QUANTIFIED AGING IN SECONDARY ORGANIC AEROSOLS
AND CONTRIBUTIONS BY SMALL PRECURSOR COMPOUNDS

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## Acknowledgement

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An aerosol is technically defined as a suspension of fine solid or liquid particles in a gas. Atmospheric aerosols are small enough to remain suspended in the air, with a diameter varying from a few nanometers to tens of micrometers. Aerosols play a key role in many environmental processes: They markedly affect the radiative balance in the Earth’s atmosphere and play a central role in climate. In contrast to greenhouse gases, aerosols have mainly a cooling effect on the global climate. However, the uncertainties in anthropogenic radiative forcing are highest for aerosol effects. Atmospheric aerosols also have an adverse impact on human health. It is now well established that exposure to ambient aerosols is associated with damaging effects on the respiratory and cardiovascular systems.

A wide variety of natural and anthropogenic sources contribute to atmospheric aerosols, thus also their chemical composition varies strongly. Aerosols are often classified according to their particle size ranges, their sources (natural or anthropogenic) or related to their state during formation pathway: Directly emitted particles are called primary aerosols, while those formed by nucleation or condensation processes from gaseous precursors are named secondary aerosols. Sources of primary aerosols are, e.g., biomass burning, combustion of fossil fuels, volcanic eruptions and wind-driven suspension of soil, mineral dust, sea salt and biological materials. Aerosols resulting from the condensation of compounds formed by chemical degradation of biogenic and anthropogenic volatile organic compound (VOC) precursors are called secondary organic aerosols (SOA). The formation of semivolatile, low-volatility, and possibly non-volatile compounds that make up SOA is governed by a complex series of reactions of a large number of organic species, so the experimental characterization and theoretical description of SOA formation presents a substantial challenge. It is estimated that 10 000 to 100 000 different organic compounds are present in the atmosphere. The mean lifetime of these particles suspended in air is about one week.

Organic aerosol makes up a large fraction (20 to 90%) of the submicron particulate mass. Recent results show that SOA, formed by atmospheric oxidation of gas-phase species, accounts for a large fraction of the organic aerosol burden. Despite much recent progress in our understanding of SOA formation chemistry, current “bottom-up” models based on parameterizations of laboratory experiments cannot explain the magnitude and evolution of atmospheric SOA. Explicit chemical models are still not able to predict ambient SOA concentrations or the degree of oxidation accurately, and they are too complex for large-scale models. A better understanding of the chemical evolution of organic aerosol is required to reduce unacceptable aerosol-related uncertainties in global climate simulations and to improve air quality.

Due to the central role assigned to SOA this work is almost exclusively dealing with this topic. The main posed questions are:

- Does hydroxyl radical (OH, referred to here as OH for simplicity) aging significantly increase the concentration of first-generation biogenic SOA?
- How is it possible to determine the mean OH concentration — the dominant atmospheric oxidant — at smog chambers with the available instrumentation?
- How can we make different experiments more comparable between each other, and how can we compare lab studies with those performed in the atmosphere?
Summary

– What is the effect of SOA aging with regard to physical properties (hygroscopicity, volatility)?
– Is methane — the most abundant and fairly unreactive VOC in the atmosphere — contributing to SOA mass? If yes to what extent?

The Multiple Chamber Aerosol Chemical Aging Study (MUCHACHAS) tested the hypothesis whether OH aging significantly increases the concentration of biogenic SOA. OH is the dominant atmospheric oxidant, and MUCHACHAS employed environmental chambers of very different designs, using multiple OH sources to explore a range of chemical conditions and potential sources of systematic errors. This way we were able to isolate the effect of OH aging, confirming the hypothesis while observing corresponding changes in SOA properties. The mass increases are consistent with an existing gap between global SOA sources and those predicted in models, and can be described by a mechanism suitable for implementation in those models.

As implied before, OH is not only responsible for SOA aging, it is also the primary cleansing agent of the lower atmosphere: it is the key reactant for the degradation of most compounds emitted from biogenic and anthropogenic sources into the troposphere. Globally, OH radicals are mostly produced by photolysis of ozone (O3) and the subsequent reaction of the formed excited oxygen atoms with water vapor. Owing to its central importance, absolute measurements of OH concentrations are crucial and they are needed to determine the progress of photochemical aging. A useful metric is the photochemical age defined as OH exposure, which can be used as a chemical clock (OH clock). The OH clock corresponds to the OH concentration integrated over time. This chemical time dimension makes experiments, e.g., between different smog chambers more comparable than other widely used clocks such as “time after lights on” (TALO) or “time after start of secondary organic aerosol formation”. Suitable tracers to be measured by proton transfer reaction mass spectrometry (PTR-MS) were evaluated to establish a (photo-) chemical clock based on OH exposure. The OH concentration was obtained by applying an adequate fit to the decay curve of the tracer. Several OH tracers for PTR-MS were evaluated and a new, universal OH tracer (butanol-d9) was presented together with various applications of the OH clock.

The influence of atmospheric aerosols on climate is based on the direct aerosol effect by scattering sunlight and on the indirect aerosol effect by changing cloud properties and characteristics. Hygroscopicity, the degree of water uptake by particles, is an important parameter for both effects. Volatility in turn is a key property of the organic components of the gas and particulate phase and it determines the SOA formation and the partitioning between the phases. Hygroscopicity and volatility of particles in general are important physical properties closely linked to size and chemical composition of the aerosol. The volatility and its temporal evolution provide some insight in the chemical composition and related processes. The water uptake of several inorganic substances has been studied for years and is well understood, but they are typically mixed with carbonaceous substances in the atmospheric aerosol. The hygroscopicity of fresh and aged SOA and combustion aerosols is not well known so far and is of interest for their effects on climate and on human health. Therefore aging processes need to be simulated and investigated under controlled conditions.

During MUCHACHAS the evolution of pure SOA from the gaseous precursor α-pinene was investigated: SOA was formed during ozonolysis and followed by aging with OH radicals in a smog chamber. The particles’ volatility and hygroscopicity were characterized and used as sensitive physical parameters to reveal the possible mechanisms responsible for the chemical changes in the SOA composition during aging. Four distinct reaction phases of the experiment were found. The connection between hygroscopicity and chemistry of SOA was also investigated. The water uptake was linked to the organic mass spectra during the chemical and photochemical oxidation of several organic precursors. SOA hygroscopicity was
found to strongly correlate with the relative abundance of a specific ion signal. An empirical linear relation was determined for smog chamber and ambient measurements. Both, volatility and hygroscopicity were measured with a so called “volatility and hygroscopicity tandem differential mobility analyzer” (V/H-TDMA).

Due to their high volatilities small carbonyls and hydrocarbons have been considered for a long time as irrelevant to aerosol formation. If oxidation products of methane - this fairly unreactive and volatile hydrocarbon - are able to contribute to the aerosol mass, then every existing volatile organic carbon should be able to contribute to the aerosol mass.

Carbon yields of methane, the most abundant volatile organic compound in the atmosphere, were investigated at the PSI smog chamber. This was done in the presence of an inorganic and an organic seed aerosol (from 1,3,5-trimethylbenzene or α-pinene oxidation). The carbon yields of methane were determined to be between 0.01% and 0.2% — depending mainly on whether one applies a wall loss correction or not. The upper limit is wall loss corrected, the lower one is not. The atmospheric relevance was found to be small: The methane contribution of the atmospheric aerosol carbon mass was estimated to be maximally 1.25%. Nevertheless these findings imply that all VOCs are able to contribute to some extent to SOA mass.


Aufgrund ihrer zentralen Rolle in der Atmosphäre befassen wir uns hier fast ausschließlich mit SOA. Die wichtigsten Fragen, die hierbei gestellt werden, sind:

- Kann die Konzentration der ersten Generation an biogenen SOA durch die Alterung mittels Hydroxyl-Radikale (OH) erheblich erhöht werden?
- Wie kann die mittlere OH-Konzentration in Smog Kammern mit "herkömmlichen" Instrumenten bestimmt werden?
Zusammenfassung

- Können verschiedene Experimente untereinander besser vergleichbar gemacht werden? Wie könnten allenfalls Laborstudien mit Messungen in der Atmosphäre besser verglichen werden?
- Was ist der Effekt von SOA-Alterung in Bezug auf die physikalischen Eigenschaften (Hygroskopizität und Volatilität)?
- Leistet Methan — das am häufigsten vorkommende und ziemlich reaktionsträge VOC — einen Beitrag zur SOA-Masse? Falls ja, in welchem Umfang liegt er?

Während der “Multiple Chamber Aerosol Chemical Aging Study” (MUCHACHAS) Kampagne testeten wir die Hypothese, ob eine Alterung der Aerosole durch OH die Konzentration der ersten Generation an biogenen SOA erhöht. In der Atmosphäre ist OH das dominierende Oxidationsmittel. Während MUCHACHAS wurden in Klimakammern (Smog-Kammern) unterschiedlichen Designs und mit Hilfe verschiedener OH Quellen eine Reihe von chemischen Bedingungen getestet und mögliche systematische Fehlerquellen eruiert. Auf diese Weise konnte die zuvor gestellte Hypothese, dass durch OH bedingte Alterung der Aerosole die Konzentration an biogenen SOA erhöht werden kann, bestätigt werden. Der entdeckte Massenanstieg durch SOA-Alterung könnte die bestehende Kluft zwischen globalen SOA-Quellen und der in den Modellen vorhergesagten SOA Massen erklären.


Die Hygroskopizität von frischen und gealterten SOA und diejenige von Partikeln aus Verbrennungsprozessen ist bisher eher unbekannt und ist deshalb von grossem Interesse, um die Auswirkungen auf das Klima und die menschliche Gesundheit zu quantifizieren. Dabei

Aufgrund ihrer hohen Flüchtigkeit wurden kleine Carbonyle und Kohlenwasserstoffe lange Zeit als nicht relevant für die Bildung von Aerosolen betrachtet. Sollten Oxidationsprodukte von Methan — diesem reaktionsträchtigen und flüchtigen Kohlenwasserstoff — in der Lage sein, einen Beitrag zur Aerosol-Masse zu leisten, dann müsste dies für jede existierende Art von VOCs der Fall sein.

Methan ist die am häufigsten vorkommende flüchtige organische Verbindung in der Atmosphäre. Ihre Kohlenstoff-Ausbeute für Aerosole wurde an der PSI-Smogkammer untersucht. Dies wurde in Gegenwart sowohl eines anorganischen wie auch eines organischen Träger-Aerosols (gebildet aus der Oxidation von 1,3,5-Trimethylbenzol oder α-Pinen) durchgeführt. Die atmosphärische Relevanz für diesen Befund bleibt jedoch klein: Der Beitrag des Methans am gesamten atmosphärischen Aerosol-Kohlenstoff wurde auf maximal 1% geschätzt. Trotz geringer atmosphärischer Relevanz wurde mit dieser Studie zum ersten Mal gezeigt, dass prinzipiell alle flüchtigen organischen Verbindungen zu einem gewissen Grad zur Masse von SOA beitragen können.
1

Introduction

1.1 Atmospheric aerosols

1.1.1 Definition, properties

Atmospheric aerosols, defined as “liquid or solid particles suspended in air” (Seinfeld and Pandis, 2006), play a key role in many environmental processes. Aerosols scatter and absorb solar and terrestrial radiation, influence cloud formation and participate in heterogeneous chemical reactions in the atmosphere, thereby affecting the abundance and distribution of atmospheric trace gases (Andreae and Crutzen, 1997; Haywood and Boucher, 2000). As a result, aerosols markedly affect the radiative balance in Earth’s atmosphere and play a central role in climate (IPCC, 2007). In addition to their climatic relevance aerosols exert an adverse impact on the human health and it is now well established that exposure to ambient aerosols is associated with damaging effects on the respiratory and cardiovascular systems (Pope and Dockery, 2006; Davidson et al., 2005; Harrison and Yin, 2000). Atmospheric aerosols are, by definition, small enough to remain suspended in the air, with a diameter varying from a few nanometers (nm) to tens of micrometers (µm). Often they are classified into four distinct modes defined as the nucleation mode (particle diameter \(D_p \leq 10\) nm), the transient nuclei or Aitken mode (10 nm \(\leq D_p \leq 0.1\) µm), the accumulation mode (0.1 µm \(\leq D_p \leq 2.5\) µm) and the coarse mode (\(D_p \geq 2.5\) µm).

Particles present in the atmosphere can be directly emitted (primary aerosols) or can be formed by nucleation or condensation processes (secondary aerosols). Secondary aerosols are formed after chemical transformation of gaseous precursors into semi-volatile or low-volatility species that condense into the particle phase (see also 1.1.3).

Primary emissions of particles and gaseous precursors for the formation of secondary aerosols can have either natural (e.g. mineral and volcanic dust, sea salt, dimethyl sulfide (DMS), volcanic sulfur dioxide (SO\(_2\)), biogenic volatile organic compounds) or anthropogenic sources (soot, SO\(_2\) from fuel combustion, nitrogen oxides (NO\(_x\)), anthropogenic volatile organic compounds) (Seinfeld and Pandis, 2006). Aerosol resulting from the condensation of low volatility compounds formed by chemical degradation of biogenic and anthropogenic volatile organic compound (VOC) precursors is called secondary organic aerosol (SOA). Understanding SOA — their formation, composition and aging — is a major task in today’s atmospheric research since SOA presents a major fraction of the total organic aerosol.
1.1.2 Aerosol climate impact

Aerosols have been identified as having a significant contribution to climate change [IPCC, 2007]. However, aerosol loading and properties are highly variable in time and space making it difficult to assess their impact on climate. Finally several parameters are needed for determining the ability of an aerosol particle to act as a cloud condensation nuclei (CCN), namely its size, chemical composition and mixing state (e.g. IPCC, 2001). Increases in ambient concentrations of CCN and ice nuclei (IN) due to anthropogenic activities can modify the microphysical properties of clouds, thereby affecting the climate system (e.g. IPCC, 2001). Several mechanisms are involved, as presented schematically in Fig. 1.1 [IPCC, 2007].

![Figure 1.1 Schematic diagram showing the various radiative mechanisms associated with cloud effects that have been identified as significant in relation to aerosols. The small black dots represent aerosol particles; the larger open circles cloud droplets. Straight lines represent the incident and reflected solar radiation, and wavy lines represent terrestrial radiation. The filled white circles indicate CDNC. The unperturbed cloud contains larger cloud drops as only natural aerosols are available as CCN, while the perturbed cloud contains a greater number of smaller cloud drops as both natural and anthropogenic aerosols are available as CCN. The vertical gray dashes represent rainfall, and LWC refers to the liquid water content. (From IPCC, 2007).](image)

**The direct radiative forcing of tropospheric aerosols:** The direct aerosol effect is defined as the mechanism by which the aerosols scatter and absorb radiation, thereby altering the earth’s radiative balance ([IPCC, 2007]). Scattering aerosols have a net negative effect while absorbing aerosols may have a negative or a positive effect depending on the ratio of scattering to absorbing material, their vertical distribution and the surface albedo below the aerosol layer.

**Aerosol indirect effect:** The indirect effect is defined as the mechanism by which the aerosols modify the microphysical and hence the radiative properties, amount and lifetime of clouds ([IPCC, 2007]). The indirect aerosol effect is split into two parts in the [IPCC (2007)] report:

- The 1st indirect effect (also named cloud albedo or Twomey effect) describes the fact that aerosol particles increase the number of cloud droplets in clouds therefore decreasing their size at a fixed liquid water content. As a result, the cloud albedo (defined as the reflected radiation to the incident radiation) increases and the clouds are brighter.
- The 2nd indirect effect (also named the cloud lifetime effect or the Albrecht effect) describes the microphysically induced effect on the liquid water content, cloud height, and lifetime of clouds. In other words: aerosol enhancements have also been hypo-
1.2 Gas phase

thesized to lead to an increased drizzle suppression (thus increasing the liquid water content), increased cloud height and/or increased cloud lifetime.

**Aerosol semi-direct effect:** The aerosol semi-direct effect is the mechanism by which absorption of shortwave radiation by tropospheric aerosols leads to heating of the troposphere that in turn changes the relative humidity and the stability of the troposphere and thereby influences cloud formation and lifetime (IPCC, 2007).

1.1.3 Secondary organic aerosols

Aerosol resulting from the condensation of low volatility compounds formed by chemical degradation of biogenic and anthropogenic VOC precursors is called secondary organic aerosol (SOA). SOA accounts for 64 to 95% of the total organic aerosol mass depending on the location of the measurements (Zhang et al., 2007). The SOA contribution is generally more important in rural areas than in urban sites.

The importance of SOA in the atmosphere has been underestimated until not so long ago. Current “bottom-up” models based on parameterizations of laboratory experiments still cannot explain the magnitude and evolution of atmospheric SOA. Explicit chemical models are still not able to predict ambient SOA concentrations or degree of oxidation accurately, and they are too complex for large-scale models (Jimenez et al., 2009). The conversion of inorganic gases such as sulfur dioxide, nitrogen dioxide and ammonia into particulate phase sulfate, nitrate and ammonium is now fairly well understood (Hallquist et al., 2009). However, there is considerable uncertainty over the SOA formed when the atmospheric oxidation products of VOCs undergo gas-particle transfer (Hallquist et al., 2009). The formation of low-volatility (semivolatile and possibly nonvolatile) compounds that make up SOA is governed by a complex series of reactions of a large number of organic species, so the experimental characterization and theoretical description of SOA formation presents a substantial challenge (Kroll and Seinfeld, 2008).

1.2 Gas phase

1.2.1 Volatile organic compounds

There is a large variety of compounds that can be classified as VOCs. These compounds have a sufficiently high saturation vapor pressure to evaporate (partly or completely) to the atmosphere. VOC sources can be both biogenic and anthropogenic. Biogenic VOCs represent an important part of the total VOC emissions. Guenther et al. (1995) have developed a global model to estimate emissions of VOCs from natural sources (excluding methane): Isoprene (C5H8, 44% of the annual global VOC flux), monoterpenes (C10H16, e.g. α-pinene, 11% of the annual global VOC flux), sesquiterpenes (C15H24) and other VOCs emitted by plants or bacteria belong to this class of compounds (Guenther et al., 1995). There is also a wide variety of anthropogenic VOCs: Alkanes (methane, propane and many others), alkenes (e.g. ethene, 1,3-butadiene), benzene derivatives (e.g 1,3,5-trimethylbenzene (TMB), polynuclear hydrocarbons (PAHs)) and solvents (e.g. acetone) could be cited as a few examples. In the atmosphere, VOCs can be oxidized by ozone (O3), hydroxyl radical (OH, referred to here as OH for simplicity) or nitrate radicals (NO3). These oxidation reactions mostly take place in the gas phase. The complexity of the situation is compounded further by the fact that each VOC can undergo a number of atmospheric degradation processes to produce a range of oxidized products, which may or may not contribute to SOA formation and growth (Hallquist et al., 2009). Goldstein and Galbally (2007) estimated that 10 000 to 100 000 different organic compounds are present in the atmosphere.
1.2.2 Hydroxyl radical

The key to understanding tropospheric chemistry begins with the hydroxyl radical (OH). As OH is unreactive toward O2, once produced, it survives to react with virtually all atmospheric trace species (Seinfeld and Pandis, 2006). The most abundant oxidants in the atmosphere are O2 and O3, but these molecules have large bond energies and are generally unreactive, except with certain free radicals; this leaves the OH radical as the primary oxidizing species in the troposphere (Seinfeld and Pandis, 2006). Another exception is the reaction of alkenes with O3.

OH plays a central role in the chemical degradation of VOCs. Typical concentrations of OH in the atmosphere are between 1 and 2·10^6 cm^-3 (Lelieveld et al., 2008). The most widely applied OH concentration measurement technique is laser-induced fluorescence (LIF) combined with a gas expansion, also known as fluorescence assay with gas expansion (FAGE). Other methods are chemical ionization mass spectrometry (CIMS) or differential optical absorption spectroscopy (DOAS). The OH concentration can also be measured indirectly from the decay of a tracer compound. OH is the major oxidizing species in the lower atmosphere. Thus it is the driving factor for the aerosol aging.

1.3 Gas-particle interaction

1.3.1 Gas-particle partitioning theory and the volatility basis set (VBS) approach

(Section adapted from Hallquist et al. (2009))

The phase partitioning of SOA is generally described using the theoretical foundations on organic aerosol phase partitioning developed by Pankow in the 1990s (Pankow, 1994b). Later it was extended by Odum to SOA formation (Odum et al., 1996). The fundamental concept is that SOA comprises a mixture of semi-volatile organic compounds that partition between the gas and particle phases. Partitioning of each compound is described by an equilibrium partitioning coefficient \( K_{p,i} \) (m^3·µg^-1), or equivalently (Donahue et al., 2006) its inverse, the saturation vapor concentration, \( C_i^* \) (µg/m^3):

\[
\frac{C_i^p}{C_i^g} = K_{p,i} \cdot C_{OA} = \frac{C_{OA}}{C_i^*} \tag{1.1}
\]

where \( C_i^g \) is the mass concentration of species \( i \) per unit volume of air (µg/m^3) in the gas phase, \( C_i^p \) is the mass concentration per unit volume of air (µg/m^3) in the particulate phase, and \( C_{OA} \) is the mass concentration per unit volume of air (µg/m^3) of the total absorbing particle phase. \( C_{OA} \) refers only to the portion of the particulate matter participating in absorptive partitioning (an organic aerosol into which semi-volatile organics can partition and possibly the aqueous portion of the particles in the case of highly water-soluble organics). Thus a sphere of Aquadag, fullerene soot or glassy carbon e.g. would not count as \( C_{OA} \).

Note that as long as some absorbing mass is present, some fraction of a given semi-volatile compound will partition into the particle phase, even if its gas-phase concentration is below its saturation concentration, \( C_i^* \). Equation 1.1 can be used to obtain the fraction \( F_i \) of a semi-volatile compound in the particle phase:

\[
F_i = \frac{C_i^p}{C_i^p + C_i^g} = \frac{C_{OA} \cdot K_{p,i}}{1 + C_{OA} \cdot K_{p,i}} = \frac{1}{1 + C_i^*/C_{OA}} \tag{1.2}
\]
Hence as the amount of absorbing material \((C_{OA})\) increases, compounds of greater volatility (larger \(C_i^*\)) will increasingly partition into the particle phase. When \(C_i^* = C_{OA}\), half of the semi-volatile mass of species \(i\) resides in the particle phase. In case that \(C_{OA}\) is much greater than \(C_i^*\), essentially all of the semi-volatile species \(i\) is in the particle phase.

In the first basic model of SOA formation in smog chambers using partitioning theory, Odum et al. (1996) represented the process by the generation of \(n\) semi- (or non-) volatile products, e.g., \(P_1, P_2, \ldots P_n\), and showed that the SOA yield, or mass fraction, \(F_{OA}\), defined as the mass of SOA produced \((\Delta M_{OA})\) when a certain mass of a precursor hydrocarbon \((\Delta M_{HC})\) is oxidized can be derived from Equation 1.1 and expressed as:

\[
F_{OA} = \frac{\Delta M_{OA}}{\Delta M_{HC}} = C_{OA} \sum_i \alpha_i \cdot K_{p,i} \equiv \sum_i \frac{\alpha_i}{1 + C_{OA} \cdot K_{p,i}}
\]

where \(\alpha_i\) is the mass-based stoichiometric yield of compound \(i\). The “volatility distribution” of the oxidation products is represented by the product yields \((\alpha_i)\) and partitioning coefficients \((K_{p,i})\). The traditional approach to representing SOA formation, as embodied in the 2-product model Odum et al. (1996), is based on fitting an empirical gas-particle partitioning model to chamber SOA yield data as a function of the mass concentration of absorbing aerosol Zhang and Seinfeld (2012). The two-product \((n = 2)\) version of Equation 1.3 was used by Odum et al. (1996) because adding more products did not improve the fit to the yields obtained from the chamber studies. As a result, the two-product model has been used as the standard means of representing laboratory SOA yield data in many experimental and modeling studies (Seinfeld and Pankow, 2003; Kanakidou et al., 2005).

