increasing the condensation sink by having a higher seed surface area. In general our design objective is to have a suspended seed condensation sink at least  $10\times$  greater than the vapor-wall collision frequency. For the CMU chambers, with a vapor wall-loss frequency of approximately  $0.1 \text{ min}^{-1}$  (Ye et al., 2016a), this means that the ideal seed condensation sink is of order  $1 \text{ min}^{-1}$ . The critical



Figure 4.12: The effect of varying particle-to-wall condensation sink ratio by varying the number of seeds at 3 ppb  $\alpha$ -pinene and 50 ppb ozone. (a) has a CS ratio of 0.3; (b): CS ratio = 1; (c): CS ratio = 3; (d): CS ratio = 10. The CS ratio describes how likely an organic molecule would hit a particle versus the wall. The key area is the grey area denoting the bulk vapor (the sliver between the teal and red), which comes from reacted products that have not yet condensed into the particle phase. In 4.12d, there is sufficient seed concentration to condense most of the vapors into the particle phase (mass of particles on walls and bulk suspended). Conversely, in 4.12a, the lack of seeds causes a buildup of bulk vapor, most of which is then lost to the walls.

parameter is the ratio of the seed condensation sink to the wall-loss rate constant.

Figure 4.12 shows the locations of vapors given an initial particle-to-wall condensation sink (CS) ratio for a hypothetical mix of 3 ppb  $\alpha$ -pinene and 50 ppb ozone. The CS ratio describes how likely an organic vapor molecule is to hit a particle versus the wall. For low CS ratios there is a buildup of ozonolysis products (Figure 4.12a, denoted in gray), showing a delay of condensation of vapors to particles. The majority of these vapors are thus lost to the walls. Even in Figure 4.12b, where the initial CS ratio is 1, more of the mass is lost to the walls than is condensed onto particles. This is due to particle wall loss, which decreases the available surface area in the bulk chamber. As CS ratio increases, the



Figure 4.13: How the condensation sink (CS) ratio changes over the course of a chamber run, depending on the initial CS ratio. Each run has the same initial condition: 3 ppb  $\alpha$ -pinene and 50 ppb O<sub>3</sub>. The number of seeds is increased by half decades each time. (a) has a CS ratio of 0.3; (b): CS ratio = 1; (c): CS ratio = 3; (d): CS ratio = 10. At a low CS ratio (Figure 4.13a), fewer seeds mean that each seed grows more. Because the CS is dependent on the surface area of the particle, a faster growth of the surface area results in an increase in the particle condensation sink. At high seed concentrations, the bump in the CS ratio does not occur because each seed receives little organic mass. However, CS is also dependent on the particle number concentration. Therefore, as shown in all of the figures, the CS ratio steadily drops over the course of a chamber run as particles themselves are lost to the walls. The specific value of CS ratio at which the growth rate effect disappears is dependent on the amount of precursor and the oxidation rate of precursors.

bulk vapor concentrations decrease as higher particle condensation rates collect most of the organic mass.

The CS ratio is dependent on the particle number concentration and particle diameters. Over the course of an experiment, there are competing processes that affect the CS through these two variables. The particle number concentration decreases due to particle wall loss. The particle diameter increases due to condensation. However, the rate at which the diameter increases is also dependent on the particle number. Figure 4.13 shows the change



Figure 4.14: Locations of organic products from 3 ppb  $\alpha$ -pinene with varying concentrations of ozone and CS ratios. (a) shows the result of 500 ppb O<sub>3</sub> with a CS ratio of 1; (b): 5000 ppb O<sub>3</sub>, CS ratio of 1; (c): 5000 ppb O<sub>3</sub>, CS ratio of 100. Given a seed concentration, increasing the ozone concentration causes  $\alpha$ -pinene to react faster, resulting in a higher condensation driving force and a higher organic particle mass after a shorter period. However, half of the vapors are still lost to the walls. By increasing the CS ratio, or seed concentration, by two orders of magnitude, all of the condensible vapors can be captured in the particle phase.

in CS ratio over time across the four aforementioned runs. At low CS ratios (Figure 4.13a, or low particle concentrations, condensation has a greater effect on the diameter of each particle. This causes the CS ratio to increase at the beginning before decreasing later from particle wall loss. As the CS ratio increases, the effect of particle diameter decreases, as each particle is growing slower. By Figure 4.13d, the diameter growth effect is negligible.