With increasing understanding of the nature and complexity of SOA formation, the limitations of representing laboratory data with a two-product model have two major issues:

- the wide range of \(C_{OA}\) (which is the mass concentration per unit volume of air (in \(\mu g/m^3\))) in the atmosphere
- the ongoing oxidation of semi-volatile organics in both the gas and particle phases

Donahue and co-workers (e.g. Donahue et al., 2006; Presto and Donahue, 2006) have proposed the use of a “volatility basis set (VBS)” to address these issues. The VBS consists of a group of lumped compounds with fixed \(C^*\) (saturation concentration of the products) values, comprising up to 9 “bins” separated by one order of magnitude each in \(C^*\) at 300 K. Using the VBS different SOA-forming reactions can be mapped onto the same set of bins over the range of organic aerosol mass concentration typical of ambient conditions (~0.1-100 \(\mu g/m^3\)) while maintaining mass balance for more volatile co-products as well. Aging reactions within the VBS can be added easily if the kinetics and volatility distribution of the products can be measured or estimated. Figure 1.2 shows how experimental SOA yield data from the \(\alpha\)-pinene + \(O_3\) reaction can be fitted to the VBS given a mass balance constraint that the total mass of gaseous and particulate phase products is about 1.4 times the mass of \(\alpha\)-pinene reacted (the mass gain is from added oxygen). The inset to Fig. 1.2 shows the partitioning when 26 \(\mu g/m^3\) of \(\alpha\)-pinene is oxidized to give 1 \(\mu g/m^3\) of SOA, making clear that under typical ambient conditions most of the first-generation products are vapors of a wide range of volatilities.

### 1.3.2 SOA aging

As already mentioned in Section 1.1.3 there is considerable evidence that vapor-particle transformation is dynamic and organic aerosol formation can be induced by gas-phase aging.
reactions that yield products with lower vapor pressures than their parents, yet on the other hand, the heterogeneous oxidation of organic particles can generate products with higher vapor pressures that evaporate from the particles (Hallquist et al., 2009). As the SOA aging often comes along with oxidation processes and hydroxyl radical plays a very important role in the chemical degradation of VOCs, it is indispensable to know the OH concentration.

Jimenez et al. (2009) presented in 2009 a unifying model framework describing the atmospheric evolution of organic aerosol (OA). They find OA and OA precursor gases evolve by becoming increasingly oxidized, less volatile, and more hygroscopic, leading to the formation of oxygenated organic aerosol (OOA). The simplified schemes based only on volatility (see Section 1.3.1) cannot represent the broad diversity in physicochemical properties of organic species, such as polarity, solubility, carbon number, and reactivity, and thus may not reproduce the formation rates, properties, or atmospheric fates of OA (Jimenez et al., 2009). This was the motivation for developing a 2D volatility basis set (2D-VBS) modeling framework using OA volatility \( C^* \) and oxidation state (here approximated by oxygen content, O:C) as its two basis vectors (Jimenez et al., 2009). The 2D-VBS simulates photochemical aging using a functionalization kernel and a fragmentation kernel, a branching ratio between these two pathways, and a simple representation of differing homogeneous and heterogeneous oxidation by the OH — as shown in Fig. 1.3 (Jimenez et al., 2009).

### 1.3.3 Small carbonyls and methane

Small carbonyls are ubiquitous oxidation products of VOCs from a variety of sources and have been considered as non-relevant for the aerosol formation due to their high volatilities which makes them unlikely to undergo effective partitioning to the particulate phase.
1.3 Gas-particle interaction

Figure 1.3 Oxidation can occur in the gas or condensed phase, and reactions transform material. Reactions form three categories: fragmentation, functionalization, or oligomerization, based on whether the carbon number decreases, stays the same, or increases. This model here shows the first two pathways. The branching ratio ($\beta$) between these pathways is critical. Functionalization will reduce volatility considerably, whereas fragmentation can generate more-volatile species, which are less likely to partition to the OA (Figure adapted from Jimenez et al., 2009).

However, identification of oligomers from reactive uptake of glyoxal, the smallest dicarbonyl, as well as of methylglyoxal and glycolaldehyde on seed aerosols or their aqueous phase reactions (e.g. Kroll et al., 2006; Healy et al., 2008; Volkamer et al., 2009) suggests that small carbonyl compounds in the atmosphere can be involved in oligomerisation and hence in SOA formation. As a result, their precursors, e.g., acetylene, which produces a high yield of glyoxal during its atmospheric oxidation, may indirectly contribute to SOA formation as well (Volkamer et al., 2009).

The identification of oligomers and organosulfates in SOA (e.g. Kalberer et al., 2004; Iinuma et al., 2004, 2005; Baltensperger et al., 2005; Samburova et al., 2005; Dommen et al., 2006; Surratt et al., 2006) has established that SOA formation from VOC degradation is not solely driven by the volatility of the gas-phase products formed, but is also influenced by the propensity of degradation products to undergo further reactions in the condensed phase, and how this depends on conditions such as water content, dissolved ions and pH (Hallquist et al., 2009). Condensed-phase reactions that increase the molecular weight can strongly reduce the volatility distribution of the organics. Thus even acetylene ($C_2H_2$), the smallest hydrocarbon after methane, can produce significant SOA due to the high yield of glyoxal from its degradation (Volkamer et al., 2009). In theory the oxidation of methane can also contribute to SOA if e.g., the radical products such as $CH_3O_2$, $CH_3O$, or photolysis products of HCHO react to form species with much lower volatility (Hallquist et al., 2009).

In atmospheric research, methane ($CH_4$) plays a key role due to its very high radiative forcing. Spahni et al. (2005) report that preindustrial $CH_4$ concentrations over Antarctica have not exceeded 773 ($\pm 15$) ppb during the past 650 000 years. During the last 250 years the $CH_4$ concentration increased from about 7000 ppb up to almost 1.8 ppm. Methane has increased as a result of human activities related to agriculture, natural gas distribution and landfills. Methane is also released from natural processes that occur, for example, in wetlands. Methane concentrations are not currently increasing in the atmosphere because growth rates decreased over the last two decades (IPCC, 2007). As methane is the most abundant VOC in the atmosphere and as its oxidation chain is well known (Fig. 1.4) it might be also an interesting subject of study in aerosol research.
1.4 Motivation and thesis outline

There seems to be clear evidence that the Earth’s climate is changing and that human activities contribute to this perturbation by causing changes in Earth’s atmosphere in the amounts of greenhouse gases, aerosols, and cloudiness. This could lead to several severe problems (e.g. of adaptation) for the next generations. According to the IPCC (2007) report, the largest range of uncertainty in the radiative forcing is coming from the direct and indirect aerosol effect. In addition to their climate impact, aerosols do exert an adverse impact on human health. The exact mechanisms and the contributing compounds however are rather unknown. In order to reduce negative impacts for the present and future generations it is inevitable to study aerosols, to know their chemical composition and sources as well as their physical and chemical properties.

Based on the facts described in Section 1.3.3 the question emerges, whether the ubiquitous small carbonyls in the atmosphere contribute to aerosol and if so, what are the SOA formation yields of these carbonyls and which are their precursors? Moreover, in the most recent years with the help of high resolution mass spectrometry a fairly high oxygen/carbon (O/C) ratio was observed in SOA from aged ambient aerosol Aiken et al. (2008). A possible explanation for this high O/C ratio is the fact that small highly oxygenated species (like e.g. formaldehyde, glyoxal and methylglyoxal) are involved in the oligomerisation processes. Consequently further questions rise, such as: If these small carbonyls are involved in the oligomer formation, what are their yields and what is the mechanism? To address these questions it might be worth to have a look at the simplest and most abundant VOC in the atmosphere — methane (CH₄) — where the first steps of oxidation are well known (see also Fig. 1.4). In case that the oxidation products of CH₄ — this fairly unreactive compound — can be found in the aerosol, it is evident that every existing VOC should be able to contribute to
1.4 Motivation and thesis outline

Beside the SOA formation another major challenge in today’s aerosol research is the SOA aging. Kalberer et al. (2004) demonstrated that the degree of oligomerization increases with SOA aging time, while Paulsen et al. (2006) showed that also the remaining volume after thermal treatment increases with aging time. Another form of SOA aging is occurring via heterogeneous oxidation, i.e., rapid uptake of oxidants such as OH which do oxidize organic particles. One of the first-order questions germane to the chemical evolution and semi-volatile organic compounds is whether a given process generates products with a lower or higher volatility compared to the initial compound. Within the MUltiple CHamber Aerosol CHemical Aging Study (MUCHACHAS) the hypothesis was tested whether the OH aging significantly increases the concentration of first-generation biogenic SOA (see Chapter 3). In this context, the determination of OH concentration is essential and by using the integrated OH exposure as a chemical time dimension, enables us to make chamber studies more comparable with atmospheric measurements. In Chapter 4 this OH based metric for aerosol aging is introduced: The “OH clock” uses the OH exposure as a chemical time dimension. Several of its applications are then presented in the Chapters 5 and 6. In addition the “OH clock” permits to pin down other — non OH related — driving factors, as shown in Chapter 6, Section 6.3.

As mentioned, Chapter 4 is treating the OH topic in further detail and some possible tracers for an indirect hydroxyl radical OH measurement technique at smog chambers are discussed. In addition a new OH tracer compound will be presented, which appeared to be very useful for smog chamber studies. Thus OH will play a major role throughout this work (Chapters 3 to 7) as it was the case for the MUCHACHAS. The main focus in Chapter 5 however is on volatility and hygroscopicity of aged SOA originated from α-pinene ozonolysis: The changes in volatility and hygroscopicity reveal the possible mechanisms responsible for the chemical changes in the SOA composition during aging.

Chapter 7 puts the focus on the carbon yield determination of methane. The effects of ambient conditions such as relative humidity, acidity and composition of the seed aerosol and NOx level on the SOA formation yields are also systematically investigated. The seed aerosol might be necessary for some small carbonyls to react with, as they might do under ambient conditions where always an inorganic/organic aerosol is available onto which oxidation products can condense. Therefore we use a method to determine the SOA formation potential from methane in the presence of organic seed aerosols. This method is based on labeling the precursor with 13C — a stable isotope of carbon. The discrimination of the oxidation products of the 13C labeled reactant from the unlabeled organic seed aerosol can then be made by offline isotope ratio mass spectrometry (IR-MS), which measures the 13C/12C ratio. These measurements were done in collaboration with the “Ecosystem Fluxes Group” of the Laboratory of Atmospheric Chemistry (LAC). All the further details are presented in Chapter 7.
2 Instrumentation

2.1 PSI smog chamber

The environmental reaction smog chamber at Paul Scherrer Institute (PSI) (Figure 2.1) was built to simulate particle formation and growth similar to that expected in the atmosphere. It consists of a Teflon® bag enclosing a 27 m³ volume, which can be continuously flushed with pure air. Four xenon-arc lamps placed in the housing can simulate irradiation by sunlight in the chamber. In addition 80 UV lights (Philips, Cleo performance 100 W) located underneath the smog chamber bag can be illuminated to accelerate the aging process. The walls of the housing are covered with aluminum plates to maximize the light intensity and to enhance light scattering or diffusion. A more detailed description of the smog chamber was published by Paulsen et al. (2005). An input system allows the injection of several gaseous species (like e.g. water, NO₂, O₃, SO₂ and VOC).

![Figure 2.1 Sketch of the PSI smog chamber. (From Paulsen et al., 2005).](image)

The temperature (controlled by two cooling units), the relative humidity (RH) and gas phase species (O₃ and NO₂) can be monitored. The aerosol size distribution can also be acquired by a scanning mobility particle sizer (SMPS). Supplementary instrumentation (i.e. aerosol mass spectrometer (AMS), proton transfer reaction mass spectrometry (PTR-MS), cloud condensation nuclei counter (CCNC), volatility/hygroscopicity tandem differential analyzer (V/H-TDMA)) is optional and is used according to the needs of the experiment.
2.2 Proton transfer reaction mass spectrometry (PTR-MS)

Molecules with a proton affinity higher than the one of water are detected by PTR-MS since only these molecules undergo a proton transfer reaction. All common constituents of ambient air ($\text{N}_2$, $\text{O}_2$, Ar, $\text{CO}_2$, etc.) have a lower proton affinity than water. So the air itself acts as a buffer gas and only volatile organic compounds (VOCs), which are usually present in very small densities, get ionized. The fact that common VOCs and oxygenated VOCs except alkanes and small alkenes/alkynes exhibit sufficient proton affinities, makes PTR-MS a suitable tool for measuring most of the common organic trace gases in the atmosphere (Hellen et al., 2008).

The advantage of this system is that — compared to electron impact ionization — the energy transfer in the proton transfer reaction process is very low. This effectively suppresses fragmentation and leads to mass spectra that are easy to interpret. As summarized by de Gouw and Warneke (2007) the further main advantages are:

- The product ion signal is proportional to the VOC mixing ratio.
- PTR-MS allows numerous VOCs of atmospheric interest to be monitored with a high sensitivity and rapid response time (1-10 sec).
- PTR-MS does not require any sample treatment such as drying or pre-concentration.

The commercially available instrument for proton transfer reaction mass spectrometry (see Fig. 2.2) consists of three main parts (adapted from www.ionicon.com):

1. In the ion source $\text{H}_3\text{O}^+$ ions are produced within a hollow cathode discharge and injected into the drift tube.
2. In the drift tube, a (mostly) non-dissociative proton transfer from the $\text{H}_3\text{O}^+$ ions to the VOC trace gases in the sampled air occurs.
3. A quadrupole mass filter is situated in the analyzing system. In conjunction with a secondary electron multiplier, the quadrupole allows mass separation and detection of the ions.

![Figure 2.2 Sketch of the main parts for proton transfer reaction mass spectrometry (PTR-MS). The sketch was taken from www.ionicon.com](http://www.uibk.ac.at/ionen-angewandte-physik/umwelt/research/pics/animation.gif)

A major disadvantage of PTR-MS with a quadrupole mass spectrometer (MS) is that it determines the mass of product ions at unit mass resolution, which is not a unique indicator.
of the VOC identity. It is clear that isomers cannot be distinguished, and the interpretation of mass spectra is further complicated by the formation of cluster ions and the fragmentation of product ions (de Gouw and Warneke, 2007). Despite transmission correction and normalization to the primary ion counts of the values, one has to calibrate the instrument. This is done at the same humidity and temperature as measurements and by using gas standards. The latest used gas standard (from AiR Environmental, Inc.) contained most of the VOCs of interest such as acetone, isoprene, 3-pentanone, toluene, TMB and α-pinene.

### 2.3 Isotope ratio mass spectrometry (IR-MS)

In isotope ratio mass spectrometry (IR-MS), element isotope ratios are determined very accurately and precisely. Complex compounds are reduced to simple molecules prior to measurement, for example, organic compounds are combusted to CO₂, H₂O and N₂ (ASMS, 2012). Isotope ratio measurements are useful in a wide range of applications, for example, metabolic studies using isotopically enriched elements as tracers; climate studies using measurements of temperature-dependent oxygen and carbon isotope ratios in foraminifers; rock age dating using radiogenic isotopes of elements such as lead, neodymium or strontium; and source determinations using carbon isotope ratios (ASMS, 2012). In stable isotope ratio mass spectrometry, the stable isotopic composition of samples is measured relative to the isotopic composition of a working gas. This measured isotopic composition must be converted and reported on the respective international stable isotope reference scale for the accurate inter laboratory comparison of results (Paul et al., 2007). This data conversion procedure is commonly called normalization.

In contrast to conventional stable isotope ratio measurements, where the ratios of \(^{13}\)C/\(^{12}\)C vary very little, we are operating with 99% labeled precursor VOCs. The distinction between the labeled precursors and the unlabeled organic seed aerosol will be unambiguous. The aerosol samples are collected on tin foil in an impactor and on quartz filter. Both samples are burnt under oxygen in an elemental analyzer (EA-1110, Carlo Erba Thermo- quest, Milan, Italy) coupled (in continuous flow mode) to the inlet of the IR-MS instrument. Until 2012 the latter has been a “Delta S” type from Thermo Science Finnigan. Since 2012 the IR-MS analysis for stable \(^{13}\)C isotopes is done with the “MAT 253” type from Thermo Science Finnigan. The carbon excess — which is the amount that stems from the labeled precursor VOC — is finally determined by subtracting the background \(^{13}\)C percentage from the measured \(^{13}\)C percentage. This calculation holds for the assumption, that 100% of the considered precursor VOC is labeled with \(^{13}\)C. In actual fact the labeled percentage of \(^{13}\)C is 99. The resulting error is negligible.

### 2.4 Chemical modeling with the Master Chemical Mechanism

The Master Chemical Mechanism (MCM) was initially developed to compute the photochemical ozone creation potential (POCP) of atmospheric relevant organic compounds (Saunders et al., 2003; Jenkin and Hayman, 1999). Now it is a near-explicit chemical mechanism which describes the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted VOCs. Currently, the degradation of methane and 142 non-methane VOCs is represented. The most up-to-date version is MCMv3.2. However we were mainly using version 3.1, which was already adapted to the PSI smog chamber to simulate the experiments performed therein (Metzger et al., 2008). Regarding the aerosols it might be a disadvantage of this model that it only contains gas-phase reaction and takes
neither condensation of low volatility species nor condensed phase reactions into account.

Concerning the MCM we could build up on a great work that was achieved by my predecessor Axel Metzger. He focused on the evaluation and refinement of the MCM. They substantially extended the number of experiments and variations of experimental conditions for aromatics compared to previous studies. The results showed that the MCM provides a consistent description of the photo-oxidation of TMB/NO\textsubscript{x} mixtures for a range of conditions. In all cases the agreement between the measurement and the simulation decreased with decreasing VOC-NO\textsubscript{x} ratio and in addition with increasing precursor concentration. A significant underestimation of the decay rate of TMB and thus underestimation of the reactivity in the system, consistent with results from previous appraisals of the MCM, was observed. They also showed that there is enhanced nitrous acid (HONO) formation in the presence of VOCs and proposed a photo-enhanced conversion of NO\textsubscript{2} to HONO on the chamber walls to be responsible for this. Implementation of such a reaction considerably reduced the well known discrepancies between model and measurements. This process is of importance for all chamber related mechanism evaluations and is now implemented in the model for the PSI smog chamber. Axel Metzger and co-workers could also show that this photo-enhanced HONO formation is not restricted to TMB photo-oxidation but also occurred in other chemical systems (e.g. α-pinene).

The almost “standardized” determination of the OH concentration in the smog chamber enables us to compare the reactivity in the modeled system with the one in the chamber and — if needed — implement an artificial OH source into the model to compensate for this discrepancy. For this PhD thesis, the MCM was mainly used as a planning and controlling tool.
3

Aging of Biogenic Secondary Organic Aerosol via Gas-Phase OH Radical Reactions

3.1 Introduction

Organic aerosol (OA) comprises a large fraction of fine-particle mass (PM\textsubscript{2.5}) (Jimenez et al., 2009). In the developed world, 1–2% of deaths are blamed on inhalation of PM\textsubscript{2.5} (Pope et al., 2009), and the leading uncertainty in climate forcing is the interplay between the number of fine particles large enough to nucleate cloud droplets and the amount of sunlight reflected by those clouds (IPCC, 2007). Oxidation and condensation of organics play a major but uncertain role in both phenomena.

Traditional models treat most OA as non-volatile primary OA (POA), augmented by SOA (Hallquist et al., 2009), and they underpredict OA concentrations by a factor of 3–


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My contribution to this publication was to run the PSI smog chamber, measure the VOCs and determine the mean OH concentration in the chamber, attending the meetings, presenting my results and commenting on the paper.

Supporting Information (including the Fig. S1 to Fig. S6) can be found on www.pnas.com.
α-Pinene is a major biogenic SOA source, sometimes used to represent all SOA in global models (Kanakidou et al., 2005; Hallquist et al., 2009). However, less than 20% of the carbon from fresh α-pinene oxidation condenses in chambers at room temperature (Shilling et al., 2009); the remainder is gaseous (Fig. 3.1a). This “chamber” SOA is modestly oxidized, with an oxygen to carbon ratio (O:C) < 0.4 (Shilling et al., 2009). It is unambiguously semi-volatile; yields rise with increasing SOA mass loading (Odum et al., 1996; Presto and Donahue, 2006) and decreasing temperature (Saathoff et al., 2009), and the SOA evaporates upon heating (An et al., 2007; Tritscher et al., 2011; Salo et al., 2011) and after isothermal dilution (Grieshop et al., 2007).

In contrast, ambient OA is highly oxidized (0.5 ≤ O:C ≤ 1.0) (Jimenez et al., 2009; Ng et al., 2010) and not very volatile (Huffman et al., 2009). Ambient SOA is much less volatile than ambient POA (Huffman et al., 2009). Consequently, “chamber” SOA does not represent the atmosphere. Our hypothesis is that homogeneous gas-phase aging by OH is a major missing process connecting chamber studies to the atmosphere. Considerable attention has been paid to heterogeneous uptake of oxidants to particles (Pöschl et al., 2007; Rudich et al., 2007), and recently gas-phase oxidation of semi-volatile primary emissions (Robinson et al., 2007), but the degree to which gas-phase oxidation can age chamber SOA is uncertain (Kalberer et al., 2004; Rudich et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009).

OA resides in the atmosphere for about one week (Wagstrom and Pandis, 2009), while the gas-phase lifetimes of major semi-volatile SOA constituents are far shorter. Typical α-pinene products pinonaldehyde, cis-pinonic acid, and pinic acid all have lifetimes of only a few hours for summertime conditions (Vereecken and Peeters, 2002). Without question, oxidation of semi-volatile SOA vapors will perturb the equilibrium phase partitioning of these constituents. Because almost all of the first-generation products are less volatile than α-pinene (Fig. 3.1a), many second-generation products should be even less volatile, leading to increased SOA mass. That could rectify the shortfall in model OA predictions (Spracklen et al., 2011). However, SOA concentrations alone are not the only property of interest; the “target” for OA chemistry includes high oxidation state and low volatility (Jimenez et al., 2009; Ng et al., 2010).

POA sources emit compounds over a wide range of volatility, and oxidation of those vapors dramatically transforms OA properties. After emissions are diluted to ambient concentrations (evaporating semi-volatile compounds), OH exposure results in large increases in aerosol mass and oxygen content (Robinson et al., 2010). However the aging mechanism driving this enhancement is uncertain. The first few hours of chamber data on POA aging can be reproduced with a simple mechanism that irreversibly drives semi-volatile organics to lower volatility (Robinson et al., 2007). Extended to aging SOA, this mechanism improves model agreement in both mass and O:C in short-term box model simulations of Mexico City (Dzepina et al., 2009), but for biogenic SOA it leads to a severe over-prediction of rural OA concentrations in the Southeastern U.S. (Murphy and Pandis, 2009). Consequently, the effects of aging on biogenic SOA remain highly uncertain despite its immense importance.

### 3.2 Experimental Design

MUCHACHAS was designed to separate biogenic SOA formation from aging by OH, and to constrain the effects of that aging. The design is presented as a model simulation in Fig. 3.1b. The model employs a mechanism based on a priori consideration of how oxidation influences volatility. By employing multiple state-of-the-art chambers, MUCHACHAS was able to separate systematic effects such as wall losses and radical sources from the fundamental OH aging process occurring in all of the chambers and by extension the atmosphere.
3.2 Experimental Design

To reduce systematic issues associated with wall losses, light sources, and chamber size, we conducted parallel experiments in four very different chambers described in the methods section. These include Teflon (SAPHIR, PSI, CMU) and aluminum (AIDA) walls with large (SAPHIR, AIDA) and medium (PSI, CMU) volumes. OH was produced by HONO photolysis (SAPHIR, PSI, CMU), alkene ozonolysis (AIDA, PSI, CMU), and HOOH photolysis (CMU). Photolysis was driven by sunlight (SAPHIR), quasi-solar lamps (PSI), and 350 nm UV lamps (CMU). The critical design feature permitting isolation of the aging effect was the near stepwise introduction of OH after the initial SOA formation had reached completion.

Wall and dilution losses impede chamber studies, which are mass balances (Matsunaga and Ziemann, 2010); they must be modeled. Particle wall losses are high in small chambers (CMU = 0.4 h⁻¹, PSI = 0.17 h⁻¹) and low in large chambers (AIDA = 0.014 h⁻¹, SAPHIR...
= 0.04 – 0.16 h\(^{-1}\) depending on fan and roof state). Dilution is significant in SAPHIR (0.034 h\(^{-1}\)). Any loss of condensable vapors other than the target chemical loss or condensation to suspended particles is an unseen part of the mass balance. Direct vapor wall losses are high only in aluminum-walled AIDA (0.36 h\(^{-1}\)) (Saathoff et al., 2003b, 2009). For the teflon chambers (SAPHIR, PSI, and especially CMU, where \(2/3\) of the mass is on the walls at \(t = 0\)), vapor condensation to particles after deposition to the walls is a major uncertainty.

### 3.3 Model Description

The mechanism behind Fig. 3.1b is built on the 2D volatility basis set (2D-VBS) framework. The 2D-VBS classifies organics based on volatility (\(C^*\)) and oxidation extent (Donahue et al., 2011, 2012b; Kroll et al., 2011; Jimenez et al., 2009). To construct a lumped mechanism, described in detail in the supplemental material, we discretize this 2D space into bins and consider the changes to \(C^*\) and O:C caused by OH oxidation. Reaction with OH transforms source organics in one bin to products distributed among many other bins. Here vapors react with OH at \(3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), while heterogeneous OH uptake is either 5 times slower (with the same product distribution) or negligibly slow. While the gas-phase OH rate constants are uncertain, there is no doubt that the organic vapors will react with OH rapidly, and there is also no doubt that heterogeneous OH uptake is much slower.

For the full product distribution we describe two processes via generalized oxidation “kernels” (Fig. S1): functionalization, where the carbon number is conserved and products move to lower volatility and higher oxidation state, and fragmentation, where products are spread widely over lower carbon numbers and thus (mostly) higher volatility and oxidation state (Chacon-Madrid et al., 2010; Kroll et al., 2011).

Functionalization always forms products with lower volatility than the reactant; one generation of chemistry in our model makes products with \(C^*\) decreased by \(1 – 6\) (mostly 2 – 4) orders of magnitude, consistent with average addition of one -OH and one =O group per oxidation step (Donahue et al., 2011). Fragmentation generates products over a wide volatility range. Fragmentation is a two-step process: initial fragments are distributed between the \(C^*\) of the reactant and the largest \(C^*\) in the model, but half of these fragments are radicals that immediately functionalize to form lower \(C^*\), more oxygenated stable products. Some fragmentation products are thus less volatile than the precursor. In addition, fragments can also functionalize in a subsequent oxidation step; for both of these reasons fragmentation products must be tracked because they can contribute to SOA formation. These two processes are reasonably well constrained for hydrocarbons (Atkinson, 1997; Lim and Ziemann, 2009); we assume this extends to more oxidized organics.

A key element of the mechanism is the branching ratio between functionalization and fragmentation for lumped species in a given 2D-VBS bin. Here the effect of increasing oxygenation can be described. This branching ratio is uncertain, and so we rely on an empirical parameterization. Early models had no fragmentation (Robinson et al., 2007; Dzepina et al., 2009), but data reported by Kroll et al. (Kroll et al., 2009) showed that fragmentation increases dramatically as O:C rises from \(0\) to roughly \(0.5\). Jimenez et al. (Jimenez et al., 2009) parameterized the branching ratio with O:C\(^{1/6}\). Because the kernels are based on mechanistic insight from VOC oxidation, we limit adjustment to this single \textit{ad hoc} parameter (Fig. S2), with O:C\(^{1/4}\) giving the best model-measurement agreement. The important feature is the rapid increase in fragmentation for functionalized compounds. Our simulations are most sensitive to branching at the O:C of first-generation products (80% fragmentation at O:C = 0.4).
3.4 Results

The mechanism is bounded by several constraints. First-generation volatility distributions (Fig. 3.1a) are well constrained by chamber-SOA formation data. It is very likely that second-generation products will be, on average, less volatile and thus SOA mass yields will rise with continued OH oxidation (Fig. 3.1b). However, complete oxidation to CO$_2$ includes complete volatilization; eventually mass yields must fall, and particles do shrink after intense OH exposure \cite{Kroll et al., 2009}. The mechanism thus interpolates between the (observed) rising mass yields between the first and second generations and the inevitably decreasing yields over longer timescales. The uncertainties are the magnitude and timing of the maximum in Fig. 3.1b and how this varies with photochemical conditions (i.e. VOC: NO$_x$, UV light, etc.).

3.4 Results

In all experiments a chamber was prepared by thorough cleaning and then filled with clean air and at least one tracer to follow OH radical production. We then added ozone and \textalpha-pinene and allowed the reaction to proceed to completion. This generated a collection of first-generation reaction products in both the vapor and condensed phases as in Fig. 3.1a. This dark interval (the shaded region in Figs 3.1b and 3.2) served as a control and continued long enough to constrain the wall-loss parameters. After the dark interval we turned on an OH-radical source and monitored changes in the SOA.

Representative results from each chamber for similar OA concentrations are shown in Fig. 3.2. OH exposure almost always led to a significant increase in SOA concentrations. The model used in Fig. 3.1b, with additional treatment of wall losses, is shown with solid green curves in Fig. 3.2 while the dashed curves show model runs with no OH aging. Wall losses caused the observed mass concentration increase from OH aging to be much less than the twofold increase intrinsic to the mechanism (upper solid curve in Fig. 3.1b) because we assumed that wall-bound particles behave like suspended particles and thus consume some of the condensable vapors (Figs S3 – S5). The step function in OH makes the effect of aging evident even in experiments with low OH and high wall losses.

For the complete MUCHACHAS dataset, the different chambers and OH sources spanned a wide range of conditions. Dark OH production from TME ozonolysis \cite{Lambe et al., 2007} was used in AIDA (exclusively) and also at PSI and CMU. HONO photolysis at PSI (Fig. 3.2c) and CMU (Fig. S5) produced more OH and sharper initial SOA concentration increases. The natural photolysis in SAPHIR \cite{Rohrer et al., 2005} produced the lowest OH concentrations (typical of ambient OH) and consequently the smallest net SOA concentration increase.

For temperature-dependent experiments in AIDA we controlled the \textalpha-pinene concentrations to keep the fresh SOA level constant. At 253 K, more than half of the carbon was in the condensed phase, while at 313 K less than 10% was. We observed greater aging mass increases at elevated temperatures, consistent with the larger pool of vapors available for OH oxidation. Our model also predicts larger fractional increases for lower SOA concentrations at 300 K, because a greater fraction of the carbon is in the gas phase (lower curves in Fig. 3.1b).

The different chamber loss mechanisms taken together constitute an experimental advantage. For example, we clearly observed rapid loss of organic acid vapors to the AIDA walls for directly injected cis-pinonic acid \cite{Müller et al., 2012}. The mass loss for AIDA experiments (Fig. 3.2b) was because of semi-volatile vapor loss, consistent with other isothermal observations \cite{Grieshop et al., 2007, Vaden et al., 2011}. At PSI and CMU, however, particle diameters were stable after SOA formation, and mass losses were associated with particle number loss via deposition to the walls.
We observed much more than SOA concentration changes. The oxygen to carbon ratio (O:C) clearly increased after OH production (Fig. 3.3a, measured with a high-resolution aerosol mass spectrometer (HR-AMS) (Jimenez et al., 2009)). Individual fragment ions showed more nuanced behavior. Despite the nearly constant SOA mass late in the dark period, the AMS spectra evolved steadily, at a rate independent of external parameters (ozone concentrations, OH concentrations, etc.). We call this evolution “ripening” to distinguish it from OH-driven chemical aging. During ripening, $f_{44}$ (the fraction of the organic signal at $m/z = 44$, predominantly CO$_2$) rose, $f_{43}$ (mostly CH$_3$CO$^+$) fell, but O:C remained roughly constant (DeCarlo et al., 2013).

We observed cloud condensation nucleus (CCN) activity (Frosch et al., 2011), volatility via tandem differential mobility analysis (V-TDMA) (Salo et al., 2011; Tritscher et al., 2011), and subsaturated water uptake via hygroscopicity TDMA (H-TDMA) (Tritscher et al., 2011). The CCN activity of the organics was largely unaffected by either ripening or OH oxidation (Frosch et al., 2011). Volatility (Fig. 3.3b) showed a consistent temporal pattern in AIDA, PSI, and SAPHIR, responding to ripening and to OH aging (Tritscher et al., 2011).
3.4 Results

Figure 3.3 Additional changes to SOA properties and constituents during OH aging experiments. (a) Typical evolution of molar oxygen to carbon ratio (O:C, magenta circles) modeled with the 2D-VBS (magenta curve). The model reproduces the increase in O:C for the first 1.5 h well. Afterwards model and measurements diverge, either because oxygenation in the model is too aggressive or because OH levels (and consequently aging) declined later in the experiment. The sharp early drop in the model arises from fresh SOA growth; the least volatile constituents have the highest O:C. (b) Volatility data combine a steady decrease in volatility (increase in volume fraction remaining) unrelated to OH exposure with a sharp increase in volatility immediately after OH exposure, suggesting that fresh semi-volatile SOA addition dominates over aging of existing semi-volatile SOA. (c) Gas-phase fraction of cis-pinonic acid (magenta circles) and levels of MBTCA (red triangles) vs. temperature in AIDA. Separate experiments with pure cis-pinonic acid showed conclusively that MBTCA is formed from cis-pinonic acid oxidation by OH in the gas phase. These results show that as the cis-pinonic acid is sequestered in the condensed phase at low temperatures, the MBTCA formation is reduced proportionally.

Salo et al., 2011). Volatility measured by the volume fraction remaining at a fixed elevated temperature decreased progressively during ripening, increased sharply with the introduction of OH, and then reverted to a more gradual progressive decrease after roughly 1 hour of OH aging. Though the average volatility of the SOA increased with OH aging, this masked a concurrent broadening of the volatility distribution. This broadening suggests that while the newly added mass formed from OH aging had fairly high volatility, this aging also formed a significant amount of very low volatility material. During the ripening period the unsaturated hygroscopicity observed with H-TDMA remained roughly constant (Tritscher et al.,
Production of low volatility organics via OH aging was confirmed by measurement of individual products. In AIDA, organic acids were measured with atmospheric pressure chemical ionization mass spectrometry (APCI-MS) (Müller et al., 2012). We observed the phase partitioning of acids shown in Fig. 3.1 (e.g. the cis-pinonic acid partitioning in Fig. 3.3c), and established conclusively that the triacid MBTCA is produced from gas-phase oxidation of cis-pinonic acid by OH. MBTCA in SOA increased sharply after OH formation. Production was correlated with the fraction of cis-pinonic acid in the gas phase (Fig. 3.3c), suggesting that this triacid is effectively a first-generation product of cis-pinonic acid. To confirm this, we introduced a mixture of pinic and cis-pinonic acids into AIDA; only when cis-pinonic acid vapors were being actively added to the chamber while OH was also being generated did the MBTCA signal rise (Müller et al., 2012).

3.5 Discussion

MUCHACHAS experiments were carefully designed to separate initial SOA formation from subsequent exposure to OH radicals in an aging step, and to ensure that substantial concentrations of OH were produced during that step. The results confirm dramatic aging effects and strongly suggest that the major effect of OH reactions is to enhance SOA concentrations by a factor of 2-4 (Fig. 3.1b). The fundamental result is that gas-phase reactions of semi-volatile SOA vapors are clearly an important part of OA evolution, and these experiments substantially extend the timescale of the chamber studies.

Model-measurement agreement varies between experiments. It is best for the AIDA and PSI experiments, with the highest and most intense OH exposure relative to wall losses. The fresh SOA prediction ($t \leq 0$ in Fig. 3.2) is based on the scavenger-free SOA mass yields in Fig. 3.1. (Henry and Donahue, 2011). SOA production is known to vary with conditions (VOC:NOx, UV light, etc. (Hallquist et al., 2009)) that were not kept constant in different experiments. We did not attempt to model those differences because the essential and invariant feature is that a large pool of vapors can react with OH radicals during aging. Consequently, we adjusted the initial $\alpha$-pinene by $\leq 10\%$ to match the SOA level at $t = 0$ so that the aging data are easy to compare with the model in Fig. 3.2.

We could have adjusted chamber-specific parameters further in order to match experimental data. As an example, the observed aging growth in the CMU chamber (Fig. 3.2d) is larger than the model; this could be due to the large modeled flux of condensible vapors to particles on the wall, but we lack sufficient evidence to “tweak” this parameter. Such adjustments would be as likely to mask chamber-specific systematic errors as to provide new insight. Instead we applied a common model that reproduces the general features of all the chamber experiments; this makes a stronger case for our main conclusion regarding OH-initiated aging of biogenic SOA. The differences between the model and measurements reflect real uncertainties that will not be reduced by model- and chamber-dependent parameter tuning.

The MUCHACHAS findings also highlight significant remaining uncertainties that must be addressed before a complete aging mechanism can be described. One is the degree of fragmentation. Without fragmentation the 2D-VBS rapidly converts vapors to SOA with $\sim 180\%$ mass yields because of added oxygen (blue dash-dot curve, Fig. 3.1b). The preferred mechanism peaks at $\leq 50\%$ (lower green curves, Fig. 3.1b). Low fragmentation may be suitable for high molecular weight POA vapors (Robinson et al., 2007), but not lighter and more oxygenated biogenic SOA. The empirical O:C$^{1/4}$ relation for the fragmentation branching ratio captures this difference, but it is quantitatively uncertain. As shown in the supplemental
material, different numerical values of this parameter result in different SOA enhancements from aging, but the overall conclusion that OH oxidation results in a substantial SOA mass increase is robust.

Another uncertainty is the nature and effect of ripening, which may well be oligomerization (Kalberer et al., 2004). Some properties evolve, such as volatility, while others remain roughly constant, such as organic mass and CCN activity. Furthermore, the MUCHACHAS experiments were carried out at medium to low relative humidity and thus avoided (by design) potential aqueous-phase aging reactions, which could well be important in the atmosphere.

UV photolysis may also affect the oxidized SOA. Experiments at CMU showed a strong UV effect; in the extreme case, with weak OH formation ($\sim 10^6 \text{ cm}^{-3}$) via HOOH photolysis using 360 nm UV lights, SOA mass diminished monotonically during aging. For HONO photolysis the SOA initially rose, consistent with the PSI results in Fig. 3.2, but fell again after OH concentrations declined from $\sim 10^7$ to $\sim 10^6 \text{ cm}^{-3}$. With TME + ozone OH production, SOA concentrations rose on aging with OH production in the dark (as in Fig. 3.2), but the rise halted if the UV lights were turned on (Henry and Donahue, 2012). The same effect may be evident in the SAPHIR data, as shown in Fig. 3.2: OA concentrations initially rose upon aging but ultimately failed to increase as rapidly as our model predicted, again when OH production was relatively weak in the presence of UV light (in this case sunlight).

A final uncertainty is the effect of heterogeneous OH uptake, with limiting behavior indicated by the solid and dashed curves in Fig. 3.1b. The differences between the curves are substantial; both accommodation coefficients for OH and the resulting mechanisms are highly uncertain for atmospheric aerosols. OH uptake clearly oxidizes organic particles (Kroll et al., 2009), causing the oxidation state to rise and carbon numbers to decrease (Kroll et al., 2011). For the model producing the dashed green curves in Fig. 3.1b we presume that the homogeneous gas-phase and heterogeneous mechanisms are the same despite the different rates, which is probably not true. Because of gas-phase diffusion limitations heterogeneous oxidation is almost certainly a factor of 5-20 slower than the corresponding homogeneous oxidation (Lambe et al., 2009), but the heterogeneous oxidation timescale is still shorter than the aerosol residence timescale (Wagstrom and Pandis, 2009). If the mechanism including heterogeneous oxidation is valid, as shown with the dashed curves in Fig. 3.1b, this could partly counteract the mass increases of aging, though the average concentrations would still be elevated and variable. Furthermore, the residual aerosol would be highly oxidized and distributed down to very low volatility, consistent with observations in remote locations (Ng et al., 2010; Hildebrandt et al., 2010).

### 3.6 Conclusions

OH aging strongly influences biogenic SOA properties and concentrations throughout the aerosol life cycle in the atmosphere. Aging can significantly increase SOA concentrations beyond first-generation mass yields, by a factor similar to the disagreement between some models and observations (Hallquist et al., 2009; Spracklen et al., 2011). The interval in Fig. 3.1 spans $\sim$ 1 week in the atmosphere, yet many photochemical models currently only describe the gray interval ($t \leq 0$), or even simply assume a constant mass yield at $t = 0$ by parameterizing SOA formation as a fraction of the terpene flux from the biosphere. Based on the MUCHACHAS results, this is clearly inadequate, and the mechanism presented here provides at least a partial solution to a more accurate representation.

An ongoing challenge is to isolate the various effects influencing OA over the week or so average residence time in the atmosphere. OA comprises thousands of molecules, making
complete elucidation a formidable challenge; a hypothesis of MUCHACHAS was that meaningful average behaviors could be described and applied to atmospheric simulations. This first step demonstrates the influence of OH aging chemistry on biogenic SOA, and the potential application of OH aging in regional and global models to accurately simulate organic aerosol mass concentrations and properties.

Materials

Chambers: Carnegie Mellon University (CMU) 12 m$^3$ teflon chamber (Presto et al., 2005); the Paul Scherrer Institute (PSI) 27 m$^3$ teflon chamber (Paulsen et al., 2005); the Karlsruhe Institute of Technology 84.5 m$^3$ Aerosol Interaction and Dynamics in the Atmosphere (AIDA) aluminum chamber (Saathoff et al., 2003a); and the Forschungszentrum Jülich 270 m$^3$ Simulation of Atmospheric Photochemistry in a large Reaction chamber (SAPHIR) double-walled teflon outdoor facility (Rohrer et al., 2005). The CMU (Presto et al., 2005) and PSI (Paulsen et al., 2005) chambers are similar. However, the CMU chamber relies on 360 nm UV lights for illumination, while the PSI chamber uses filtered Xe lamps to produce quasi solar light. For MUCHACHAS each chamber was held near 298 K. The AIDA chamber has temperature and pressure control over a very wide range (188 – 333 K, 0.01-1100 hPa) (Saathoff et al., 2003a); SOA experiments were conducted at 253, 273, 293, and 313 K and 1013 mb, while the cis-pinonic acid oxidation experiments were conducted at 283 K. Finally, the SAPHIR chamber is housed within a completely retractible outdoor enclosure. Illumination is solar, and conditions are nearly ambient (it is held slightly over atmospheric pressure to ensure that any leakage goes out of the chamber, and it is typically slightly warmer than ambient due to radiational heating).

Instrumentation: All experiments included a proton-transfer reaction mass spectrometer (Lindinger et al., 1998; Presto et al., 2005), a scanning mobility particle sizer, an Aerodyne aerosol mass spectrometer (Jayne et al., 2000; DeCarlo et al., 2006), and either a thermodenuder (An et al., 2007) or a volatility tandem differential mobility analyzer (Tritscher et al., 2011; Salo et al., 2011). Most experiments measured SOA hygroscopicity, either with tandem differential mobility (Tritscher et al., 2011) measurements below 100% RH or with cloud condensation nucleus counting (Asa-Awuku et al., 2009; Frosch et al., 2011) above 100% humidity or both.

At AIDA we employed an atmospheric pressure ionization mass spectrometer (Müller et al., 2012) and filter solvent extraction GC/MS to measure condensed-phase organic acids, while at PSI ion chromatography was employed to measure selected acids in both phases. At SAPHIR, OH and HO$_2$ radicals were measured directly using Laser Induced Fluorescence (Hofzumahaus et al., 2009).

OH Sources: We used several different OH radical sources. These were the dark reaction of ozone and tetramethyl ethylene (Lambe et al., 2007) (CMU, AIDA, PSI), UV photolysis of hydrogen peroxide at 360 nm (Kroll et al., 2006; Hildebrandt et al., 2009) (CMU), and photolysis of nitrous acid in the near UV (CMU, PSI, SAPHIR). The different sources result in different balances between OH, HO$_2$ and organic peroxy radicals, different peroxy radical oxidation pathways (especially under high and low NO$_x$ conditions) and different amounts of photolysis of oxygenated organic oxidation products.
4

OH clock determination by proton transfer reaction mass spectrometry at an environmental chamber

4.1 Introduction

The hydroxyl free radical (OH) is the primary cleansing agent of the lower atmosphere (IPCC, 2007); it is the key reactant for the degradation of most compounds emitted from biogenic and anthropogenic sources into the troposphere (Ehnhalt, 1999, Lelieveld et al., 2004). Globally, OH radicals are mostly produced by photolysis of ozone ($O_3$) and the subsequent reaction of the formed excited oxygen atoms with water vapor. Minor sources include the photolysis of nitrous acid (HONO) and hydroperoxides, as well as the ozonolysis of alkenes. The major secondary OH source, i.e. from other radical species, is the reaction of nitric oxide (NO) with hydroperoxy radicals. Lifetimes of OH vary between 1 s and 10 ms in clean and polluted environments, respectively, due to the rapid reactions of OH with atmospheric trace gases (Schlosser et al., 2009).

Owing to its central importance, absolute measurements of OH concentrations are crucial and they are needed to determine the progress of photochemical aging. A useful metric is the photochemical age defined as OH exposure which can be used as a chemical clock (OH clock). The OH clock corresponds to the OH concentration integrated over time. This chemical time dimension makes experiments e.g. between different smog chambers more comparable than other widely used clocks such as “time after lights on” (TALO) or “time after start of secondary organic aerosol (SOA) formation” and has been applied already in other publications.
e.g. Hennigan et al. (2010). Also for comparisons between lab studies and atmospheric measurements the OH clock is a fundamental parameter – especially since the photochemical age has been determined in many atmospheric studies.

Atmospheric OH is hard to measure (Brune, 1992), since low OH concentrations require extremely sensitive detection techniques and OH reacts efficiently at wall surfaces, requiring precautions to avoid instrumental OH loss. Another reason is that most other atmospheric species are much more abundant, raising the potential for interferences in OH detection. Furthermore, stable calibration mixtures for OH do not exist (Schlosser et al., 2009).

However, the large-scale concentrations and long-term trends of OH concentrations in the atmosphere can be inferred indirectly using global measurements of trace gases for which emissions are well known and their primary sink is the reaction with OH. According to IPCC (2007), the best trace gas used to date for this purpose is methyl chloroform. Other gases that are useful OH indicators include $^{14}$CO, which is produced primarily by cosmic rays (Lowe and Allan, 2002). Another useful gas is the industrial chemical HCFC-22. It yields OH concentrations similar to those derived from methyl chloroform, but with less accuracy due to greater uncertainties in emissions and less extensive measurements (Miller et al., 1998). Indirect measurements of OH concentrations using methyl chloroform have established that the globally weighted average OH concentration in the troposphere is roughly $10^6$ cm$^{-3}$ (Prinn, 2001; Krol and Lelieveld, 2003). A similar average concentration is derived using $^{14}$CO (Quay et al., 2000).

Tropospheric OH was detected for the first time by Perner et al. (1976) using differential optical absorption spectroscopy (DOAS). Schlosser et al. (2009) report that the most widely applied OH concentration measurement technique is laser-induced fluorescence (LIF) combined with a gas expansion, also known as fluorescence assay with gas expansion (FAGE). LIF instruments directly measure OH concentrations with high sensitivity and can be built compact for mobile operation. Chemical ionization mass spectrometry (CIMS) is an OH concentration measurement technique with very high sensitivity and good mobility for ground and aircraft field campaigns comparable to LIF instruments (Eisele and Tanner, 1991; Berresheim et al., 2000). Long-term monitoring of OH concentrations has only been demonstrated using CIMS (Rohrer and Berresheim, 2006). OH concentration measurements using DOAS are currently only operated by researchers at the Jülich Forschungszentrum in field and chamber campaigns (Dorn et al., 1996; Brauers et al., 2001; Schlosser et al., 2007). According to Schlosser et al. (2009) all three techniques (DOAS, LIF, CIMS) involve elaborate, expensive, custom-made experimental setups. Therefore, worldwide less than ten research groups measure atmospheric OH concentrations using these techniques. Other techniques, e.g. the salicylic acid scavenger method (Salmon et al., 2004) or the radiocarbon tracer method (Campbell et al., 1986) do not have the degree of accuracy, sensitivity and time resolution provided by LIF, CIMS, and DOAS (Schlosser et al., 2009).

Many researchers over the last decades have used the VOC ratio method to determine average OH concentrations and its photochemical age in an air parcel. Calvert (1976) made the first indirect estimates of the average ambient concentration of the OH from the observed rates of removal of hydrocarbons of different OH-reactivities. This concept of using reactive tracers to determine the OH concentration has been discussed (and improved) in several publications in the past, like e.g.: Singh et al. (1981); Roberts et al. (1984); McKeen et al. (1990); Satsumabayashi et al. (1992); Blake et al. (1993); McKenna et al. (1993); Kramp and Volz-Thomas (1997). Other studies use the ratio of NO$_2$ to NO$_y$ to determine the photochemical age (Kleinman et al., 2008; Slowik et al., 2011).

These ambient measurements emphasize the need of using the OH clock also in smog chamber studies – as this has just begun to be done in the last few years. Based on the findings
of Poppe et al. (2007) at the SAPHIR chamber in Jülich, this indirect technique works also at environmental chambers. The decay of several hydrocarbons by hydroxyl radicals was measured with gas chromatography and proton transfer reaction mass spectrometry (PTR-MS, described by Lindinger et al., 1998) while the OH was measured with DOAS. The combination of these measurements yielded reaction rate constants in good agreement with the reference rate constants taken from the Master Chemical Mechanism (MCM3.1).

Direct OH concentration measurement in chambers are difficult to maintain over long time periods, as for most OH measurement techniques (except DOAS) very high flow rates are required. Also, most species reacting with OH in chambers have lifetimes of many minutes to hours and thus the chamber-averaged OH concentration must be known. OH is likely not uniform in most chambers, and in situ methods like LIF or CIMS will not necessarily constrain this average.