In addition to the CS ratio, the condensation rate is affected by the reaction rate. The reaction rate is simply the product of the reaction rate constant, the  $\alpha$ -pinene concentration, and the ozone concentration. At higher ozone concentrations, more precursors become products, creating a greater condensation driving force, resulting in more particle mass. Organics with higher volatilities are also more likely to enter into the particle phase due to higher aerosol loading. Figure 4.14a and Figure 4.14b show the reservoirs of organic products at 500 ppb ozone and 5000 ppb ozone, respectively. Compared to Figure 4.12b, which has the same  $\alpha$ -pinene and seed concentrations, here organic aerosol mass is formed faster and concentrations are higher. We can also see evaporation of organics off the particles toward the walls as the run continues, as  $C^t$  grows while  $C^s + C^d$  shrinks. However, we would like to avoid vapor wall losses altogether, if possible. Figure 4.14c shows that it is possible to minimize the wall loss by increasing both the reaction rate and the condensation sink in the chamber. In this case, almost all of the organics condense to particles before slowly being lost to the walls. It is trivial to extrapolate the green condensed-phase concentration back to the "correct" value; unfortunately, this comes at the expense of running the chemistry extremely quickly, and potentially perturbing the gas-phase chemistry (especially the yields of HOMs due to auto-oxidation).

## 4.4 Conclusion

In this work, we took a dynamic 1-D volatility basis set model developed for CLOUD experiments at CERN and adapted it to  $\alpha$ -pinene ozonolysis experiments conducted in the CMU smog chamber. Based on the mass yield distribution from CLOUD, we found that our model overpredicts the organic mass produced and the resulting yields over the course of an experiment. However, we demonstrated that chamber experiments need to be treated dynamically, because there is a delay between the formation of low volatility vapors and the condensation of these vapors to particles. This delay at least partially resolves the issue of the existence of low volatility compounds that do not seem to show up in Odum plots – they exist, but show up at higher aerosol loading than expected because of the time it takes for them to condense.

We found that substantial oligomerization is consistent with both the CLOUD and the CMU chamber results. By allowing semivolatile organics in the condensed phase to form dimers with lower volatility compounds, we showed that it is possible to replicate the data from CLOUD experiments. It is likely that oligomerization plays a role in organic aerosol formation, but how substantial a role remains to be determined. Because of the many parameters available to explain the current set of observations (HOM yields, oligomer fraction, mass accommodation coefficients, vapor wall losses, RO<sub>2</sub> auto-oxidation rates, etc.), only a very carefully designed series of experiments will fully constrain this problem.

We emphasize that the ratio of vapor-particle condensation sink to the vapor-wall loss sink is critical to interpretation of smog-chamber data. At low initial CS ratios, most of the organic vapors produced are lost to chamber walls. As the CS ratio increases, more of the mass goes to the particles, but the suspended mass concentration does not scale with the CS ratio. Because of particle wall loss, the organics on suspended particles are driven to the walls. For the same reason, the condensation sink to the remaining particles also decreases over time. Therefore, merely increasing the condensation sink does not always increase the concentration of bulk organic particle mass. Ideal chamber conditions require both high CS ratios and high oxidation rates (by boosting ozone concentrations). At high oxidation rates, all of the  $\alpha$ -pinene is immediately reacted into low volatility compounds, and the high CS ratio allows these compounds to quickly condense onto seed particles. This allows all the organics to be collected onto seeds before wall losses in either the vapor or suspended phase can have a large effect. However, this condition may in turn interfere with the unimolecular gas-phase auto-oxidation chemistry that produces the HOMs in the first place. Consequently, direct measurements of the gas-phase HOM yields during such experiments are critical to the overall interpretation of the experimental data.

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Chapter 5

# **Conclusions and future work**
## 5.1 Conclusions

The health and climate impacts of organic aerosols make their formation an important area of research. In this work, we developed models based in the VBS framework to track the aging of volatile organic compounds, especially  $\alpha$ -pinene, and how the formation of low volatility compounds result in aerosols.

First, we modeled the formation of organonitrates from the introduction of  $NO_x$  to  $\alpha$ -pinene aging in a 2-dimensional VBS. By adding a second 2D-VBS layer to represent organonitrates, we specifically tracked the production and reactions of organonitrates. Under high NO<sub>x</sub> conditions, the contribution of organonitrates to overall mass can be similar to non-nitrate organics even though the N:C and the mass of the nitrate group( $-ONO_2$ ) can be low. Higher volatility precursors such as  $\alpha$ -pinene were shown to produce lower mass as the concentration of NO<sub>x</sub> increases. Low volatility precursors or higher mass loadings showed enhanced mass in the presence of NO<sub>x</sub>. This showed the importance of NO<sub>x</sub> in the aging of organic compounds, and demonstrated the capability of the VBS to model organonitrate chemistry. We showed that the overall effect of NOx on aerosol mass changes as NO<sub>x</sub> increases—and the effect is especially pronounced in first generation chemistry. As organic emissions pass through a NO<sub>x</sub>-concentrated region, such as a city, the aging chemistry may vary significantly between suburbs, city limits, and city center. In addition, as we have shown in this work, the identity and volatility of the organic compound is also an important determinant in how much organic aerosol is produced when NO<sub>x</sub> is introduced. As we continue to limit concentrations of NO<sub>x</sub> through emissions controls for health and environmental reasons, the concentration of aerosols generated from the same precursors will change. It is thus important to continue conducting chamber experiments to investigate the effect of  $NO_x$  on organic precursors, and to continue creating models that can predict aerosol formation as NO<sub>x</sub> levels change.