Against this background, a method of feasibly determining OH concentrations with instruments commonly installed at environmental chambers would be highly valuable. One possibility in this context is the use of an adequate OH tracer that can be monitored by PTR-MS. Changes in the tracer concentration over time can be expressed as:

$$\frac{d[\text{tracer}]}{dt} = -k \cdot [\text{OH}] \cdot [\text{tracer}] \quad (4.1)$$

In the case of constant OH concentration levels, one can integrate Eq. (4.1) to get Eq. (4.2):

$$\ln([\text{tracer}]) = -k \cdot [\text{OH}] \cdot t + \ln([\text{tracer}]_0) \quad (4.2)$$

Plotting the natural logarithm (ln) of the tracer concentration versus time ($t$), results in a slope that equals $-k \cdot [\text{OH}]$. The OH concentration is therefore:

$$[\text{OH}] = -\frac{\text{slope}}{k} \quad (4.3)$$

In order to use a direct oxidation product of the reaction of a reagent with OH as an OH tracer, one has to modify Eq. (4.2), using the relation between the amount of the reacted reagent and the produced product:

$$[\text{product}] \cdot q = [\text{reagent}]_0 - [\text{reagent}] \quad (4.4)$$

Where $q$ is the proportionality factor between the “reagent reacted” and the “product produced” by the reaction with OH.

The analogous of Eq. (4.2) would then be:

$$\ln(1 - \frac{[\text{product}]}{[\text{reagent}]_0/q}) = -k \cdot [\text{OH}] \cdot t \quad (4.5)$$

Plotting the left side of Eq. (4.5) versus time ($t$), results in a slope that equals $-k \cdot [\text{OH}]$. The OH concentration is then calculated again with Eq. (4.3).

In our case, the ideal OH tracer has to be detectable by PTR-MS (which requires that its proton affinity is higher than the one of water), react only with OH, and have no interference with other compounds at the tracer’s mass-to-charge ratio ($m/z$). The last point pertains mainly to an instrument with a quadrupole mass spectrometer at unit mass resolution. Furthermore the tracer should exhibit a certain reactivity (neither too fast nor too slow) such that changes in concentration during the course of an experiment are measurable.

In this paper, we discuss three OH tracers which were used to determine the OH concentration during an α-pinene (AP) ozonolysis and aging campaign where we suggest the
use of an OH based dimension: the OH clock. Furthermore a new, deuterated OH tracer for PTR-MS is presented, together with the investigation of its reaction rate constant with OH. This deuterated OH tracer exhibits a characteristic \( m/z \) unlikely to interfere with any other compounds.

### 4.2 Experimental setup

#### 4.2.1 MUCHACHAS

The Multiple Chamber Aerosol Chemical Aging Study (MUCHACHAS) was designed to test the hypothesis that hydroxyl radical oxidation significantly alters the levels and properties of SOA [Donahue et al., 2011]. The typical design of a MUCHACHAS experiment is shown as schematic in Fig. 4.1 (see also Tritscher et al., 2011). The precursor in all experiments was AP. This precursor first reacted with \( O_3 \) to form SOA. Then, after nearly all the precursor was consumed, this SOA and partially oxidized gas-phase species were exposed to OH from different sources in order to observe additional production and aging of SOA by OH. The overall results of the MUCHACHAS campaign are presented in [Donahue et al., 2012a], and only a short summary on the experimental details is given here (see also Tritscher et al., 2011).

![Figure 4.1](image)

**Figure 4.1** Schematic of the experiments during the MUCHACHAS campaign at the PSI smog chamber. Formation of secondary organic aerosol (SOA) mass (wall-loss corrected) from the volatile organic precursor \( \alpha \)-pinene (AP) takes place during the first part in the dark with ozone (\( O_3 \)). The aging of the SOA and gaseous products from ozonolysis was then investigated under different conditions. The data can be plotted against several time axes as “time after AP injection was started” and “time after the OH reaction started” or against a “chemical clock” as \( O_3 \) exposure and OH exposure. During ozonolysis and reaction with OH the four different periods of our experiments are indicated above the figure: \( O_3 \) induced condensation, ripening, OH induced chemical aging with substantial mass gain, and OH induced chemical aging without significant mass gain (reproduced from Tritscher et al., 2011).
In all experiments, the clean PSI smog chamber – described in Paulsen et al. (2005) – was humidified to $\sim 50\%$ RH and O$_3$ was added in a first step. After about 20 min, when O$_3$ was homogeneously distributed in the chamber, the precursor AP was injected. We conducted experiments at two atmospherically relevant precursor mixing ratios of 40 ppb and 10 ppb AP. The reaction started immediately via ozonolysis of the C=C double bond in AP, forming particles (first generation SOA). The OH formed by the ozonolysis will mainly react with AP, as long as it is still present in excess. Ozonolysis lasted a few hours until at least 90\% of the AP precursor had reacted. This phase is subdivided into a O$_3$ induced condensation and a ripening period (see Fig. 4.1).

In a next step, 20 ppb of 3-pentanol was added as an OH tracer. Then SOA was aged by exposure to OH generated from either photolysis of HONO or ozonolysis of tetramethylethylene (TME) (IUPAC name: 2,3-dimethyl-2-butene) (Epstein and Donahue, 2008). A HONO level of 15–20 ppb (as measured by a long path absorption photometer; LOPAP) in the chamber was reached by passing pure air (2 l min$^{-1}$) through a custom built vessel containing sulfuric acid (0.01 M H$_2$SO$_4$) and sodium nitrite (3 $\times$ 10$^{-3}$ M NaNO$_2$). The vessel and the HONO system are described elsewhere (Taira and Kanda, 1990). The flow from the HONO generator was passed through a filter to ensure that only the gas phase HONO without particles entered into the chamber. The addition of HONO started about one hour before the lights were turned on. The goal was to perform these experiments in a low-NO$_x$ regime. In contrast, for some high-NO$_x$ photolysis experiments, 50–80 ppb NO was added aside from HONO. For OH experiments in the dark, TME was continuously injected from a gas cylinder (Messer, TME 1000 ppmv in N$_2$ 5.0) at a flow of 10 ml min$^{-1}$. The O$_3$ level was usually chosen to be higher in the TME experiments compared to HONO photolysis experiments because O$_3$ was also consumed by the ozonolysis of TME. This second phase of the experiment, i.e. reaction and aging with OH could be divided into an OH induced chemical aging with and without significant mass gain (see Fig. 4.1).

The OH concentration in the environmental chamber was derived from the decay of 3-pentanol and from a specific intermediate product of AP and pentanol oxidation. In total, the following three OH tracers were tested:

- 3-pentanol, which was injected additionally,
- the formation of 3-pentanone (also named diethyl ketone), a direct oxidation product of the reaction of 3-pentanol with OH,
- pinonaldehyde (PA), an ozonolysis product of AP.

The OH concentration integrated over time is used as a chemical clock to bring all experiments on a comparable time scale. One application of the OH clock for the MUCHACHAS campaign has been published by Tritscher et al. (2011). The rate constants used to calculate OH concentrations and the OH clocks were: $k_{3\text{-pentanol}}$(298.15K) = 1.22 $\times$ 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Wallington et al., 1988) for 3-pentanol and $k_{PA}$(298.15 K) = 3.9 $\times$ 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2011) for PA.

### 4.2.2 Butanol-d9

The mass spectra in PTR-MS show generally low signal intensities at even mass-to-charge ratios ($m/z$) due to the protonation of the compounds (M+H$^+$). Owing to its unusual mass-to-charge ratio ($m/z$ 66, [M+H$_2$O]$^+$), 9-fold deuterated butanol (butanol-d9; n-butanol (D9, 98\%); IUPAC name: [1,1,2,2,3,3,4,4,4-$D_9$] Butan-1-ol) promises to be a suitable OH tracer. The rate constant $k_{n\text{-butanol}}$ of undeuterated n-butanol with OH is quite well known (according to IUPAC the reliability is $\Delta \log(k) = \pm 0.15$ at 298 K; IUPAC, 2011), however, due to the kinetic isotope effect (KIE) it differs from the k-value of deuterated butanol. The investigation of the rate constant of butanol-d9 with OH was done relative to the well known k-value (reliability: $\Delta \log(k) = \pm 0.1$ at 298 K; IUPAC, 2011) of 2-butanone (also named methyl...
ethyl ketone) as a reference compound. Additionally we injected the “MUCHACHAS-tracer” (3-pentanol).

The experiments were performed at the PSI smog chamber and the OH tracers were monitored by PTR-MS with a quadrupole detector. Butanol-d9, 2-butanone and 3-pentanol were injected in 20 to 30 min time intervals – in order to ensure homogeneous distribution in the chamber – and they all had a mixing ratio of approximately 20 ppb. As an OH source, HONO plus light was used – similar to the MUCHACHAS HONO photolysis experiments: the addition of HONO started one hour before the lights were turned on, reaching a level of approximately 15 ppb. In order to enhance the OH concentration – and unlike during the MUCHACHAS campaign – additional UV lights were used (black lights emitting mainly between 320 and 400 nm; manufactured by Cleo Performance; in total 80 tubes with 100 W per tube).

4.3 Results and discussion

4.3.1 MUCHACHAS

Figure 4.2 shows the time trends of AP and the three potential OH tracers during a MUCHACHAS experiment with HONO as OH source (with additional NO). After injection, AP rapidly decays due to ozonolysis and produces among other products PA (observed as \(m/z\) 151, \([\text{M+H-H}_2\text{O}]^+\)). Subsequently 3-pentanol (\(m/z\) 71, \([\text{M+H-H}_2\text{O}]^+\)) is injected before the start of OH production. Thereafter \(m/z\) 71 and \(m/z\) 151 decrease while the pentanol oxidation product 3-pentanone (\(m/z\) 87) is produced.

Figure 4.2 indicates the disadvantage of 3-pentanol (red line) as an OH tracer: during the ozonolysis of AP, one or more compounds are produced appearing at the signal \(m/z\) 71 of 3-pentanol. Several AP ozonolysis experiments (without adding 3-pentanol, not shown in Fig. 4.2) revealed that one fraction of the ozonolysis products at \(m/z\) 71 reacted away as soon as the OH source was turned on, while another fraction did not and appeared to remain at a constant level. The decreasing fraction could be a fragment of PA and leads to a systematic overestimation of the OH concentration – most notably right after the OH production starts.

For PA there is no known interference with other compounds at \(m/z = 151\). One of the biggest advantages of PA is that it is present in all the AP ozonolysis experiments and does not require additional injections. However, a major disadvantage of PA is that it reacts almost four times faster with OH than 3-pentanol. Furthermore the initial PA concentration depends on the initial AP concentration. Therefore this tracer is not ideal for longer experiments with high OH concentrations – especially when the initial AP concentration is low. Another drawback of PA and pentanone, which cannot be seen from Fig. 4.2, is that some other reactions may interfere: PA reacts with NO\(_3\) and undergoes photolysis, while pentanone photolyzes as well and is decomposed by the reaction with OH. However, these superposing reactions are very slow and should not significantly influence the OH concentration determination. PA has little utility in experiments where not all AP is consumed prior to the onset of OH production since it is still formed (at \(m/z\) 151) while one would like to determine the OH concentration from the decay of its \(m/z\) signal.

The interference at pentanone’s \(m/z\) 87 is quite small. However experiments without 3-pentanol addition revealed that just after the ozonolysis of AP the signal of \(m/z\) 87 in PTR-MS jumps up to a higher level and remains constant until the lights are turned on, from where on a further increase in the signal is monitored. The initial signal, before turning
4.3 Results and discussion

Figure 4.2 Three potential OH tracers measured by PTR-MS and used for the OH concentration determination during the MUCHACHAS campaign at the PSI smog chamber. The unit of the tracers is normalized counts per second (ncps) while the unit of $\alpha$-pinene (grey dots) is parts per billion (ppb). The apparent 3-pentanol signal (red line, $m/z$ 71) increases already during the ozonolysis of $\alpha$-pinene and indicates an interference with other compounds. 3-pentanone (green line) is a direct oxidation product of 3-pentanol with OH and is monitored at $m/z = 87$. Pinonaldehyde (blue line, $m/z$ 151) is an ozonolysis product of $\alpha$-pinene and reacts several times faster with OH than 3-pentanol. The pinonaldehyde concentration depends on the initial $\alpha$-pinene concentration. A few hours after the OH source has been turned on, the pinonaldehyde is generally depleted. The lower panel presents the signal on a log-scale.

As is seen from the lower panel of Fig. 4.2 – from a 10 ppb AP experiment – the decay of $\ln([PA])$ and $\ln([3\text{-pentanol}])$ is not linear on a logarithmic scale. This is either due to an interference with other compounds at the tracer’s specific $m/z$ or due to interfering reactions, or it indicates that the OH concentration is not constant over the course of the experiment. Eq. (4.3) cannot be applied. Thus, dealing only with slowly changing OH concentrations over time, the evolution of $\ln([PA])$ versus time was first fitted with an exponential function and then its derivative was used to calculate the slope at each point, as shown exemplarily in Fig. 4.3. The calculated OH concentrations agreed well with those modeled with version 3.1 of the Master Chemical Mechanism (MCMv3.1) (Jenkin and Hayman, 1999; Saunders et al., 2003). The OH concentrations based on 3-pentanol and 3-pentanone were additionally inserted in Fig. 4.3 which shows a 40 ppb AP experiment. While OH concentrations derived from pentanone are similar to those from PA, 3-pentanol as an OH tracer shows a large discrepancy.

OH clocks from all three tracers were produced using an exponential fit on the data. This is not a universal solution for all cases, but it seemed to work best in most of our experiments. Comparing the OH clocks 4 h after the OH source was turned on, there is – in the high AP experiments – a clear discrepancy between 3-pentanone and PA on the one side.
and 3-pentanol on the other. In these experiments with an AP mixing ratio of about 40 ppb the discrepancy between the OH clocks could be more than a factor of two. In contrast, for the low AP experiments (about 10 ppb AP) they still concur within 33% (calculated relative to PA) even 4 h after lights on. The increasing discrepancy over time between the tracers can be explained by the fact that after 4 h the tracer PA was usually consumed. It is obvious that PA is a more suitable OH tracer for AP ozonolysis experiments with a high initial AP concentration. Conversely, since PA is produced from AP, for experiments with an initial AP mixing ratio well below 10 ppb, PA is unsuitable as a tracer, unless more sensitive methods for PA determination can be used.

Figure 4.3 Determination of the OH concentration from pinonaldehyde (m/z 151) under varying OH levels. The upper plot shows the ln(m/z 151) decay measured by the PTR-MS (gray dots) and a fit (orange line) to the data, while the bright green line represents the slope of the fitted curve at each time point. The lower panel shows a comparison between the calculated (red) and modeled (dark green) OH concentration. The experiment lasted more than 24 h, the initial α-pinene mixing ratio was about 40 ppb and the OH was produced from the ozonolysis of tetramethylethylene.

The extent to which the OH concentration determination is limited by this low concentration of the fast reacting PA and the interference at m/z 71 can be underlined by a result of another experiment, where the 3-pentanol was injected after the PA (and the interfering compounds at m/z 71) had reacted: during this three-day experiment, the SOA formation started every day with the ozonolysis of 40 ppb AP without cleaning the chamber in between. Based on the PA tracer the OH concentration was very stable from the second day on. In order to avoid interference from other compounds at m/z 71, the 3-pentanol was injected 6.5 h after lights on. At that time all the interfering compounds were depleted and the determined OH concentration based on 3-pentanol was in quite good agreement with that based on the PA tracer: it was higher by less than 18% when compared to the PA tracer.

This discussion makes it clear that 3-pentanol, 3-pentanone and PA have clear drawbacks, and a “universal” OH tracer, which could also be applied in very complex systems – such as diesel car exhaust or two-stroke moped exhaust (see below) – is still needed.

We conclude that for the MUCHACHAS campaign 3-pentanone and PA as determined by PTR-MS are useful OH tracers while 3-pentanol is more problematic – especially for experiments with a higher AP concentration. The OH clocks based on 3-pentanone and PA agree quite well during the first 4 h after turning on the OH source. For experiments with a lower AP concentration all three tracers seem to concur quite well. In any case they all
4.3 Results and discussion

Figure 4.4 Mass-to-charge ratios for potential OH tracers during a EURO1 (a) and a EURO2 (b) moped experiment monitored by PTR-MS. The mass-to-charge ratios 62, 64, and 66 would correspond to 5-, 7- or 9-fold deuterated butanol. The unit (ppb) is calculated assuming a proton transfer rate constant of $2 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$ as a default value.

definitively do have clear drawbacks and none of them is useful for long experiments with a high OH dose.

### 4.3.2 Butanol-d9

Figure 4.4 shows three m/z, measured by PTR-MS during two moped exhaust oxidation experiments, which could be of interest as potential OH tracers. Figure 4.4a relates to a EURO1 moped and Fig. 4.4b to a EURO2 moped (both two-stroke engines). The signal at m/z 62, 64 and 66 would interfere with 5-, 7-, or 9-fold deuterated butanol, respectively. At m/z = 66 there is hardly any signal, not even after 20 h of experiment (Fig. 4.4a). Similar results were found for the exhaust from a four-stroke EURO2 moped, a diesel car and even wood burning (all not shown). Therefore, the 9-fold deuterated butanol is adequate also for such complex gas mixtures.

The rate constant of butanol-d9 with OH was determined using 2-butanone as a reference compound. 2-butanone is observed at m/z = 73. Similarly, we also repeated the evaluation of the rate constant of 3-pentanol with this method. Kinetic data can be obtained using the expression

$$
\ln \left( \frac{[\text{tracer}]_0}{[\text{tracer}]_t} \right) = \frac{k_{\text{tracer}}}{k_{\text{reference}}} \cdot \ln \left( \frac{[\text{reference}]_0}{[\text{reference}]_t} \right)
$$

(4.6)

where [reference]$_0$ and [tracer]$_0$ correspond to the measured initial concentration of the reference and the tracer compound, respectively.

Figure 4.5 shows the results from two similar experiments with 20 ppb of 2-butanone, 3-pentanol and butanol-d9 each. From the slopes (which correspond to the ratios of the rate constants) it can be concluded that the rate constant of 2-butanone with OH is about three times lower than the one of butanol-d9, and almost 10 times lower than the one of 3-pentanol. The slopes of linear least-squares analyses of the individual and the combined data sets of both experiments are summarized in Table 4.1 together with the rate constants for butanol-d9 and 3-pentanol. The fit uncertainty in Table 4.1 indicates the 95% confidence level. This also applies to the reliability confidence interval for the reference compound 2-butanone. As the fit uncertainty is very small, the confidence bands would overlap on the fitting line in Fig. 4.5. Therefore, we show the prediction bands on a 95% confidence level and not the confidence bands.
OH clock determination by proton transfer reaction mass spectrometry

Chapter 4

The slopes represent the ratios of the rate constants of the considered OH tracers (butanol-d9 and 3-pentanol) plus OH and the reference compound (2-butanone) plus OH. Table 4.1 gives an overview of the slopes and the resulting $k_{OH}$-values for butanol-d9 and 3-pentanol. The bright colors (red and blue) indicate the prediction bands of the fit on a 95% confidence level. The confidence bands would overlap with the fit and are therefore not shown here.

Using the IUPAC recommended $k$-value of $1.106 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ ($k_{2\text{-butanone}} = 1.5 \times 10^{-12} \times e^{-90/T}$ at $T = 295.15 \text{ K}$) for 2-butanone and taking the slopes through both data sets (in each case) results in $k_{\text{butanol-d9}} = 3.4(\pm 0.88) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ and $1.09(\pm 0.29) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ for 3-pentanol (Table 4.1).

For butanol and its 9-fold deuterated analog (butanol-d9) we obtain a KIE of 2.5 ($k_{H} = 2.5(\pm 1.2)$) using $k_{\text{butanol}} = 8.52(\pm 3.51) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ [IUPAC, 2011]. This is very much in line with the fundamental primary KIE of about 2.8 derived for H-abstractions by OH with a minimal reaction barrier height [Sage and Donahue, 2005]. Our rate constant for pentanol is 9% lower than reported by Wallington et al. (1988), who measured it using an absolute technique, and 17% lower than the one of Hurley et al. (2008), who also used a relative technique. The main reason for this bigger discrepancy probably comes from using different reference compounds, which then again do have differing rate constants from literature. Hurley et al. (2008) used for one of their two reference compounds ($C_2H_4$) a rate constant that is almost 8% higher than the preferred values from IUPAC [IUPAC, 2011].

However, the reference compound used here also has a few drawbacks: 2-butanone reacts quite slowly with OH. This might result in a slightly increased uncertainty for the determined $k_{\text{butanol-d9}}$. Furthermore it photolyzes. This systematic error might also explain to some extent the slightly lower $k_{3\text{-pentanol}}$ value resulting from the experiments presented, compared to those reported by Wallington et al. (1988) and Hurley et al. (2008). Even though according to the MCM model simulation for the PSI smog chamber and assuming that the photolysis rate of 2-butanone is not more enhanced by the new UV lamps than the photolysis rate of O$_3$, the photolysis should not be responsible for more than 5% of the 2-butanone decay. This is especially true as the absorption cross section of 2-butanone – as reported by Martinez et al. (1992) – has its maximum at a wavelength of 295 nm and gets very low in the UVA range above 315 nm. This error estimation is based on a conservative OH concentration assumption of
Table 4.1 Slopes of the linear regression fit lines shown in Fig. 4.5. The two columns on the right side contain the resulting absolute rate constants (\(k_{3\text{-pentanol}}\) and \(k_{\text{butanol-d9}}\)) for the reaction of 3-pentanol and butanol-d9 with OH by using 2-butanone (\(k_{2\text{-butanone}} = 1.103 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)) as a reference compound. The uncertainties are given in parentheses and represent the 95% confidence interval. For the \(k_{\text{OH}}\)-values they are obtained by calculating the error propagation from the fit uncertainties and the reliability of the reference compound.

<table>
<thead>
<tr>
<th>Date</th>
<th>Slope of the linear regression fit line</th>
<th>(k_{\text{OH}}) (295 K) [10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slope 3-pentanol</td>
<td>slope butanol-d9</td>
</tr>
<tr>
<td>15 April 2011</td>
<td>10.08(±0.56)</td>
<td>3.15(±0.06)</td>
</tr>
<tr>
<td>18 April 2011</td>
<td>9.63(±0.52)</td>
<td>2.98(±0.06)</td>
</tr>
<tr>
<td>Fit of both experiments</td>
<td>9.87(±0.38)</td>
<td>3.08(±0.05)</td>
</tr>
</tbody>
</table>

2.5 \times 10^7 \text{ cm}^{-3}, while the determined OH concentration was about 15% higher. An experiment designed to determine the photolysis rate of butanone at the PSI smog chamber revealed that this systematic error should be less than 3%. Furthermore, we cannot exclude small interferences at the m/z 71 (of 3-pentanol) caused by oxidation products of 2-butanone (or less probable oxidation products of butanol-d9). The (opposed) interference of 3-pentanol at 2-butanone’s m/z 73 was tested and is marginal.

A first application of the butanol-d9 as an OH tracer was performed in moped exhaust experiments. Figure 4.6 shows a comparison of the OH clocks based on butanol-d9 and toluene (a commonly used OH tracer in emission experiments, e.g. [Hennigan et al., 2011]) for two moped experiments, by using \(k_{\text{toluene}} = 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at \(T = 295.15 \text{ K}\) [UPAC, 2011]. The butanol-d9 based OH clock is slightly higher than the toluene based OH clock and the discrepancy increases with time. For this later stage of the experiment the butanol-d9 seems to be clearly superior to the toluene and works even after 20 h of the experiment. It is possible that an interfering compound at toluene’s m/z is formed very slowly or injected together with the toluene and leads to the observed discrepancy. Figure 4.4 clearly shows that this does not happen for m/z 66 of butanol-d9.

4.4 Summary and conclusions

Suitable tracers to be measured by PTR-MS were evaluated to establish a (photo-) chemical clock based on OH exposure. The OH concentration is obtained by applying an adequate fit to the decay curve of the tracer.

The use of an OH clock as a “chemical time dimension” might be very useful, particularly for inter-experiment comparisons or between lab studies and atmospheric measurements. The OH clock is only applicable where OH is the main oxidant species.

Three OH tracers were tested during an AP campaign: 3-pentanol, which was injected additionally, 3-pentanone (a direct oxidation product of the reaction of 3-pentanol with OH) and PA (an ozonolysis product of AP). The latter reveals no interferences with other compounds at its m/z, but its initial concentration depends on the amount of AP injected and it is depleted much faster by OH radicals than 3-pentanol. 3-pentanol interferes at its m/z 71 signal with one or more ozonolysis products of AP and becomes unsuitable in experiments.
Figure 4.6 Comparison of the OH clocks based on butanol-d9 and toluene, respectively, as OH tracers for two experiments. Both tracers were fitted with a polynomial fit of the fourth degree. The fit lasts over 20 h in the first experiment (orange) and over five hours in a second one (black). After five hours, the toluene based OH clock reveals a slightly (about 10%) lower OH exposure than the one based on butanol-d9. The discrepancy increases with time and reaches more than 30% after 20 h. Note that in the 24-h-experiment the tracer (butanol-d9) was injected only 2.5 h after the lights were turned on.

with a high AP concentration. 3-pentanone interferes only little with other compounds and results in OH concentrations similar to those based on PA.

By using a deuterated hydrocarbon as an OH tracer chances are higher to avoid these interferences. Butanol-d9 is a very promising OH tracer which reacts only with OH and reveals no interferences with other compounds in the (PTR-MS) m/z signal. Its rate constant was determined to be $k_{\text{butanol-d9}} = 3.4(\pm0.88) \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

A first application of butanol-d9 as an OH tracer reveals reasonable and reproducible results. A comparison to toluene, another OH tracer often used in photochemical processing of emissions, shows a very good agreement up to several hours after the OH production starts. For a later stage of the experiment the butanol-d9 seems to be clearly superior to toluene. We would like to point out here that other compounds than n-butanol-d9 would be preferable tracers when analytical techniques other than PTR-MS are used.
5

Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber

5.1 Introduction

Secondary organic aerosols (SOA) are a major constituent of the atmospheric particulate matter and originate from chemical transformation of primary volatile organic compounds (VOC) to lower volatility products that partition into the condensed phase. Many studies have already been performed on SOA formation and properties (see e.g. references in Hallquist et al. 2009). One of the major challenges for SOA studies is the multi-component composition of SOA with only few known substances among thousands of unknown species. Field measurements show changing SOA properties with oxidative aging, but detailed studies of these processes under ambient conditions in the lab are challenging and thus scarce (Rudich et al., 2007).

State-of-the-art chemical transport and box models cannot reproduce the measured ambient organic aerosol concentrations (i.e. directly emitted primary organic aerosol (POA) and SOA formed from various precursors) with currently known chemical and physical mechanisms (Volkamer et al., 2006; Hodzic et al., 2010). One important challenge in modeling SOA...
mass in the atmosphere or under laboratory conditions is the correct implementation of the
gas-particle interactions such as the partitioning effect (Pankow, 1994a,b). Recently the volat-
ility basis set (VBS) approach was introduced (Donahue et al., 2006; Robinson et al., 2007;
Jimenez et al., 2009), lumping the various organic compounds together according to their ef-
effective saturation mass concentration (C*) in order to describe the semi-volatile nature of the
SOA particles including their gas-particle partitioning behavior. C* is the mass equivalent
of the saturation vapor pressure, which controls volatility. Volatility is a key property of the
organic components of the gas and particulate phase and it determines the SOA formation
and the partitioning between the phases.

Laboratory experiments e.g. in chambers span a wide range of semi-volatile oxygenated
organic aerosol (SV-OOA), but low-volatility oxygenated organic aerosol (LV-OOA), as found
in ambient measurements of aged air masses, is still difficult to study and reproduce under
laboratory conditions (Jimenez et al., 2009). The atomic oxygen to carbon ratio (O:C ratio)
of SOA can be used to roughly split the mass to SV-OOA and LV-OOA components. It also
allows the classification of organics within the VBS framework.

Formation of SOA involves oxidation of semi-volatile vapors from primary emissions to
less volatile species which partition into the organic aerosol. In a simplified picture we start
with a pure volatile hydrocarbon species which is oxidized to different first generation ox-
idized products of a large range of volatilities. From the low volatility species a secondary
organic aerosol is formed while the volatile and semi-volatile species form a large pool of
organic mass in the gas phase in equilibrium with the particle phase. This aerosol can be
further processed, which is called aging; this includes various processes changing the proper-
ties of the particles (Qi et al., 2010). Most of the oxidation will take place in the gas phase
and either generates more SOA via further functionalization (adding more oxygen to the
carbon backbone) or fragmentation upon oxidation of the semi-volatile gases. Heterogeneous
oxidation is much slower than gas phase oxidation due to mass-transfer limitations. Hetero-
geneous reactions include functionalization and fragmentation as well as some transformation
reactions of functional groups (alcohol to carbonyl). Additional reactions in the condensed
phase such as oligomerization have also been observed (Kalberer et al., 2004). Functional-
ization and fragmentation lead to an increase in the O:C ratio while oligomerization may
increase or decrease it depending on the process (Reinhardt et al., 2007). Functionalization
always decreases volatility while fragmentation forms species in a wide range of volatilities
albeit mostly at lower volatilities. Oligomerization converts monomers to larger, less volatile
compounds. The expected effects of the three main processes on particle volatility are
summarized in Tab. 5.1.

Atmospheric aerosols are composed of inorganic and organic substances, including SOA
components. They have an influence on global climate via the direct aerosol effect by scatter-
ing sunlight and via the indirect aerosol effect by changing cloud properties and characteristics
(Lohmann and Feichter, 2005). Hygroscopicity, the degree of water uptake by particles, is
an important parameter for both effects and has been studied for different SOA types (Bal-
tensperger et al., 2005; Varutbangkul et al., 2006; Prenni et al., 2007; Duplissy et al., 2008;
Jurányi et al., 2009; Qi et al., 2010). A positive correlation between hygroscopicity and O:C
ratio has been shown recently (Jimenez et al., 2009; Chang et al., 2010; Massoli et al., 2010;
Duplissy et al., 2011). The following equation for the hygroscopicity parameter $\kappa$ can be
derived from Petters and Kreidenweis (2007) to represent the hygroscopicity of an aerosol:

$$\kappa = \nu_w \times \frac{\rho_s}{M_s} \times i_s,$$  \hspace{1cm} (5.1)

where $\nu_w$ is the partial molar volume of water, $M_s$, $\rho_s$ and $i_s$ the molar mass, density and
effective van’t Hoff factor of the solute, respectively. $\nu_w$ is in good approximation constant
5.1 Introduction

Table 5.1 The three main chemical processes and their expected influence on volatility and hygroscopicity, and on additional parameters: van’t Hoff factor $i_s$: the ratio of density to molar weight of solute, $\rho_s/M_s$. Symbols represent: + expected to increase, - expected to decrease, $\sim$ only minor change expected. For hygroscopicity ($\kappa$) see also equation 5.1. Note that if the chemical processes result in a substantial aerosol mass gain, then the resulting changes of particle volatility and hygroscopicity are determined by the relative difference between the properties of the previous and added SOA mass, and consequently the trends indicated in Tab. 5.1 are not applicable.

<table>
<thead>
<tr>
<th>Process</th>
<th>Volatility</th>
<th>VFR</th>
<th>$i_s$</th>
<th>$\rho_s/M_s$</th>
<th>Hygroscopicity ($\kappa$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalization</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$\sim$</td>
<td>$+$/$\sim$</td>
</tr>
<tr>
<td>Oligomerization</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>$\sim$</td>
<td>$-$</td>
</tr>
<tr>
<td>Fragmentation</td>
<td>$+$/$\sim$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
</tbody>
</table>

across the water activity range of interest. This leaves $i_s$ and $\rho_s/M_s$ as the two key factors determining particle hygroscopicity ($\kappa$). The expected effect of the three main chemical processes on $i_s$ and $\rho_s/M_s$ and thus $\kappa$ is also summarized in Tab. 5.1.

Functionalization typically increases $i_s$ slightly due to positive interactions between polar functional groups and water [Petters et al., 2009]. Additional dissociation effects would also increase $i_s$, though the degree of dissociation of carboxyl and hydroxyl groups is likely very small. Only a small increase, if at all, is expected for $M_s$ and $\rho_s$, and thus changes of $\rho_s/M_s$ will be small. $\kappa$ is thus expected to increase slightly under the influence of functionalization.

Oligomerization strongly increases $M_s$ with little effect on $\rho_s$, resulting in a decrease of $\rho_s/M_s$. Only small changes are expected for $i_s$. Overall a decrease of $\kappa$ is expected under the influence of oligomerization, though the effect becomes smaller with increasing $M_s$ [Petters et al., 2006].

Fragmentation strongly decreases $M_s$ with little effect on $\rho_s$, resulting in an increase of $\rho_s/M_s$. Only small changes are expected for $i_s$. Overall an increase of $\kappa$ is expected under the influence of fragmentation.

Equation 5.1 describes the hygroscopicity of completely dissolved solutes. Particle hygroscopicity would be reduced if the SOA was only partially soluble. Functionalization and fragmentation increase the solubility, while oligomerization decreases the solubility. The potential effects of functionalization, fragmentation or oligomerization on particle hygroscopicity caused by solubility changes have equal sign as the effects of changes of $i_s$, $\rho_s$ and $M_s$. Thus the summary of the effect of the three main chemical reactions on particle hygroscopicity as presented in Tab. 5.1 remains valid also under the influence of solubility limitations.

The chemical and physical characterization of SOA is often discussed separately [Hallquist et al., 2009]. So far it is not clear how oxidation (aging) changes the amount and properties of SOA. Here we investigate the aerosol physical properties of SOA volatility and hygroscopicity as a function of the oxidant exposure under controlled conditions. Comparing trends of volatility and hygroscopicity may shed light on the dominant processes in the course of SOA aging.

These measurements were conducted at the Paul Scherrer Institute (PSI) smog chamber within the scope of the MUCHACHAS (Multiple Chamber Aerosol Chemistry and Aging Studies) campaigns. MUCHACHAS took place in several chambers in Europe and the US with different points of emphasis for a similar set of experiments. The main emphasis for the
MUCHACHAS experiments at the PSI smog chamber was the aging of α-pinene (AP) SOA with OH under dark and light conditions.

The typical design of the MUCHACHAS experiments is shown as schematic in Fig. 5.1. The precursor in all experiments described here was AP. The concept was to first form SOA from ozonolysis, allow it to stabilize after nearly all the precursor was consumed, and then to expose the first-generation SOA and partially oxidized gas-phase species to OH radicals in order to observe changes caused by OH aging.

A change of the VFR and/or the κ value during processing of atmospheric aerosols may occur either by addition of SOA mass (by condensation) or by an exchange of molecules in the SOA by other molecules with different properties. The former process increases the SOA mass by definition, while the latter keeps the SOA mass roughly constant and may occur either by heterogeneous reactions on the surface of the SOA particles, condensed phase reactions like oligomerization or by an evaporation - gas-phase oxidation - recondensation cycle. Thus, when there is a substantial change in the aerosol mass by addition of new molecules to the aerosol phase with time, the condensation mechanism may be assumed to be dominant, while, when the mass stays roughly constant the exchange mechanism is the likely dominant process. In the light of this, we assign the following four dominating mechanisms to four different periods of our experiments (see Fig. 5.1): O₃ induced condensation; ripening; OH induced chemical aging with substantial mass gain; OH induced chemical aging without significant mass gain. In the condensation periods, the physical (VFR, κ) and chemical (O:C ratio) properties are believed to mainly vary as a result of the additional condensing material, in contrast to chemical transformation of the SOA during periods without significant change of the mass.

5.2 The experimental setup

5.2.1 Smog chamber and associated instruments

The air in the 27-m³ Teflon bag in a temperature controlled chamber with four filtered xenon lamps providing quasi-solar illumination is monitored by several gas and aerosol phase instruments described in detail in Paulsen et al. (2005). Here we mention the main instruments relevant for this paper and the experimental procedure. The particles volatility and hygroscopicity were characterized with a volatility and hygroscopicity tandem differential mobility analyzer (V/H-TDMA, see Sect. 5.2.2). The aerosol particle number size distribution (diameter D = 20 - 800 nm) and chemical composition were measured with a scanning mobility particle sizer (SMPS) and an Aerodyne high resolution time of flight aerosol mass spectrometer (AMS). The AMS detects inorganic and organic aerosol species quantitatively and is described elsewhere in detail (DeCarlo et al., 2006). It allows the chemical quantification and characterization of several types of fragments of the SOA with a time resolution of a few seconds (e.g. Alfarra et al. 2006). The organic aerosol mass measurement from the AMS was wall-loss corrected to account for the losses to the chamber walls. Assuming that the wall loss rate is first order and independent of size we used an exponential fit asymptotically decreasing to zero to correct for the losses (Pathak et al., 2007). In the following the terms ”organic aerosol mass” or ”SOA mass” always relate to wall-loss corrected organic particulate mass. A very useful parameter derived from AMS data is the oxygen to carbon ratio (O:C ratio) (Alken et al., 2007, 2008), which was linked to the hygroscopicity properties of the aerosol (Duplissiy et al., 2011).

The gas-phase instruments include NOₓ monitors (Monitor Labs 9841A, Thermo Environmental Instruments 42C) and ozone monitors (Monitor Labs 8810, Environics S300). A proton transfer reaction mass spectrometer (PTR-MS) from IONICON was deployed as well.
5.2 The experimental setup

Figure 5.1 Schematic of the main features of the smog chamber experiments during MUCHACHAS. Formation of secondary organic aerosol (SOA) mass (wall-loss corrected) from the volatile organic precursor α-pinene (AP) takes place during the first part in dark with ozone (O\textsubscript{3}). The ozonolysis is followed by OH chemistry to age the SOA. The data can be plotted against several time axes as "time after AP injection was started" and "time after the OH reaction started" or against a "chemical clock" as O\textsubscript{3} exposure and OH exposure. During ozonolysis and reaction with OH the four different periods of our experiments are indicated above the figure: O\textsubscript{3} induced condensation, ripening, OH induced chemical aging with substantial mass gain, and OH induced chemical aging without significant mass gain.

The high sensitivity PTR-MS (Lindinger et al., 1998) is able to detect VOCs in real-time with a very low detection limit (ppt level). From the measurement of the precursor α-pinene we calculated "AP reacted". However, after injection of AP into the ozone (O\textsubscript{3}) containing chamber the initial concentration was not directly measured because AP needs to mix first and already starts to react with O\textsubscript{3}. It was therefore determined from fitting the AP concentration trend back to the injection time.

5.2.2 V/H-TDMA instrument

We built a new V/H-TDMA instrument which is described and characterized in more detail here. The tandem differential mobility analyzer (TDMA) technique (Rader and McMurry, 1986) is a common technique to characterize aerosol properties. The H-TDMA technique is well established and a suitable method to measure the hygroscopicity of submicrometer aer-
osol (Swietlicki et al., 2008). Our combined volatility and hygroscopicity tandem differential mobility analyzer (V/H-TDMA) runs volatility and hygroscopicity scans in parallel (Fig. 5.2). The aerosol is conditioned before entering the first differential mobility analyzer (DMA1) by passing through a diffusion dryer and a Kr-85 bipolar charger to bring the particles into charge equilibrium. All DMAs are situated in a temperature controlled, well insulated housing at 20°C. DMA1 size selects a dry (RH < 15%), quasi-monodisperse aerosol, which is split into a heater and a humidifier flow (0.3 L/min each). Two additional DMAs scan the humidified or heated particles (DMA2 and DMA3, respectively) which are then counted with the condensation particle counter for hygroscopicity (CPC_H) and for volatility (CPC_V), respectively.

The H-TDMA part is based on the design of a previous instrument (Duplissy et al., 2008, 2009). The individual sheath air flows are operated in closed loops and the flows are maintained with blowers (Fig. 5.2), which is controlled by laminar flow elements combined with differential pressure sensors and proportional-integral-derivative (PID) controllers. A separate humidifier loop with bubbler (not shown in Fig. 5.2) supplies the humidifier with humid air. The humidifier section is situated in a second, temperature controlled housing at 24°C. The aerosol can be humidified up to a controlled relative humidity (RH) of 97 ± 1% with a residence time of ~26 s (between DMA1 and DMA2).

Measurement of the deliquescence RH of ammonium sulfate (AS) and other salts e.g. sodium chloride (NaCl) are used for the calibration of the dew point mirror (see Fig. 5.2) to assure accurate RH measurement. The correct absolute sizing of the DMAs is periodically checked with polystyrene latex (PSL) spheres having dry diameters $D_0$ between 100 and 350 nm. The correct sizing of the DMAs with respect to each other is frequently checked by conducting a series of measurements without heating and humidifying. This relative calibration of DMA1 with DMA2 / DMA3 is important to detect small instrumental drifts which would affect the precision of the growth factor measurements (the error in $D/D_0$ is typically < 1%).

The heater in the V-TDMA part is custom-built and consists of an inner linear brass...
5.2 The experimental setup

tube (70 x 2.2 cm) surrounded by capillary tubes containing a heating wire. The small space between these capillary tubes allows for a rapid cooling with pressurized air. The temperature sensor in the center of the inner tube (see Fig. 5.2) controls the heater temperature \( T \) in a range from 25 - 200\(^\circ\)C (\( \pm 2\)\(^\circ\)C). Modeling of the temperatures and flow streamlines inside the heater suggests a laminar flow and a homogeneous temperature distribution after at most 15 cm from the inlet. The calculated plug flow residence time (RT) in the heater for 25 - 200\(^\circ\)C is 24.4 - 15.4 s at a constant aerosol flow of 0.6 L/min. The aerosol flow is diluted with filtered, pure air before (0.3 L/min) and after the heater (0.4 L/min) to maintain correct aerosol flows in all parts of the instrument. Measurements of the aerosol particles’ average “traveling time” from the outlet of DMA1 to the inlet of DMA3 (including heater and tubing) was found to be 23 ± 2 s at 30\(^\circ\)C. The RT is longer compared to other heaters employed in TDMA (Paulsen et al., 2005; Jonsson et al., 2007; Villani et al., 2007) and thermodenuder (Burtscher et al., 2001; Wehner et al., 2002). This typically results in a lower remaining aerosol volume at a specific temperature. As particle concentrations are rather small, a denuder is not needed in our system because the inner surface of the heater offers much larger surface for the vapors to condense than the aerosols. Nucleation, an indicator for re-condensation of vapors, was not observed in the V-TDMA.

In general the parameters obtained from the TDMA are the growth factor GF(RH), and shrinking factor SF(\( T \)) defined as the ratio of humidified diameter \( D(RH) \), or heated diameter \( D(T) \) and initial dry and non-heated diameter \( D_0 \), respectively:

\[
GF(RH) = \frac{D(RH)}{D_0} \quad (5.2)
\]

\[
SF(T) = \frac{D(T)}{D_0} \quad (5.3)
\]

The raw growth or shrinking factor distributions measured by the H- and V-part are analyzed using the TDMAinv approach (Gysel et al., 2009) in order to obtain inverted and calibrated probability density functions (PDF). Details on this data analysis procedure and especially on the used TDMAinv approach are found in Gysel et al. (2009). In the following the hygroscopic growth factor (GF) always refers to the number weighted mean GF (1\(^{st}\) moment) of the inverted GF-PDF, and the shrinking factor (SF) to the volume weighted mean SF (3\(^{rd}\) moment) of the inverted SF-PDF. Instead of SF the volume fraction remaining (VFR), defined as VFR = SF\(^3\), is chosen to present the volatility data.

In this study the H-TDMA was typically operated at a constant high RH of 95%. The GFs measured in the RH range between 93 - 97% were recalculated to 95.0% RH following Gysel et al. (2009), using a single-parameter growth curve parametrization for correcting small RH differences. The used RH correction in a small band of ± 2% RH minimizes systematic biases when reporting temporal evolution of GF at constant target RH. This is especially of importance when overall changes in the GF evolution are not large. The V-TDMA heater was running mainly at 70\(^\circ\)C (with a plug flow RT of 21 s) and only data in the range \( T = 68 - 72\)\(^\circ\)C were considered in the analysis. We minimized pyrolysis in the heater by using a low thermodenuder temperature with a relatively long residence time. During a few experiments the heater temperature was varied (from 25 to 200\(^\circ\)C) to measure the VFR as a function of temperature, resulting in a thermogram plot.

Typically particles are small in the beginning of an SOA experiment, but grow very rapidly during the ozonolysis and stabilize at a diameter of a few hundred nanometers. Several \( D_0 \) in the diameter range across the mode of the size distribution were selected for the H-TDMA and V-TDMA measurements at a time and the diameter range covered was gradually

43
increased to follow the temporal evolution of the mode. For low AP experiments $D_0$ ranged from 50 to 150 nm and for high AP precursor concentrations the $D_0$ range was from 75 to 250 nm.

We present results from the hygroscopicity measurements mainly as hygroscopicity parameter $\kappa$ (see also equation 5.1, Petters and Kreidenweis 2007) to account for the size dependence of the GF (Kelvin effect). $\kappa$ was calculated assuming the surface tension of pure water. A $\kappa$ of 0 corresponds to GF = 1. The use of $\kappa$ allows for direct comparison of hygroscopic growth factor measurements made at different dry diameters. It is also a convenient quantity to explore the water activity dependence of particle hygroscopicity by comparison of studies presenting $\kappa$ values from H-TDMA or CCNC measurements made at different water activities.

The V-TDMA was characterized with laboratory generated particles of known chemical composition to allow for a comparison of the results with other systems. The instrument residence time, diameter, and concentration of aerosols are important factors for heater characterization. Figure 5.3 shows the VFR for different compounds and particle diameters as function of the heater temperature.

Panel A in Fig. 5.3 displays the VFR of NaCl, which is known to be non-volatile up to temperatures clearly above 200°C (Scheibel and Porstendoerfer, 1983), and thus the VFR measured by the V-TDMA is expected to be unity across the whole temperature range. The very small observed decrease in VFR to $\sim$0.97 at 200°C might be either a restructuring effect, which would result in a more compact structure and therefore smaller effective volume, or evaporation of impurities from the nebulizing process of NaCl. A similarly stable volatility behavior is observed in other studies (e.g. Modini et al. 2010). The plot of NaCl shows also the high precision of the instrument with less than $\pm$ 2% for VFR in a wide temperature range. Thermophoretical losses at 200°C were determined to be 10 - 15% in particle number for NaCl particles with $D_0 = 35 - 200$ nm. This is in the range of other thermodenuders (Huffman et al., 2008; Park et al., 2008). We consider the losses as less relevant because the instrument is not quantitative in particle mass or number but rather measures the physical properties volatility and hygroscopicity.

Cictric acid (Fig. 5.3B) was chosen as a reference substance because it is of rather high volatility similar to SOA; VFR starts to decrease at $T > 70^\circ$C. At temperatures above 110°C particles with $D_0 \leq 300$ nm are completely evaporated in our instrument. A small size-dependence due to kinetic reasons is seen: smaller particles tend to evaporate faster than larger particles (see e.g. Riipinen et al. 2010).

Ammonium sulfate particles (AS) (Fig. 5.3C) are often used for heater characterization; in our system AS particles start to volatilize at temperatures $T > \sim 100^\circ$C. All AS particles volatilize completely (i.e. VFR < 0.15) at temperatures above 150°C. In addition we show in panel C some AS thermograms from studies that we will use later for comparison of SOA thermograms (see Sect. 5.3.1). Some studies need a somewhat higher temperature to volatilize AS, but show a very similar slope (Jonsson et al., 2007; Meyer et al., 2009). The study from An et al. (2007) shows very different, earlier volatilization of AS compared to our system, where VFR of AS decreases at temperatures around 75°C and 150°C is needed to volatilize the particles with $D_0 = 100$ and 200 nm completely. There are also studies where AS starts to volatilize around 110°C, but does not evaporate completely even at temperatures above 230°C (Huffman et al., 2008). However, the AS curves in this paper show a high variability and are therefore not included in Fig. 5.3C. The mass fraction remaining from AMS measurements for polydisperse AS in Wu et al. (2009) looks similar to our VFR thermogram of AS. It is characterized by a rapid decrease of the mass fraction remaining between 120°C and 160°C.

Villani et al. (2007) present an overview table with 160 - 180°C at $D_0 = 15 - 150$ nm as lowest volatilization temperature for AS in their V-TDMA instrument while other studies report even higher temperatures.
5.2 The experimental setup

Overall our instrument seems to be in a good temperature and residence time range for volatilization measurements of AS. Nevertheless, organic substances (e.g. citric acid) with relatively high volatility might be better suited to characterize a thermodenuder system than salts like AS because they often evaporate already at lower temperatures, i.e., more gentle heating is needed.

The calibration measurements presented in Fig. 5.3 show also the high precision of the V/H-TDMA instrument. The variance of precision at a constant temperature (same substance and $D_0$) is about 0.005 in VFR, which means clearly below 1%. This demonstrates the high reproducibility of the VFR data and the same is true for the GF and $\kappa$ measurements (not shown here). The important factor is the precise sizing of the particles, which can be done very well with DMA systems. The absolute accuracy of the volatility and hygroscopicity data is influenced by further parameters e.g. temperature and RH measurements leading to higher absolute uncertainties. The absolute quantification is less important in this study than the temporal changes. Therefore we report the results with errors showing the reproducibility of the observations during the temporal evolution in the chamber.