The CLOUD experiments quantified the formation of (E)LVOCs from  $\alpha$ -pinene ozonolysis, and we developed a dynamic VBS model to track the growth of freshly nucleated particles. The model showed that the raw data from the nitrate-CIMS is insufficient to explain the growth detected. One possibility is the charging efficiency of the instrument, which may be lower for higher volatility compounds, implying that there is a substantial concentration of LVOCs that was undetected. When we scaled the LVOCs, the model is capable of reproducing the CLOUD experiments. In addition, we showed that the Kelvin effect has a strong effect on particles smaller than  $\sim 4$  nm. Because of this, ELVOCs are the main contributors to growth of particles smaller than the Kelvin diameter. Subsequently, as a particle size increases past the Kelvin diameter, LVOCs become the driver of growth.

Finally, we explored the discrepancy between prior  $\alpha$ -pinene ozonolysis yields and the existence of (E)LVOC yields. Two experiments conducted in the CMU smog chamber was modeled in the dynamic VBS using an adapted yield distribution from CLOUD. We showed that there is a delay in the condensation of organics to seeds, resulting in lowered yields similar to those in prior experiments. A dynamical treatment of chamber experiments is therefore critical to modeling aging experiments. We also explored oligomerization as an alternative mechanism of (E)LVOC production and aerosol growth, and show that the oligomerization model is consistent with CLOUD results. Lastly, the model demonstrated the importance of ratio of the vapor-particle condensation sink to the vapor-wall loss sink. In order to capture most of the oxidized vapors, a chamber would require both a large reaction rate through higher ozone levels, and higher seed concentrations. However, this may introduce other issues, such as interference in the auto-oxidation chemistry that produces HOMs.

The step from an equilibrium model to a dynamic model changes the way we think about chamber experiments. Where we used to think that low volatility compounds would immediately condense, we now know that it requires a short period to do so and that this time makes all the difference in mass yields. The movement of molecules of oxidized species is integral to its particle condensation or wall absorption—which one occurs more often is affected by the concentration of seeds and the chamber walls. Thus, we will have to be more aware of these aspects as we design, perform, and analyze chamber experiments, juggling the need to have higher CS ratios and higher oxidation rates without introducing new physical or chemical processes.

Our current models involve some hypotheticals, such as the charging inefficiency of the nitrate-CIMS, the semi-volatile yields and the oligomerization rates. While they are all within reason, it is by no means an end point. Further evidence constraining these variables is imperative to creating a more realistic model. We hope that this model can be used as a starting point to inform and design chamber experiments that account for the effects of oxidation rates, precursor loading, and seed concentrations. In turn, we hope that future experiments will probe current assumptions within the model and help refine the parameters, such as the mass yields and the chemical and physical processes, upon which the model is constructed.

## 5.2 Future Work

Vapor wall loss is a process that involves many factors, some of which are highly chamber specific (e.g. material of wall, the presence of turbulent mixing). It involves the diffusion of a molecule through the boundary layer of the chamber walls, and being taken up into the wall. In a model developed by Zhang et al., (2014), the vapor wall loss depends on the equivalent aerosol mass of the chamber walls, the mass accommodation coefficient to the walls, and the coefficient of eddy diffusion. These are not simple parameters to characterize, but further experiments exploring the limits of these parameters in the chamber experiments would help constrain the dynamic model.

The dynamic VBS model for  $\alpha$ -pinene ozonolysis is currently constrained by the results of CLOUD. CLOUD data is limited by the inefficiency of the nitrate-CIMS in its detection of LVOCs. It would be helpful to characterize the charging efficiency of the nitrate-CIMS, in order to better inform the current model. Better constraints from the nitrate-CIMS would allow consideration of other possible processes, such as oligomerization and RO<sub>2</sub> autooxidation rates.

It is now clear that dynamics must be considered in chamber experiments; thus the work on organonitrate formation may be redeveloped in that context. Given the production of HOMs under low- $NO_x$  ozonolysis, further experiments would need to be conducted to determine the distribution of products.