5.2.3 Smog chamber operation

In all experiments, the clean smog chamber was humidified to ~50% RH at a temperature of 21 ± 1°C and these conditions stayed stable during the course of experiments. In a first step O$_3$ was added to the chamber. After about 20 min when the O$_3$ was distributed homogeneously in the bag the precursor AP was injected. We conducted experiments at two precursor concentrations of 40 ppb (“high”) and 10 ppb (“low”) $\alpha$-pinene mixing ratio,
Chapter 5 Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber

resulting in atmospherically relevant organic aerosol mass concentrations. The reaction resulted in immediate particle formation (first-generation SOA) from the reaction products of ozonolysis of the C=C double bond in AP. As no OH scavenger was used about 30% of AP will react with OH radicals based on model calculations. Ozonolysis lasted a few hours until at least 90% ± 5% of the AP precursor had reacted before the OH aging period was started (Fig. 5.1).

In a next step, 20 ppb of 3-pentanol was added. Pentanol reacts with OH only, and thus its decay can be used as an OH tracer, in the same way as specific intermediate products. SOA was exposed to OH aging by either photolysis of HONO or ozonolysis of tetramethylethylene (TME) with the IUPAC name: 2,3-dimethyl-2-butene [Epstein and Donahue, 2008]. The former are named ”HONO photolysis experiments” throughout this study and the latter are called ”dark OH (TME) experiments”. A list with details of all conducted experiments is given in Tab. 5.2.

TME ozonolysis is the OH source in dark OH (TME) experiments, however in some of these experiments we turned the lights on in the smog chamber to increase the OH source from photolysis of ozone during a part of the experiment. We introduced also additional experimental conditions with turning lights on and off during some experiments; one TME experiment was partly performed with UV lights on. All experiments with these special light conditions are commented in Tab. 5.2.

A HONO level of 15 - 20 ppb (as measured by a Long Path Absorption Photometer (LOPAP)) in the chamber was reached by passing pure air (2 L/min) through a custom built vessel with sulfuric acid (0.01 M H$_2$SO$_4$) and sodium nitrite (3x10$^{-3}$ M NaNO$_2$). The vessel and the setup of the HONO system we used are described elsewhere [Taira and Kanda, 1990]. The flow from the HONO generator was passed through a filter to ensure that only the gas phase HONO without particles entered into the chamber. The addition of HONO started about one hour before the lights were turned on. In some high-NO$_x$ photo-chemical experiments (Tab. 5.2, exp. No. 6 - 8) 50 - 80 ppb NO was added in addition to the HONO. TME was continuously injected from a gas cylinder (Messer, TME 1000 mol ppm in N$_2$ 5.0) at a flow of 10 mL/min to maintain a TME mixing ratio between 0.5 - 1.5 ppb. The ozone level was usually higher in the TME experiments compared to HONO photolysis experiments because O$_3$ was also needed for the ozonolysis of TME.

Different time axes as shown in the concept figure (Fig. 5.1) are used in the following. The progress of the experiment is described by either ”time after AP injection” (relating to the start of the ozonolysis reaction) or ”time after OH started” (relating to the start of the OH aging by lights on or start of TME injection) in units of hours (h). In addition two ”chemical clocks” are used to represent the experiments with respect to their exposure to O$_3$ or OH, respectively. The O$_3$ exposure (in ppb h) serves as chemical clock during the ozonolysis, and the OH exposure (in cm$^{-3}$ h) is used during the reaction period with OH. The OH concentration was calculated from the decay rate of pinonaldehyde as measured by PTR-MS (see [Barmet et al. (2012)]). Pinonaldehyde is a reaction product of AP ozonolysis and proved to be a better tracer than pentanol [Barmet et al., 2012]. OH concentrations in the experiments were between 2x10$^6$ and 10$^7$ cm$^{-3}$ (see Tab. 5.2). Due to the fast reaction of pinonaldehyde with OH the OH exposure was limited to about 15x10$^6$ cm$^{-3}$ h.

5.3 Results and Discussion

First we present thermograms (temperature ramping in the V-TDMA heater) of some SOA experiments for comparison with reference substances (Sect. 5.2.2) and with other studies (Sect. 5.3.1). However, the main focus in this paper is on the temporal evolution of κ (GF)
Table 5.2 Overview for all smog chamber experiments during the MUCHACHAS campaign 2009 at PSI with detailed experiment conditions (AP and O₃ input), OH concentration and results from the V/H-TDMA.

<table>
<thead>
<tr>
<th>exp. ID/No.</th>
<th>experiment type</th>
<th>AP input O₃ input</th>
<th>comments on the experiment type</th>
<th>log-gas-phase growth factor at RH of 95% and (κ value)</th>
<th>volume fraction remaining at temperature of 70°C</th>
<th>OH concentration [ppbcm⁻³] after 2 hours OH aging</th>
<th>comments on V/H-TDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ozonolysis only</td>
<td>26 Jan 2009 40</td>
<td>500</td>
<td>1.32 (0.063)</td>
<td>0.71 (0.087)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>ozonolysis only</td>
<td>18 Feb 2009 40</td>
<td>500 no AMS data</td>
<td>1.26 (0.069)</td>
<td>0.61 (0.087)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>ozonolysis</td>
<td>16 Jan 2009 40</td>
<td>100+300 only; H_2SO_4 during ozonolysis</td>
<td>1.37 (0.086) (0.113) (0.139)</td>
<td>0.64 (0.087) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>ozonolysis and light</td>
<td>21 Jan 2009 10</td>
<td>150+50 *OH exposure after 3 hours</td>
<td>1.38 (0.113) (0.138) (0.141)</td>
<td>0.70 (0.087) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>ozonolysis</td>
<td>11 Feb 2009 10</td>
<td>250+200 lights on/off</td>
<td>1.35 (0.086) (0.113) (0.139)</td>
<td>0.68 (0.087) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>ozonolysis and light</td>
<td>19 Jan 2009 40</td>
<td>90+20</td>
<td>1.37 (0.086) (0.113) (0.139)</td>
<td>0.66 (0.087) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>ozonolysis</td>
<td>13 Feb 2009 40</td>
<td>150+100</td>
<td>1.31 (0.086) (0.113) (0.139)</td>
<td>0.65 (0.087) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>ozonolysis</td>
<td>21 Jan 2009 10</td>
<td>200</td>
<td>1.40 (0.115) (0.138) (0.150)</td>
<td>0.71 (0.087) (0.115) (0.138)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>ozonolysis</td>
<td>14 Jan 2009 40</td>
<td>200 very short experiment</td>
<td>1.19** (0.084) (0.104) -</td>
<td>0.70 (0.087) (0.104) -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>ozonolysis</td>
<td>06 Feb 2009 10</td>
<td>200 lights on/off</td>
<td>1.40 (0.115) (0.138) (0.150)</td>
<td>0.72 (0.087) (0.115) (0.138)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>ozonolysis and dark OH, TME</td>
<td>28 Jan 2009 40</td>
<td>500+200 long exp.</td>
<td>1.29 (0.072) (0.103) (0.124)</td>
<td>0.56 (0.072) (0.103) (0.124)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>ozonolysis and dark OH, TME</td>
<td>7 Feb 2009 10</td>
<td>500 no AMS data</td>
<td>1.34 (0.086) (0.113) (0.139)</td>
<td>0.67 (0.086) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>ozonolysis</td>
<td>02 Feb 2009 10</td>
<td>500+150 long exp.; lights on +150</td>
<td>1.34 (0.086) (0.113) (0.139)</td>
<td>0.65 (0.086) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>ozonolysis</td>
<td>09 Feb 2009 10</td>
<td>500+150 lights on/off</td>
<td>1.31 (0.086) (0.113) (0.139)</td>
<td>0.60 (0.086) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>ozonolysis</td>
<td>25 Feb 2009 10</td>
<td>500 UV intensive lights in addition to TME; no AMS data</td>
<td>1.31 (0.086) (0.113) (0.139)</td>
<td>0.63 (0.086) (0.113) (0.139)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

and VFR during the ozonolysis (Sect. 5.3.2) and the OH exposure periods (Sect. 5.3.3). Thus time series at constant heater temperature (T = 70°C) in the V-TDMA and relative humidity (RH = 95%) in the H-TDMA allow for a closer look at the ongoing processes during different reaction periods (see Sect. 5.2.3). Finally, the correlation of VFR and κ (Sect. 5.3.4) will be investigated as well as the effect of additional light and the size dependence (Sect. 5.3.5) of these measured properties.

5.3.1 Thermogram of SOA and comparison with other studies

Thermograms with well known substances characterize the V-TDMA (Fig. 5.3) as discussed above. Such thermal information can also be used to gain information on the complex chemical nature of SOA. Figure 5.4 shows mean VFR values versus heater temperature for all three types of AP SOA experiments (circles). Four thermograms from other studies of AP SOA (squares) are compared to our measurements. The error bars represent the standard deviations of VFR (vertical) and the temperature (horizontal). Large vertical error bars are due to real volatility changes of the chamber aerosol during the course of the experiment and do not reflect the V-TDMA accuracy. All our thermograms are similar within these uncertainties and show no distinct D₀ or experiment type dependence.

A significant decrease of VFR starts at ~50°C and at 90°C 50% of the particle volume is volatilized. Temperatures around 150°C are required to reduce the VFR to 10%. This
is a much wider temperature range than for pure citric acid or ammonium sulfate and is explained with different compounds in the chamber SOA possessing volatilities ranging from rather semi-volatile to low-volatile. Although the three experiment types (ozonolysis, HONO photolysis and dark OH (TME) experiments) cannot be compared directly as the data were acquired at different stages of the experiments, we fitted our thermograms with an error function. The fitted error function (erf) (Fig. 5.4 black line), is only valid above 50°C. It is set to 1 as maximum and has the following equation with \( T \) as the heater temperature:

\[
VFR = 0.91 - 0.911 \times \text{erf} \left( \frac{T[°C] - 53.15}{82.5} \right)
\]  

(5.4)

This empirical function was simply chosen as it represents the observations in the most suitable way. It is helpful to extrapolate the volatility data from other experiments during this study when the temperature was set to 70°C continuously to compare e.g. with other studies. Comparison of our measurements with other AP SOA studies (squares in Fig. 5.4) shows the best agreement with the instrument and measurements from [Meyer et al. (2009), from Cappa and Wilson (2011) and Jonsson et al. (2007) for low temperatures and Hoffman et al. (2009) for higher temperatures. These and our SOA thermograms lie between the two other studies from [An et al. (2007) and Paulsen et al. (2005)] for low temperatures and [Meyer et al. (2009), ∼15 s (Cappa and Wilson, 2011), 21.2 s (Huffman et al., 2008, 2009), 23 s (this study) and 31.6 s (An et al., 2007), respectively]. If the above papers stated the centerline RT at laminar flow we converted it to plug flow RT (factor 2). Our instrument seems to have the second longest RT, at ambient temperature (see Sect. 5.2.2); only the RT from An et al. (2007) is longer. This could explain the stronger volatilization of SOA at relatively low temperatures in their study at least partly (as also seen in Fig. 5.3C). On the other hand shorter RT leads to higher VFR [Baltensperger et al., 2005 Paulsen et al., 2005], 2.8 s (Jonsson et al., 2007), ∼3 s [Meyer et al., 2009], ∼15 s (Cappa and Wilson, 2011), 21.2 s (Huffman et al., 2008, 2009), 23 s (this study) and 31.6 s (An et al., 2007), respectively. If the above papers stated the centerline RT at laminar flow we converted it to plug flow RT (factor 2). Our instrument seems to have the second longest RT, at ambient temperature (see Sect. 5.2.2); only the RT from An et al. (2007) is longer. This could explain the stronger volatilization of SOA at relatively low temperatures in their study at least partly (as also seen in Fig. 5.3C). On the other hand shorter RT leads to higher VFR [Baltensperger et al., 2005 Paulsen et al., 2005 Jonsson et al., 2007]. With our long RT we are able to use low temperatures in the heater and minimize kinetic limitations of evaporation and hope to be close to equilibrium, even though this is probably not the case as suggested recently [Riipinen et al., 2010].

The VFR of this comparison is generally following the RT, i.e. a shorter RT leads to higher VFR and vice versa. This is expected if the evaporation is kinetically limited and no equilibrium is reached in neither of these instruments [Riipinen et al., 2010]. Further reasons for small differences in the SOA thermograms may be the type of AP SOA, its concentration, and experimental conditions. Recent studies by Vaden et al. (2011) as well as Cappa and Wilson (2011) postulate a glasslike modification of the AP SOA which would even inhibit effective evaporation within a reasonable RT. Other instrumental reasons e.g. initial particle size, monodisperse or polydisperse measurement, use of a charcoal denuder after the heating section or different experimental conditions may also lead to these variations. The latter is already reflected in the scatter of our data taken from different experiments like ozonolysis and/or OH exposure. Altogether, there are many indications that evaporation studies of SOA are quite challenging and need further attention.

Overall, the comparison of thermograms gives an orientation on our V-TDMA characteristics and shows the importance of the residence time, instrument specific properties and experimental conditions. The decrease in VFR with temperature is experienced over a relatively large temperature range and offers a sensitive range from ∼60 to 100°C to study the SOA volatile properties. A constant oven temperature of 70°C was chosen to track temporal changes in the SOA volatility during the chamber reactions discussed in the following.
5.3 Results and Discussion

Figure 5.4 Mean VFR measured for SOA from three different experiment types, distinguished with greenish, reddish and bluish color, at various heater temperatures with error bars representing the standard deviation of VFR and temperature of multiple measurements during the experiment (circles). Literature data (squares) from similar SOA studies were added for comparison. The black solid line represents a fit through all measured data of this study.

5.3.2 Ozonolysis - O$_3$ induced condensation and ripening

The first step in each experiment was the ozonolysis of AP to form SOA mass (Fig. 5.1). The initial O$_3$ concentration varied with the type of experiment. Figure 5.5A shows the time trends of the fraction of AP reacted, the organic aerosol mass, the volatility as VFR, and the hygroscopicity both as $\kappa$ value and as GF at 95% RH. The markers are colored according to the initial O$_3$ concentration; filled symbols represent low AP and open symbols represent high AP input.

High O$_3$ concentrations led to a fast reaction of AP and a rapid formation of SOA (Fig. 5.5A panel (A$_1$) - (A$_2$)). It took roughly one hour to reach the “90% AP reacted” level (see vertical lines in Fig. 5.5A). At lower O$_3$ concentrations this took 2 - 3 times longer and the final SOA mass was lower. This may have two reasons. Firstly, more semi-volatile compounds are lost to the walls and do not condense on the particles. Secondly, organic radical-radical reactions are decreased, eventually leading to less semi-volatile compounds contributing to SOA.

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The physical parameters $\kappa$ and VFR data (Fig. 5.5A panel A$_2$ - A$_4$) split mainly into two groups comprising low and high concentration AP experiments. Experiments with high SOA mass have generally a higher volatility (lower VFR) and lower hygroscopicity. In case of the low AP experiments VFR increases steadily from 0.55 to 0.7 after 4.5 h of reaction. Even after most of the AP had reacted (90%-level) VFR keeps increasing. The high AP experiments show a similar but less pronounced trend. During the condensation phase VFR slightly increases. The hygroscopicity of low and high AP experiments shows a similar evolution but
separates slightly with time (Fig. 5.5 A, A5). Duplissy et al. (2008) found a distinct mass concentration dependence of GF for an α-pinene photooxidation experiment, i.e. a lower GF at a higher particle concentration. This was attributed to volatile and less oxygenated vapor condensing at higher mass concentrations lowering the GF. Here we do observe only a slightly lower GF for the high concentration experiments after the SOA has evolved, but Duplissy et al. (2008) had higher AP mixing ratios (> 120 ppb) in their study and investigated a different system (photochemistry instead of ozonolysis), which can explain the differences in the findings.

The hygroscopicity is presented in Fig. 5.5 panel A4 - A5 in terms of κ and GF. Both show the same features (small difference between high and low AP experiments) and differences between κ and GF are mainly seen during the first 1 - 2 hours of ozonolysis where the selected diameters are small and differ due to fast particle formation. In some experiments (open blue circles at about 5 h, two diameters are measured alternately) the GF seems to smooth size effects of different diameters. The presented κ values are a good proxy for the particle hygroscopicity because the diameter dependence of the Kelvin effect is taken into account (by assuming a surface tension of pure water). Thus we will present the hygroscopicity data as κ values in the following. The κ values start at about 0.04 in the beginning of all experiments and then increase during the condensation period. Thereafter, κ remains almost constant. Similar as for VFR, the low AP concentration experiments group together and show a higher κ than the high AP concentration experiments. However, the values remain within a rather narrow range of 0.08 - 0.12.

Figure 5.5B (panel B1 - B4) shows the same experiments and parameters as Fig. 5.5A1 - A4 but as a function of the O3 exposure (in ppb h). The trends of κ and VFR are split into low and high O3 concentration experiments. After about 350 ppb h 90% of α-pinene has reacted in all experiments and we would expect a similar composition of the products. However, we see at this exposure higher VFR and κ values for the low O3 concentration experiments. The reason for this could be twofold. First, radical-radical reactions are decreased leading to a somewhat different product distribution (SOA mass is also decreased, see above). Second, at low O3 concentrations it takes longer until 90% AP has reacted and the SOA had thus more time to evolve. It is clearly seen that after 350 ppb h the VFR keeps on increasing steadily although not much additional SOA mass is formed. On the other hand κ remains nearly constant. The increase of VFR could indicate an oligomerization process while this would imply a decrease of κ. Shilling et al. (2007) observed that O3 can heterogeneously oxidize aldehydes to acids which would decrease VFR and increase κ (as dissociation of acids increases the van’t Hoff factor). A control experiment with an excess of AP during the ozonolysis shows in the AMS the same chemical changes as with an excess of O3. This does not support heterogeneous oxidation as the cause of this steady increase of VFR. At present we do not have an explanation for this evolution of the SOA. We call this unspecified process or processes ripening of the SOA.
5.3 Results and Discussion

Figure 5.5 All experiments of the ozonolysis part only. The relative fraction of AP reacted, wall-loss corrected SOA mass concentration (org. mass), volatility expressed as VFR at 70°C and the hygroscopic parameter $\kappa$ are presented on different time axes, in panel (A) as "time after AP injection" and in panel (B) as "O$_3$ exposure", which is used as "chemical clock". The color indicates the O$_3$ concentration for low O$_3$ (< 400 ppb) and for high O$_3$ (≥ 400 ppb). The filled symbols represent the low $\alpha$-pinene (AP) (10 ppb) and open symbols the high AP (40 ppb) precursor concentration experiments. The panels (A$_1$) - (A$_4$) and (B$_1$) - (B$_4$) present corresponding data, respectively. In addition panel (A$_5$) shows the GF at 95% RH and (B$_5$) shows the O$_3$ concentration. The vertical lines in panel (A) indicate roughly (± 5%) the 90%-AP-reacted value for the four main experiment conditions: high/low AP (open/solid line, respectively), combined with high/low O$_3$ (orange/blue color, respectively). Exemplary error bars for volatility and hygroscopicity data represent the reproducibility. Additional scatter of the data points is caused by the fact that different dry sizes are measured.
5.3.3 SOA aging - OH induced chemical aging

During the first period of the experiment the precursor was removed by ozonolysis, forming mainly first generation and a fraction of second generation gaseous oxidation products, as well as a certain mass of SOA. We then turned on an OH-radical source and monitored any changes in the amount and properties of SOA. Figure 5.6 shows the organic aerosol mass (panel A), the VFR at 70°C (panel B), as well as \( \kappa \) and O:C ratio (panel C) for a low (green) and a high (blue) AP concentration using HONO photolysis as OH radical source. The time axis is given as "time after lights on" (TALO), which means that negative values denote the previous ozonolysis period. Immediately after the onset of the OH radical source additional SOA mass is formed. Figure 5.6A shows that after correction for wall loss the SOA mass increases by 40 - 100%. This is a lower limit as the wall loss correction presented here is conservative - the effects of aging on SOA levels will be discussed in detail in a separate publication. We divide the OH induced chemical aging period into a period with substantial mass gain (TALO \( \sim \) 0 to 2 h), and a period without significant mass gain (TALO \( \sim \) 2 to 4.5 h).

Figure 5.6 Time series of two \( \alpha \)-pinene (AP) ozonolysis experiments followed by reaction with OH from HONO photolysis. The two periods of the experiment, ozonolysis and reaction with OH, are distinguished by open and closed symbols, respectively, and green and blue color is used for the low (10 ppb) and high (40 ppb) AP precursor concentration experiment, respectively. Panel (A) shows the organic aerosol mass (wall-loss corrected), panel (B) the VFR at 70°C and in panel (C) the hygroscopicity parameter \( \kappa \) (left axis) as well as the O:C ratio (right axis). The evolution of the VFR during ripening (ca. from -3 to 0 h) was linearly fitted and extrapolated to indicate the trend expected without reaction with OH. The grey dotted lines shown in panel (C) help to guide the eye to see the changing trends of \( \kappa \) in the four periods of the experiment. Exemplary error bars in panel (B) and (C) represent the reproducibility for volatility and hygroscopicity data, respectively. Additional scatter of the data points is caused by the fact that different dry sizes are measured.

The hygroscopicity parameter \( \kappa \) (Fig. 5.6C) increases significantly by more than 30% during the OH induced chemical aging period with substantial mass gain. The increase in \( \kappa \) suggests that the SOA mass gain during aging is driven by molecules with a lower molecular
weight than the fresh SOA. This indicates the condensation of smaller molecules than the average of previous condensed phase species. The trend of \( \kappa \) levels then off and stays constant during the OH induced chemical aging period. The O:C ratio is constant or slightly decreasing during the ozonolysis, while it correlates well with \( \kappa \) during the OH induced chemical aging period. Thus OH exposure leads to condensation of higher oxidized species onto the existing SOA. During the period without significant mass gain the O:C ratio remains constant.

Contrary to this the VFR (Fig. 5.6B) abruptly decreases after OH aging commences (turning lights on) and starts to stabilize after about one hour of aging with OH radicals. In the last period of the experiment, during the OH induced chemical aging without significant mass gain, the VFR tends to increase slightly. The newly added SOA mass after the onset of OH oxidation seems to have a higher volatility (lower VFR) than the previously existing SOA from the ozonolysis. The volatility of the newly added SOA was estimated by assuming simple volume mixing, i.e.

\[
VFR_{\text{mixed}} = \epsilon_{\text{old}} \times VFR_{\text{old}} + \epsilon_{\text{new}} \times VFR_{\text{new}}
\]

where the indices "old", "new" and "mixed" stand for the SOA from the ozonolysis, the SOA added by OH-aging, and the mixed SOA particle, respectively, and \( \epsilon \) denotes the volume fractions of the SOA components in the mixed particle. Solving Eq. 5.5 for VFR_{\text{new}} provides:

\[
VFR_{\text{new}} = \frac{VFR_{\text{mixed}} - \epsilon_{\text{old}} \times VFR_{\text{old}}}{1 - \epsilon_{\text{old}}}
\]

\( VFR_{\text{mixed}} \) is directly measured by the V-TDMA. \( \epsilon_{\text{old}} \) is derived from the organic aerosol mass measurements by the AMS before and after new material was added, thereby assuming the same density for the old and new mass. \( VFR_{\text{old}} \) is obtained by extrapolating a linear fit through the last 3 hours of ozonolysis data, as indicated by the dashed lines in Fig. 5.6B. In doing so we assume that the OH exposure does not cause additional oxidation of the old SOA within this short time span as heterogeneous OH uptake is much slower compared to SOA formation by OH oxidation of gaseous precursors. Fortunately, the calculations are anyway not very sensitive to the exact value assumed for VFR_{\text{old}}.

Based on Eq. 5.6 the VFR of the newly condensed material after one hour of exposure to OH, VFR_{\text{new}}, is calculated to be 0.47 and 0.21 for the low and high precursor experiment respectively. The calculated VFR_{\text{new}} for all experiments is in a similar range from 0.09 to 0.49 (at 70°C) indicating highly volatile material. These numbers are to be taken with a grain of salt given that the simple volume mixing rule ignores e.g. the influence of absorptive partitioning and kinetic effects on VFR_{\text{mixed}}. Nevertheless, they confirm that the SOA mass added by OH aging is distinctly more volatile than the SOA mass resulting from the ozonolysis. A pathway of formation could be functionalization of volatile oxidation products reducing their volatility by one to two orders of magnitude such that they can now partition into the aerosol. This also increases the O:C ratio relative to the pre-existing SOA. However, since the increase of \( \kappa \) indicates the condensation of smaller compounds we conclude that most of the newly condensed volatile fraction occurs from fragmentation reactions. The breaking of the skeleton leads to radicals which react with molecular oxygen to form finally stable products. In this way small highly oxidized molecules of low volatility may be formed. This would be in agreement with a decrease of VFR and an increase in \( \kappa \) and O:C ratio.

In Figure 5.7 all experiments are summarized. Panels A and B group the experiments according to the type of OH radical source (HONO photolysis and dark OH (TME)) while panels C and D show the dependence of \( \kappa \) and VFR on the wall-loss corrected SOA mass.
OH exposure is used as a chemical clock to bring all experiments on a comparable time scale. Some experiments are not shown in their full experimental length because this chemical OH clock is limited in time to when the pinonaldehyde concentration was still above the limit of detection of the PTR-MS.

Figure 5.7 Volatility, expressed as VFR at 70°C, and hygroscopicity parameter κ plotted against the "chemical clock" OH exposure shown for the reaction with OH part of the experiments only. The color code in panel (A) and (B) represents the individual experiments; while the symbols shape and filling indicate the experiment type and α-pinene (AP) input concentration, respectively. The filled symbols represent the low AP (10 ppb) and open symbols the high AP (40 ppb) precursor concentration experiments. Panel (C) and (D) show exactly the same data as panels (A) and (B), now arranged in groups of experiment type and color coded by their wall-loss corrected organic aerosol mass (note that the red color ranges from 120 to max. 255 μg m$^{-3}$). Exemplary error bars at the right end of each panel represent the precision of the measurements.

Overall, the time trends of κ and VFR (Fig. 5.7A,B) are similar for all experiments and to those two experiments discussed above and shown in Fig. 5.6. The initial values of κ and VFR are somewhat variable, depending on the preparation of the SOA by ozonolysis. The κ values start at 0.07 - 0.12 and increase to 0.10 - 0.15 during the OH induced chemical aging with substantial mass gain. During the second period (after about 8x10$^6$ cm$^{-3}$ h) κ stays more or less constant. A linear regression over the whole OH induced chemical aging period results in a mean straight line of $κ = 1.37 \cdot 10^{-9} x + 0.105$ ($R^2 = 0.46$), where $x$ is the OH exposure.

The VFR decreases during the OH induced chemical aging with substantial mass gain and increases during the aging period without significant mass gain after about 8x10$^6$ cm$^{-3}$ h OH exposure. The high concentration dark OH (TME) experiment No. 11 is an exception - VFR increases during both periods as it is the experiment with the highest organic aerosol mass. Nevertheless the VFR of the newly condensing mass is still much lower than the VFR$_{old}$ as calculated from Eq. 5.6. The type of OH source, dark OH (TME) and HONO photolysis does not show differences in the particles' hygroscopicity or volatility behavior.
This also indicates that high or low NO\textsubscript{x} conditions during HONO photolysis experiments have no clear influence on $\kappa$ and VFR (see Tab. [5.2]).

In panel C and D (Fig. [5.7]) the $\kappa$ and VFR data of each experiment are colored by the SOA mass concentration measured by the AMS. The volatility of the high mass experiments is generally higher (lower VFR) than for the low AP experiments throughout the experiment. The spread of VFR becomes narrower with time. At the end of the OH induced chemical aging period $\kappa$ values are lower for high AP experiments compared to the low concentration ones.

### 5.3.4 Correlation of $\kappa$ and VFR

Here we present $\kappa$ and VFR in direct relationship to each other. We do it separately for the different periods as there can be a correlation or anti-correlation depending on the period. Figure [5.8A] shows for all available ozonolysis experiments (14 in total) a good ($R^2 = 0.80$) correlation of $\kappa$ and VFR. The observed scatter is attributed to different experimental conditions and periods. The correlation is determined by the strong trends in $\kappa$ and VFR during the O\textsubscript{3} induced condensation period.

The first hour of OH induced chemical aging is presented separately in Fig. [5.8B]. In general an anti-correlation of $\kappa$ and VFR is observed for all experiments although the magnitude and duration of this opposite trends for $\kappa$ and VFR is varying.

In some dark OH (TME) experiments we turned the lights on (and off) in the smog chamber to have an additional OH source. The idea was to check the influence on the aging process and to study the possible effects on volatility and hygroscopicity due to that. The correlation of $\kappa$ and VFR in Fig. [5.8C] allows a closer look at the temporal evolution during OH induced chemical aging and the effect of "lights on" in four dark OH (TME) experiments (No. 11 - 14, see Tab. [5.2]). Generally, the dark OH exposure experiments show a positive correlation between $\kappa$ and VFR for about the first 10 hours. Afterwards only the VFR increases further. Only an enhanced oxidation rate by turning on the lights producing more OH radicals increases VFR and $\kappa$ even more (up to $\kappa = 0.2$). It should be cautioned here that the opposing trends of VFR and $\kappa$ during the OH induced chemical aging with substantial mass gain period are buried in the scatter plot.

**Maximum hygroscopicity and minimum volatility with addition of UV light**

In one experiment we removed the UV-filters from the xenon lamps in the chamber. The combination of OH production with TME and ozone photolysis with unfiltered UV light results in a higher hygroscopicity (experiment No. 15, not shown in Fig. [5.8C]). The highest hygroscopicity ($\kappa = \sim0.21$) and lowest volatility (highest VFR = $\sim0.82$ at 70°C) of all experiments were reached in this experiment after only 4 hours of OH aging (see Tab. [5.2]). The experiment with second highest $\kappa$ and VFR after several hours of aging ($\kappa = \sim0.17$ and VFR = $\sim0.80$) was the one with dark OH and normal lights on (No. 13). However, this was a long experiment with high O\textsubscript{3} concentration and we cannot decouple the effects. We conclude that both the additional OH (e.g. TME + lights) and enough time are important for aging.

### 5.3.5 SOA aging - a closer look

In the following we present results from the second part of the experiments with the focus on the sensitivity to OH exposure (lights on/off) and the dependence of $\kappa$ and VFR on the
Figure 5.8 Correlation of hygroscopicity parameter $\kappa$ and VFR at 70°C of $\alpha$-pinene SOA for several experiments and sections of experiments. Panel (A) shows the correlation for all available experiments during the ozonolysis part only. The positive correlation of $\kappa$ and VFR can be presented by a linear fit. Panel (B) shows the anti-correlation of $\kappa$ and VFR during the first hour after OH aging was started for dark OH (TME) experiments (diamonds) and HONO photolysis experiments (triangles). The same correlation is presented in panel (C) for experiments No. 11 - 14 during the reaction with OH from TME in absence of light (open symbols), sometimes with addition of lights (closed symbols). The data shown in panel (B) and (C) are color coded by time after OH started.

Particle diameter. Figure 5.9 shows two different types of low concentration AP experiments: HONO photolysis (green traces) and dark OH (TME) experiment (yellow traces) partly with additional lights on (No. 5 and 14, see Tab. 5.2). The periods with lights on are indicated by arrows. In experiment No. 5 (green) the lights were the only OH source, in experiment No. 14 the lights were turned on and off in addition to the dark OH (TME) source. Organic aerosol mass, atomic O:C ratio (panel A and D) from the AMS and VFR as well as $\kappa$ (panel B and C) are plotted against time after OH started. Dry diameters ($D_0$) are presented in different symbols.

All TDMA data are size-specific and the size dependence of the measured hygroscopicity and volatility has not been discussed so far. In experiment No. 14 the smaller particles tend to have a higher $\kappa$ and lower VFR (higher volatility); this is not observed in experiment No. 5. The variation in $\kappa$ between different $D_0$ is typically less than $\pm 0.01$ (i.e., within uncertainty), in extreme cases up to 0.03, when comparing $D_0 = 50$ nm and $D_0 = 150$ nm. For all experiments, several sets of $D_0$ with overlapping repeats are selected in the TDMA to ensure sufficient signal and consistent measurement.
Figure 5.9 Results from low concentration α-pinene experiments No. 5 (OH from HONO photolysis, green) and 14 (OH from TME, yellow) are plotted as time series of: (A) wall-loss corrected organic aerosol mass (org. mass), (B) volatility as VFR at 70°C, (C) hygroscopicity parameter κ, and (D) O:C ratio. The lights were intermittently turned on and off during these two experiments. The double arrows above the figure indicate the periods with lights on. The symbols and colors in panel (B) and (C) indicate the dry diameter ($D_0$) for the TDMA measurement and show the size dependence of volatility and hygroscopicity. Exemplary error bars at the right end of each panel represent the reproducibility of the measurements.

Using the volatility data from the V-TDMA for experiment No. 14 from 6 - 9 h after the OH exposure as input for an evaporation model (Riipinen et al., 2010) showed a positive size dependence in the diameter range 100 - 150 nm - due to different evaporation kinetics of particles with different diameters. For this calculation, we approximated the SOA with a single component aerosol with saturation concentration of 1.2 $\mu$g m$^{-3}$ and a mass accommodation coefficient of unity, chosen to produce consistent results with the measured VFR at 100 nm. The SOA was assumed otherwise to have similar properties as the theoretical AP SOA modeled in Riipinen et al. (2010). Although this is a rough approximation, we believe it to be sufficient for this purpose of simply demonstrating the size-dependence of the evaporation kinetics. The size dependence predicted by the model is a bit stronger (VFR ranging from 0.71 to 0.83 with diameters ranging from 100 to 150 nm) than the one observed in our measurements (VFR from 0.71 to 0.75). This size dependence of the evaporation of the particles is similar to what would be expected based on dynamic evaporation calculations. It is therefore possible that the observed size dependence is rather due to kinetic effects than different chemical composition. However, the possibility of size dependent changes in the chemical composition cannot be completely ruled out either based on our data.

The two experiments No. 5 and 14 in Fig. 5.9 also illustrate well the interplay between the two periods of OH induced chemical aging on VFR. The start of OH induced chemical aging at time zero resulted in an abrupt decrease in VFR (Fig. 5.9B) while SOA mass increased.
as already discussed above. When OH production stopped (lights off in experiment No. 5) the VFR increased without significant mass gain similar to the ripening until OH started again (lights on in experiment No. 5). The VFR then stayed constant while again SOA mass slightly increased. This is an indication that again more volatile compounds are condensing compensating the aging effect by other processes. In case of the dark OH (TME) experiment (No. 14) turning lights on enhances the OH level and more SOA mass is produced. VFR does not decrease as expected but the increasing trend is stopped and VFR remains constant (best seen for small particles). This may indicate again that this ripening-like process is compensated by the condensation of volatile compounds. When lights are turned off after 4.6 h VFR starts to increase. Since further condensation is small now and SOA mass gain is not significant anymore, the non-condensational chemical aging processes become dominant again. Another lights on period after 6.6 h does somewhat slow down the increasing trend. This may be expected because at this time not much additional condensation was observed.

The effects on κ are less pronounced. In general κ (Fig. 5.9C) increased with OH exposure while without OH, when lights were off (experiment No. 5, 2 - 4 h) κ decreased significantly by about 10%. The O:C ratio correlates well with κ and shows for the dark OH (TME) experiment an almost constant and slow increase to values of 0.48 - 0.5 (Fig. 5.9D). The increasing trend for the HONO photolysis experiment (from about 0.46 to 0.52) is less visible due to relatively high noise caused by the small organic mass concentration in this experiment. The O:C ratio seems to be less sensitive to the lights on/off effects compared to VFR and κ. This has partly to do with the large noise of this parameter due to the low particle mass concentration in these low AP experiments.

5.4 Summary and conclusions

After validation and characterization of a new V/H-TDMA we measured SOA during 15 different aging experiments with 10 to 40 ppb α-pinene (AP) within the MUCHACHAS campaign in the PSI smog chamber. The retrieved parameters VFR and κ for volatility and hygroscopicity are sensitive indicators of changes in the SOA properties. We assume that the observed changes of physical properties are caused by chemical changes as a result of condensation, heterogeneous oxidation, condensed phase reactions and other processes. Two periods were discerned for each reaction period (ozonolysis and OH exposure), as seen in Figs. 5.1 and 5.6. During ozonolysis there is the O$_3$ induced condensation period and after the AP had reacted the on-going chemical and physical changes were called ripening. The OH induced chemical aging was divided into two periods with and without substantial mass gain.

The first period (O$_3$ induced condensation) forms most of the SOA mass. The exposure of the SOA and gas mixture resulting from ozonolysis to OH radicals produced up to 50% additional SOA mass. The SOA added by OH exposure was highly volatile, more oxidized and of smaller molecular mass than the SOA from ozonolysis. Based on a simple two-compound model we estimate that this new SOA forming compounds have a VFR $< 0.5$ at 70°C. The same volatility behavior was also observed with a V-TDMA during MUCHACHAS experiments at the AIDA (Karlsruhe) and the SAPHIR (Jülich) chamber (Salo et al., 2011). Once this condensation period came to an end we still observed significant changes of the aerosol properties. The κ range agrees well with the findings from other hygroscopicity studies for AP SOA (Petters and Kreidenweis, 2007; Duplissy et al., 2008).

Generally, VFR increased while κ and O:C ratio remained constant. This process appears to be independent of exposure to OH. After the end of the ozonolysis period, when most AP had reacted we also observed a steady evolution of the VFR and chemical changes...
in the AMS. We call this unknown process ripening of the aerosol. We hypothesize that this process is caused by relatively slow transformations of the condensed phase (this can include evaporation, oxidation, condensation cycles) which do not influence the SOA mass concentrations but do influence intensive physical and chemical properties (such as VFR, \( \kappa \), O:C). We conclude that the organic aerosol is continuously evolving once the SOA mass has been formed. Qi et al. (2010) also observed a steady change of hygroscopicity, volatility and chemical signature in photooxidation experiments of AP and xylene over many hours.

There were no significant differences found between dark OH (induced by tetramethyl-ethylene, TME) and light OH (induced by HONO) induced aging, and also high and low NO\(_x\) conditions had virtually no influence on the physical properties.

The combination of the physical properties volatility and hygroscopicity with chemical information from AMS is a highly suitable approach to access the complex chemical processes during formation and aging of SOA. However, there are many different processes intertwined in the aging of SOA and difficult to separate. Thus more comprehensive studies are needed which are designed such that these different processes can be better disentangled and quantified. Such studies should include sophisticated chemical analysis of specific compounds in the aerosol phase combined with a quantification of the oligomer content.
6.1 Are 2-stroke mopeds the most important source of vehicular carbonaceous aerosol?

In urban areas much of the ambient particulate matter (PM) comes from motor vehicles (European Environment Agency (EEA), 2009). Mopeds, many of which utilize 2-stroke (2-S) engines, are inexpensive and convenient and as such are a popular means of transportation globally (Rijkeboer et al., 2005). Emission reductions in other on-road vehicle types mean that carbonaceous emissions from mopeds are becoming a major issue: according to current estimates, mopeds will emit more hydrocarbons than all other vehicles combined in Europe by 2020 (European Commission, 2009). Their relative importance as a source of PM depends both on how much they emit, and on their usage, compared to other vehicles. Previous studies report substantial direct PM emissions from 2-S mopeds (Rijkeboer et al., 2005; Giechaskiel et al., 2010). However, secondary organic aerosol (SOA), originating from the reactions of atmospheric precursors rather than direct emissions, is known to dominate global OA concentrations (Hallquist et al., 2009).

Based on these facts we studied the engine exhaust from 2-S engines by focusing not only on the primary emissions but also on the secondary aerosol production potential (SAPP). We found that organic aerosol emission factors (i.e. the mass of pollutant normalized to some useful parameter, such as distance driven, CO$_2$ emitted, or fuel consumed) from 2-stroke mopeds can exceed those of other vehicles by a factor of several thousand. In a publication from Platt et al. (in preparation) we will present the emission factors in terms of OA normalized to the fuel consumed. Moreover we provide evidence of substantial secondary organic aerosol (SOA) production from 2-S moped exhaust, which means that moped emissions yield significant SOA formation. Emission factors are, calculated for OA after five hours of SOA formation, following photochemical processing during UV/visible light exposure. This corresponded to an atmospheric exposure to OH concentration of $10^6$ cm$^{-3}$ (the global annual mean OH concentration) for 12-34 hours, depending on the experiment. Furthermore we show that 2-S mopeds, including those complying with current emissions standards, may be a significant source of vehicular aerosol pollution despite comparatively low traffic mileage. Therefore it is essential that any assessment of the effect of mopeds emissions on public health and the environment consider both direct emissions and SAPP.
A first application of the 9-fold deuterated butanol (butanol-d9) as an OH tracer was performed during a moped campaign. The outcome reveals reasonable and reproducible results. A comparison to toluene, another OH tracer often used in photochemical processing of emissions, shows a very good agreement up to several hours after the OH production starts. For a later stage of the experiment the butanol-d9 seems to be clearly superior to toluene. Further details of this tracer comparison are given in section 4.3.2. The results of several moped emission campaigns — including the emission factors — will be published soon in Platt et al. (in preparation).

### 6.2 Cooking emissions might contribute to a remarkable extent to the organic aerosol mass

Recent studies, applying positive matrix factorization on ambient aerosol measurement data, revealed that cooking emissions (referred to cooking organic aerosol (COA)) seem to contribute to a remarkable extent to the organic aerosol mass (10% < COA < 20% of organic aerosol mass)(e.g. Mohr et al., 2012). Therefore it was worthwhile to characterize such a source in terms of primary aerosol emissions and the SOA formation potential upon the aging of the emitted gas phase compounds. Different systems representative of the real life cooking processes were examined, including vegetable boiling, meat grilling and vegetable frying.

Preliminary results indicate high emissions of primary aerosol from meat grilling and vegetable frying, whose MS fingerprints compare quite readily to the COA fraction obtained in the atmosphere. This feature seems to suggest that the main source of primary COA detected in the ambient environment is most likely related to release of fat and frying oil. In contrast, vegetable boiling is characterized by low primary OA emissions but a surprisingly high secondary OA formation potential (i.e. a 10 fold increase was observed in the OA mass upon the aging of the emissions), thus SOA can have an impact on total emissions from cooking. Such a feature was not observed in the case of meat cooking. Concomitant PTR-MS gas phase measurements show significant emissions of monoterpenes from vegetable cooking. According to the fragmentation pattern of the mass-to-charge ratio (m/z) signals and based on the fact that α-pinene is often referred to be a major biogenic emission, the dominant monoterpene might be even here α-pinene. These monoterpenes might be responsible for the high amounts of SOA formed during vegetable cooking, which seems to constitute a potentially important source of biogenic SOA in urban environments. E.g. the SOA yield (or mass fraction, $F_{OA}$) for SOA generated in the reaction of α-pinene and ozone under low NOx conditions using 2-butanol as an OH scavenger is about 15% ($F_{OA}$=0.15). This value was reported by Presto and Donahue (2006) for a mass concentration ($C_{OA}$) of about 20 µg/m$^3$ of the total absorbing particle phase (see also Chapter 1 Section 1.3.1). The 9-fold deuterated butanol has been used also during some of these “cooking experiments” to determine the OH exposure.

### 6.3 The link between organic aerosol mass loading and degree of oxygenation: An α-pinene photooxidation study

A series of smog chamber experiments was conducted to identify factors responsible for the discrepancy between ambient and smog chamber aerosol degree of oxygenation. An Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) is used.
to compare mass spectra from α-pinene photooxidation with ambient aerosol. Composition is compared in terms of the fraction of particulate CO$_2^+$, a surrogate for carboxylic acids, vs. the fraction of C$_2$H$_3$O$,^+$ a surrogate for aldehydes, alcohols and ketones, as well as in the Van Krevelen space, where the evolution of the atomic hydrogen-to-carbon ratio (H:C) vs. the atomic oxygen-to-carbon ratio (O:C) is investigated. Low (near-ambient) organic mass concentrations were found to be necessary to obtain oxygenation levels similar to those of low-volatility oxygenated organic aerosol (LV-OOA) commonly identified in ambient measurements. The effects of organic mass loading and OH exposure were decoupled by inter-experiment comparisons at the same integrated OH concentration. An OH exposure between 3 and 25·10$^7$ cm$^{-3}$h is needed to increase O:C by 0.05 during aerosol aging. For the first time, LV-OOA-like aerosol from the abundant biogenic precursor α-pinene was produced in a smog chamber by oxidation at typical atmospheric OH concentrations. Significant correlation between measured SOA and reference LV-OOA Pearson’s R$^2$ values larger than 0.90 for experiments with low organic mass concentrations between 1.2 and 18 µg at an OH exposure of 4·10$^7$ cm$^{-3}$h corresponding to about two days oxidation time in the atmosphere, based on a global mean OH concentration of ∼1·10$^6$ cm$^{-3}$ (Prinn, 2001). α-pinene SOA is more oxygenated at low organic mass loadings. Because the degree of oxygenation influences the chemical, volatility and hygroscopic properties of ambient aerosol, smog chamber studies must be performed at near-ambient concentrations to accurately simulate ambient aerosol properties (Ng et al., 2010; Pfaffenberger et al., 2013).

For a comprehensive comparison of all experiments described in this study, the OH exposure was utilized as the aging scale, rather than the time after lights on. The evolution of O:C as a function of organic mass concentration (wlc), both averaged for 10 min, is shown in Fig. 6.1 with each of the nine experiments marked by a different symbol and color-coded by the OH exposure. Initially, there is a period of rapid mass increase with a slow increase in O:C, followed by a later period of a continuous O:C increase with only a slight further increase in mass. The precise rate and termination point of the late-experiment mass increase are some-what uncertain due to corresponding uncertainties in the applied minimum wall loss correction method. The initial period is likely governed by condensation of early-generation, semi-volatile products and their condensation therefore yields a low increase in O:C. As aging proceeds, the gas-phase organics become more oxidized and thus more oxygenated (higher O:C) compounds condense. Additional aging of the particles is possible through repartitioning of semi-volatile condensed-phase OA to the gas phase, followed by gas-phase oxidation and recondensation of the oxygenated products. This process also increases O:C while only slightly affecting the total OA mass. Therefore, partitioning is more strongly affected by the significantly varying mass concentrations between the nine experiments than the slight mass increase within a given experiment. Higher OA mass correspond to increased condensation of semi-volatile compounds, while low-volatility compounds occur in the particle phase even at low concentrations (Donahue et al., 2006). Ng et al. (2010) also suggest that more oxygenated compounds tend to be less volatile. The reaction of less oxygenated, semi-volatile compounds with OH proceeds in the gas phase until either (1) they become sufficiently oxygenated to condense (which requires a higher level of oxygenation than at high mass concentrations) or (2) they fragment sufficiently such that they will not enter the particle phase. Both pathways lead to an increase in the net O:C for experiments conducted at low OA concentrations.

In Fig. 6.1, the color-coded squares correspond to an OH exposure of 2.5, 4, 6, 8 and 11·10$^7$ cm$^{-3}$h. Averages were calculated as ± 15 min from the given OH exposure, except for experiment 4, where a ± 30 min average was calculated. Linear (least orthogonal distance) fits of O:C as a function of OA mass concentration at 2.5, 4 and 6·10$^7$ cm$^{-3}$h OH exposure are shown by the lines in the corresponding color.
The significant dependence of O:C on the organic mass is shown by the varying slope $\Delta \text{O:C} / \Delta \text{org (wlc)}$, on average $(0.07 \pm 0.01) \% \text{ m}^3 \mu g^{-1}$. This implies that at typical atmospheric concentration levels, partitioning effects on SOA oxygenation are even more sensitive to the organic mass concentration than for the higher-than-atmospheric concentrations used in most previous smog chamber studies. Using typical atmospheric organic mass concentrations in smog chamber studies is not only crucial to reproduce the volatility and degree of oxygenation of ambient SOA, but also for accurately determine of cloud condensation nuclei activity due to the dependence of the hygroscopicity on O:C.

Figure 6.1 O:C ratio as a function of the organic mass concentration ($\mu g \text{ m}^{-3}$) in the chamber for the nine experiments. The color code indicates the OH exposure. Thirty-minute mean values at selected OH exposures are represented by colored squares (except expt. 4: 60-min average). The colored lines represent linear least orthogonal distance fits between O:C and org (wlc) at three selected OH exposures with a mean slope of $(0.07 \pm 0.01) \% \text{ m}^3 \mu g^{-1}$. (Figure from Pfaffenberger et al., 2013).
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7.1 Introduction

Particles present in the atmosphere can be directly emitted (primary aerosols) or formed by nucleation or condensation processes (secondary aerosols). Secondary aerosols are formed after chemical transformation of gaseous precursors into semi-volatile or low-volatility species that condense into the particle phase. Small carboxyls and hydrocarbons have therefore been considered as non-relevant to secondary aerosol formation due to their high volatilities, which makes them unlikely to undergo effective partitioning to the particulate phase. However, it was recently found that the oxidation of isoprene, for example, forms products of low enough volatility to partition into the particle phase of secondary organic aerosol (SOA) (e.g. Claeys et al., 2004; Healy et al., 2008; Dommen et al., 2009). Hallquist et al. (2009) conclude from a comparison between bottom-up model estimates and various top-down approaches that the global SOA budget is at present still poorly constrained. Condensed-phase reactions that increase the molecular weight can strongly reduce the volatility distribution of the organics. Thus even acetylene (C$_2$H$_2$), the smallest hydrocarbon after methane, can produce significant SOA due to the high yield of glyoxal upon oxidation (Volkamer et al., 2009). In theory the oxidation of methane could also contribute to SOA if e.g., the radical intermediate such as CH$_3$O$_2$ or the products of HCHO, CH$_3$COOH react to form species with much lower volatility (Hallquist et al., 2009).

As methane (CH$_4$) — the smallest hydrocarbon — is also the most abundant volatile organic compound (VOC) in the atmosphere, we investigated to what extent it might contribute to the total aerosol. In case that the oxidation of CH$_4$ contributes to the aerosol mass, then every existing VOC should also be able to contribute to the aerosol mass.

In atmospheric research, methane plays a key role due to its very high radiative forcing. Spahni et al. (2005) reported that preindustrial CH$_4$ concentrations over Antarctica did not exceed 773 (± 15) ppb during the past 650 000 years. In 2005, the global average abundance of CH$_4$ measured within the network of 40 surface air sampling sites operated by NOAA/GMD in both hemispheres was 1774.62 (± 1.22) ppb. The major part of this increase is anthropogenic. From 1999 to 2006, CH$_4$ remained nearly constant except for a small increase in 2002 to 2003.
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The reasons for the decrease in the atmospheric CH$_4$ growth rate and the implications for future changes in its atmospheric burden are not understood (IPCC, 2001, 2007). It is also unknown whether the observed changes reflect changes in emissions or removal pathways (sinks).

In the atmosphere methane is mainly removed by reaction with the hydroxyl radical (OH). Other minor sinks include reaction with free chlorine (Platt et al., 2004; Allan et al., 2005), destruction in the stratosphere and soil sinks (Born et al., 1990). The derived CH$_4$ lifetimes are 9.3$^{+0.7}_{-0.6}$ (total loss), 10.2$^{+0.9}_{-0.7}$ (tropospheric OH loss), and 110 (stratospheric loss) years respectively (Prinn, 2005).

Aerosol yields have been estimated from smog chamber data for a variety of reactive organic gases by various researchers over more than 30 years. There are several factors which complicate the determination of aerosol yields from smog chamber studies (Dommen et al., 2009; Hildebrandt et al., 2011):

1. During the course of the experiment aerosols are lost to the chamber walls. In the case of semi volatile species, this would reduce their partitioning into the aerosol. These losses complicate mass balance calculations (Kroll et al., 2007).
2. Under ambient conditions there is always an inorganic/organic aerosol available onto which oxidation products can condense, whereas in laboratory studies the organic particle phase is usually only formed in the process of SOA formation. If SOA is only formed after a longer induction period, semi volatile first-generation products are subject to increased wall losses and ongoing chemical degradation (Chan et al., 2007; Matsunaga and Ziemann, 2010). Thus yields measured in chambers may be substantially lower than those under ambient conditions.
3. Chemical reactions such as oligomerisation may occur in the condensed phase, depending on aerosol composition (Kalberer et al., 2004). The extent and type of these reactions may influence the aerosol yield of a precursor gas (e.g. Kroll et al., 2007). Smog chamber experiments are often performed at higher than ambient concentrations and the extrapolation to lower concentrations is not trivial.
4. There is always an equilibrium between the gas and particle phase which depends on the existing particle mass and its composition. However, experiments in chambers are usually performed with one SOA precursor and thus the composition of the SOA cannot be varied.

We do not expect SOA formation from pure CH$_4$, not even at extremely high concentrations. Therefore we used a method to determine the SOA formation potential from a precursor in the presence of organic seed aerosols. This is based on labeling the precursors with $^{13}$C — a stable isotope of carbon atoms. The discrimination of the oxidation products of the $^{13}$C labeled reactants from the unlabeled organic seed aerosol can then be made by off-line isotope ratio mass spectrometry (IR-MS), which provides the $^{13}$C/$^{12}$C ratio.

Hildebrandt et al. (2011) developed recently a new experimental method to overcome the challenge of distinguishing aerosol components from different sources, also using isotopically labeled compounds, but with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). They generated mixtures of SOA from isotopically labeled toluene and from unlabeled $\alpha$-pinene and used the HR-ToF-AMS data to separate these different SOA types.

### 7.2 Methodology

The procedure to determine the aerosol yield is similar to Dommen et al. (2009). In order to reduce the source of uncertainty induced by the conversion from measured concentrations...
of organic carbon (OC) to organic aerosol (OA) mass, we report here the carbon yields. This is possible as we measured the carbon fraction with a HR-ToF-AMS.

7.2 Methodology

7.2.1 Smog chamber

Three series of experiments were performed at the PSI smog chamber (described by Paulsen et al. (2005) — a 27 m$^3$ Teflon bag in a temperature controlled housing, with four filtered xenon lamps providing quasi-solar illumination. Additional UV lights were used (black lights emitting mainly between 320 and 400 nm; Philips, Cleo performance solarium lamps; in total 80 tubes with 100 W per tube). Before each experimental series the smog chamber was cleaned by the injection of several ppm of ozone and irradiation for 10 h with UV lights at 20$^\circ$C, followed by a flushing period with pure air and high relative humidity (above 60 %) at 30$^\circ$C for at least 20 h. One experimental series lasted between two and four days.

7.2.2 Instruments

Aerosol particle number size distribution (with a diameter between 20 and 800 nm and chemical composition were measured with a scanning mobility particle sizer (SMPS) and an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), respectively. In series 1 the AMS measured non-refractory sub-micron particles, while in series 2a and 2b a new high pressure aerodynamic lens was used to measure non-refractory particles up to 2.5 microns.

Volatile organic compounds (VOC) with a proton affinity higher than water, were measured by high sensitivity proton transfer reaction mass spectrometry (PTR-MS). The proton transfer reaction mass spectrometer from IONICON — equipped with a quadrupole mass spectrometer at unit mass resolution — is able to detect VOCs at the low ppt level and was described by Lindinger et al. (1998). Further gas phase instruments include NOx monitors (Monitor Labs 9841A, Thermo Environmental Instruments 42C with photolysis converter), ozone monitors (Monitor Labs 8810, Environics S300), CO monitor (AERO-LASER GmbH AL5002) as well as an instrument to measure formaldehyde by means of the Hantzsch reaction. The total hydrocarbon was determined using a flame ionization detector (FID) (series 1: J.U.M. Engineering GmbH J.U.M FID VE7, series 2a and 2b: Horiba Ambient THC Monitor APHA-370). During series 2a and 2b we also used a PICARRO (Picarro Cavity Ring-Down Spectrometer G2401) which is able to measure CO$_2$, CO, CH$_4$ and H$_2$O. This instrument measures only $^{12}$CO while the AL5002 measured total CO ($^{12}$CO + $^{13}$CO).

Aerosol samples were collected on tinfoil in an impactor as well as on a quartz filter, which then were burnt under oxygen in an elemental analyzer (EA-1110, Carlo Erba Thermoquest, Milan, Italy) coupled (in continuous flow mode) to the inlet of the IR-MS (Delta S for series 1 and MAT 253 for series 2a and 2b, both Thermo Science Finnigan). In addition the amount of $^{13}$C in CO and CO$_2$ from gas samples was determined by IR-MS. The impactor was built according to Williams et al. (2006).

7.2.3 Wall loss correction (wlc) and carbon mass determination

The measured aerosol mass concentration in the smog chamber is the net result of mass produced in the chamber and mass lost to the walls (Paffenberger et al., 2013). For the wall loss correction (wlc) we assumed the wall deposition rate constant ($k_{w}(t)$) of organic aerosol to be constant over the course of experiment. The wall loss rates generally depend on
particle size, turbulence in the bag, the size and shape of the bag, and particle (and/or wall) charge \cite{Pierce et al., 2008}. The $k_w$ can be estimated semi-empirically by fitting the observed decay in mass due to wall loss. This was done with a linear fit to the natural logarithm of the measured organic mass and at times in the experiment when no (or hardly any) OA is produced (see also Fig. 7.1).

**Figure 7.1** Example of a wall loss correction (here of Series 2b): The solid black line pictures the organic carbon mass measured by an aerosol mass spectrometer (AMS). The wall loss rate ($k_w$) was estimated semi-empirically by fitting the observed decay in mass due to wall loss (during the period marked in blue). The solid green line is the wall loss corrected SOA carbon mass. The bright green background indicates the roughly estimated uncertainty by varying the $k_w$ by $\pm$50%.

The gas-wall partitioning of organic compounds in a Teflon chamber is a frequently discussed topic and might be a source of systematic errors. Matsunaga and Ziemann \cite{2010} investigated gas-wall partitioning of organic compounds that included C$_8$ to C$_{16}$ n-alkanes and 1-alkenes and C$_8$ to C$_{13}$ 2-alcohols and 2-ketones in two Teflon chambers whose walls were either untreated, oxidized in sunlight, or previously exposed to SOA. They found that partitioning was nearly independent of chamber treatment, reversible, and obeyed Henry’s law. The fraction of an organic compounds that partitioned to the walls at equilibrium ranged from 0 to 65%. Values increased with increasing carbon number within an organic compounds class. Thus — as we are focused on small, volatile organic compounds — we neglected the gas-wall partitioning and included only the correction for the condensation of organic vapors into wall lost particles. This correction is based on the assumption that the ratio of the net rates of mass transfer of organic vapors to the particles in suspension and the one to the particles on the walls, respectively, are proportional to the ratio of the organic aerosol in suspension and the organic aerosol on the walls. Most previous studies have neglected this condensation of organic vapors onto the wall deposited particles and assumed a proportionality coefficient that equals zero. However more recent data are consistent with a coefficient that equals one \cite{Hildebrandt et al., 2011}. The true value — which may lie somewhere in between zero and one — remains unknown \cite{Weitkamp et al., 2007, Hildebrandt et al., 2009, 2011}. For the sake of convenience and in order to get an upper limit for the methane carbon yield we will assume a proportionality coefficient of one.

For the first experimental series (series 1) the wlc was based on the particles in suspension measured by SMPS while for series 2a and 2b the wlc was based on AMS measurements. During series 2a and 2b an aerodynamic lens was used to measure non-refractory particles up to 2.5 microns. This enabled us to observe particles outside of the SMPS detection range. In
addition it allowed us to define empirically a factor to determine the organic carbon mass of the aerosol based on the measured SMPS volume. This conversion factor was necessary to determine the organic carbon mass for series 1, where the standard AMS aerodynamic lens was used. However the use of such a conversion factor was only possible since experimental series 1 and 2a were similar in terms of organic aerosol volume, mass and size distribution.

As the wall loss procedure is based on several assumptions and uncertainties we tried to encounter this by varying the determined wall loss rate \((k_w(t))\) with \(\pm 50\%\). This leads to a spread of wall loss corrected organic carbon that is indicated with the semi-transparent green color in Fig. 7.1 and Fig. 7.2. These upper and lower limits of wall loss corrected organic carbon mass were further on used to determine the uncertainties in the methane yield calculation.

### 7.2.4 Experimental procedure

Three experimental series with labeled methane \((^{13}\text{CH}_4, 0.99 \text{ atom fraction } ^{13}\text{C}, \text{Sigma-Aldrich})\) will be discussed here in further detail (see Table 7.1). Unlike the normal experimental procedure, the smog chamber was not cleaned daily and thus the gas phase remained in the chamber for up to four days (series 2a). At the beginning of each series, the clean smog chamber was humidified to a relative humidity \((\text{RH})\) higher than 85 \(\%\) — at a temperature of 21(\(\pm 1\))\(^\circ\text{C}\). These conditions stayed stable during the course of experiments. Then, an inorganic seed was injected (nebulizing a 2 g/l solution of either ammonium sulfate (series 1) or ammonium bisulfate (series 2a and 2b) for one hour to reach sulfate concentrations between 15 and 20 \(\mu\text{g/m}^3\). 500 ppb of ozone \((\text{O}_3)\) was also added to the chamber.

<table>
<thead>
<tr>
<th>experimental series</th>
<th>date</th>
<th>duration</th>
<th>inorganic seed aerosol</th>
<th>organic seed precursor</th>
<th>NO/ HONO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td>Nov. 2010</td>
<td>3 days</td>
<td>ammonium sulfate</td>
<td>(\alpha)-pinene</td>
<td>NO</td>
</tr>
<tr>
<td>Series 2a</td>
<td>April 2012</td>
<td>4 days</td>
<td>ammonium bisulfate</td>
<td>(\alpha)-pinene</td>
<td>-</td>
</tr>
<tr>
<td>Series 2b</td>
<td>May 2012</td>
<td>2 days</td>
<td>ammonium bisulfate</td>
<td>1,3,5-TMB</td>
<td>HONO</td>
</tr>
</tbody>
</table>

In the first two experimental series (1 and 2a) SOA was formed via dark ozonolysis of \(\alpha\)-pinene (98 \%, Sigma-Aldrich). 80 ppb of \(\alpha\)-pinene was injected slowly, over the course of one hour, to avoid nucleation and the formation of a heterogeneous aerosol distribution. The ozonolysis lasted up to 3 hours. After all of the \(\alpha\)-pinene had reacted, 75 ppm of \(^{13}\text{CH}_4\) was added, and a longer period of photochemical oxidation by \(\text{OH}\) with the smog chamber lights switched on followed. On the subsequent days the chamber was refilled with up to 6 m\(^3\) of clean, humid air to compensate for the sampling losses. The inorganic and organic seed was renewed daily by nebulizing the inorganic seed (reaching sulfate concentrations up to 20 \(\mu\text{g/m}^3\)) and by injecting 80 ppb of fresh \(\alpha\)-pinene into the non-illuminated chamber (again over the course of 1 hour), that contained mainly the aged gas phase as well as the particles lost to the walls from the previous day(s). Mostly also methane was added every day (as much as 75 ppm) to compensate the daily sample loss fluxes.

The first series of experiment was conducted in November 2010 with ammonium sulfate and \(\alpha\)-pinene oxidation products as a mixed inorganic/organic seed precursor. In order to enhance the \(\text{NO}_x\) chemistry and boost the \(\text{OH}\) concentration — and thus the amount of \(^{13}\text{CH}_4\) reacted — NO was injected continuously from a gas cylinder (Messer, NO 2.8, 1005 mol ppm in \(\text{N}_2\) 5.0) at a flow of 10 ml/min from the time when the lights were switched.
on. After the last sample was taken (about 5 hours after lights were switched on) the NO injection was stopped. The continuous NO injection on the two subsequent days started after refilling the chamber, at same time as when the lights were turned on, and NO injection was stopped again after the last filter sample had been taken. On the third day nitrous acid (HONO) was used instead of NO: A HONO level of 15–20 ppb in the chamber was reached by passing pure air (2 l/min) through a custom built vessel where sulfuric acid (0.01 M H$_2$SO$_4$) and sodium nitrite (3·$10^{-3}$ M NaNO$_2$) were reacted. The vessel and the HONO system are described by Taira and Kanda (1990). Moreover (in series 1) $^{13}$CH$_4$ was added every day (as much as 75 ppm) to compensate the daily sample loss fluxes.

Series 2a was designed to be a “no-NO$_x$” experiment. In contrast to the “intermediate NO$_x$ experiment” from series 1 we targeted to increase the amount of (methyl-)peroxides. Furthermore we changed the inorganic seed from ammonium sulfate to the slightly acidic ammonium bisulfate. This might lead to an enhanced aerosol growth when the seed is acidic (Jang et al., 2002; Czoschke et al., 2003; Gao et al., 2004a,b; Iinuma et al., 2004). Similar to the first series, we had to renew the suspended particle phase about every 24 hours — due to the wall losses — and add methane as well as clean, humid air to compensate for the sampling losses. In contrast to the first series we had to add also O$_3$ every day — to maintain a mixing ratio above 500 ppb. Furthermore we stopped the addition of $^{13}$CH$_4$ for the last two days to investigate the effect of a decreasing amount of $^{13}$CH$_4$ oxidation products available in the chamber.

In a third experimental series (series 2b) ammonium bisulfate was used again as an inorganic seed precursor. In contrast to the two earlier series, $^{13}$CH$_4$ was injected before the organic seed precursor, in this case 500 ppb of 1,3,5-trimethylbenzene (1,3,5-TMB, mesitylene, 98 %, Sigma-Aldrich). The first samples were taken under a “no-NO$_x$” condition yielding a very low organic carbon SOA mass while the next samples were taken under “intermediate NO$_x$” conditions, yielding organic carbon SOA masses similar to series 1 and 2a. This “no-NO$_x$” condition was achieved by adding the $^{13}$CH$_4$ a few hours before the 1,3,5-TMB such that it can be oxidized by OH which is mainly produced by photolysis of O$_3$. The addition of 500 ppb TMB acted as an OH scavenger and almost halted the $^{13}$CH$_4$ oxidation as well as the SOA production. About 8.5 hours after the lights were switched on and the first filter/impactor samples were taken (under the “no-NO$_x$” condition), HONO was added into the chamber (similar to the third day of series 1). Thus additional OH was generated from photolysis of HONO (see also Fig. 7.1).

A second goal of these experimental series was — apart of the methane yield determination — to uncover whether formaldehyde or peroxides might be mainly responsible for the $^{13}$C enhancement in the aerosol. Therefore we tested $^{13}$C labeled formaldehyde (H$^{13}$CHO with 0.99 atom fraction $^{13}$C) and performed two different experiments, one with similar H$^{13}$CHO concentrations as expected during the methane oxidation (~40 ppb of H$^{13}$CHO), and one at very high concentration (> 800 ppb of H$^{13}$CHO), exceeding even the total amount of “methane reacted” during the methane oxidation experiments.

### 7.2.5 OH tracer

OH concentrations inside the smog chamber were calculated based on PTR-MS measurement of the decay of tracer compounds with known reaction rates with OH. In the first series pinonaldehyde, a product of α-pinene ozonolysis, was used as a tracer to infer OH concentration inside the chamber. At the end of the 2nd day 3-pentanol was injected to determine the OH concentration for the period when pinonaldehyde was used up.

In series 2a and 2b, following the approach of Barmet et al. (2012), we used an extra OH tracer (9-fold deuterated butanol, 98 %, D9, Cambridge Isotope Laboratories), further
referred to as butanol-d9. Before the lights were switched on for the first time, approximately 15 ppb butanol-d9 was inserted into the smog chamber. In series 2a the butanol-d9 had to be renewed after two days. For the OH determination we used a kinetic reaction rate constant of $3.4 \times 10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Barment et al., 2012). All other OH-reaction rate constants were taken from the Master Chemical Mechanism (MCM) (Jenkin and Hayman, 1999; Saunders et al., 2003) web page. The kinetic isotope effect (KIE) of $^{13}$CH$_4$ is very small (Cantrell et al., 1990).

7.2.6 Modeling

The first two series were modeled with version 3.1 of the Master Chemical Mechanism (MCMv3.1) (Jenkin and Hayman, 1999; Saunders et al., 2003). This allowed us to compare the determined OH concentrations for periods where such a tracer was available and to use the modeled OH concentrations for periods where no OH tracer was available. This was especially important for the first series, where we did not use butanol-d9 and determined the OH level based mainly on pinonaldehyde decay instead — an ozonolysis product of α-pinene. It also allowed us to estimate the OH concentration during the α-pinene ozonolysis. Furthermore the modeling provided insight about the fraction of formaldehyde originating from $^{13}$CH$_4$. The latter was necessary for the two extra experiments with H$^{13}$CHO.

7.3 Results and discussion

7.3.1 Initial stages of each experimental series and methane yields

For simplicity we will first focus only on the findings from the first experimental day of each series. All reported methane carbon-yields are derived from this first stage of an experimental series.

During the course of the α-pinene experiments (series 1 and 2a) the excess atom fraction of $^{13}$C (further referred to as $x^E(^{13}C)_{(SOA/blank)}$) in the SOA seed increases with photochemical oxidation time. $x^E(^{13}C)_{(SOA/blank)}$ is determined from the difference between the mole fraction of the $^{13}$C isotope in the sampled SOA and that of the blank (i.e. the sample holder) (Coplen, 2011). The $x^E(^{13}C)_{(SOA/blank)}$ corresponds to the amount that originates from the $^{13}$CH$_4$ in a preexisting SOA. After about 5 to 6 hours after light on the $x^E(^{13}C)_{(SOA/blank)}$ reached in both α-pinene experiments $7.5 \times 10^{-5}$. For the third series 1,3,5-TMB was used as an organic seed precursor. The $x^E(^{13}C)_{(SOA/blank)}$ in the aerosol reached similar but slightly lower values than those measured with the α-pinene SOA seed — despite the higher oxidation time and higher OH exposure. In the first stage of the experiment (during the “no-NO$_x$” regime) this fraction was even several times lower.

Figure 7.2 shows the first day of series 2a — with α-pinene as organic seed precursor. The green line is the wall loss corrected organic carbon mass (± wlc uncertainty), whereas the gray line indicates the $^{13}$CH$_4$ reacted. Latter was calculated based on the determined OH concentrations. The uncertainty in the wlc was determined by varying the wall loss rate by ± 50 %. The uncertainty of methane reacted comes mainly from the uncertainties of the OH tracer’s reaction rate and the reaction rate of methane plus OH. The uncertainties of methane reacted correspond to the standard deviation.

The aerosol yield ($Y$) is equal to the carbon mass of SOA produced ($\Delta M_{COA}$) multiplied by the enhanced $^{13}$C carbon fraction (coming from the labeled precursor hydrocarbon and
Chapter 7 The contribution of methane to aerosol carbon mass

Figure 7.2 Example of a typical experimental procedure: The initial stage of series 2a starts with the ozonolysis of α-pinene and the formation of SOA. The green line shows the total organic carbon mass of the aerosols. After all of the α-pinene had reacted, 75 ppm of $^{13}$CH$_4$ was added (not shown here), and a longer period of photochemical oxidation by OH with the smog chamber lights switched on followed (yellow background). The methane reacted (gray line) is based on the OH concentration determined by the decay of an OH-tracer (in this case: butanol-d$_9$). The periods where filter and tinfoil samples were taken are marked in red.

measured by IR-MS) and divided by the carbon mass of a precursor hydrocarbon that has reacted ($\Delta M_{CH_4-reacted}$), which is in our case methane:

$$Y = \frac{\Delta M_{COA} \cdot f}{\Delta M_{CH_4-reacted}}$$ (7.1)

Whereas $f$ corresponds to the $x_{E}(^{13}C)(SOA/blank)$ in percent, which is the carbon percentage of the collected aerosol that comes from the labeled precursor hydrocarbon ($^{13}$CH$_4$). It is calculated by taking the difference between the atom fraction of $^{13}$C of secondary organic carbon and the blank (in our case the sample holder) in percent: $f = x_{E}(^{13}C)(SOA/blank) \cdot 100 \%$.

Table 7.2 gives an overview of all the reported methane yields (where carbon mass was above 2 µg/m$^3$). The yields are between 0.012 % and 0.16 % — depending mainly on the type of experiment. The upper limit was reached with α-pinene as SOA seed. For series 2b (with 1,3,5-TMB SOA seed) the yields are generally lower. Especially low yields and $x_{E}(^{13}C)(SOA/blank)$ are found during the first stage of the TMB experiment (during the “no-NO$_x$” regime; not reported in Table 7.2, as the collected carbon mass was below 2 µg/m$^3$).

The addition of HONO, 8.5 hours after lights on, increased the OH production substantially and led to an enhancement in methane reacted and SOA mass produced (see also Fig. 7.1). However the observed carbon yield was about a quarter of the carbon yield in the presence of an α-pinene SOA seed. Apart from the slightly lower $x_{E}(^{13}C)(SOA/blank)$ in the aerosol (which could be due to the lower absolute $^{13}$CH$_4$ concentration), the lower SOA mass concentration might be one main reason for the lower methane yields with TMB. Another could be the different chemistry.

The atmospheric significance of these yields (between 0.012 and 0.16 %) are rather small as the following calculation reveals: The yearly CH$_4$ sink due to reaction with OH is between
Table 7.2 Aerosol carbon yields of methane under different conditions and by varying organic and inorganic precursor seeds.

<table>
<thead>
<tr>
<th>sample (hours after lights on)</th>
<th>mean $^{13}$CH$_4$ reacted [ppb] (± std. dev. [ppb])</th>
<th>yields [%] wall loss corrected (± uncertainty [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>photo-oxidation with intermediate NO$_x$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tinfoil (5 h)</td>
<td>38 (±37$^{+}_{18}$)</td>
<td>0.16 (±0.26$^{+}_{0.16}$)</td>
</tr>
<tr>
<td><strong>photo-oxidation without NO$_x$</strong></td>
<td></td>
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<tr>
<td>tinfoil (0 h)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>filter (0 h)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>tinfoil (4 h)</td>
<td>33 (±11$^{+}_{5}$)</td>
<td>0.13 (±0.11$^{+}_{0.05}$)</td>
</tr>
<tr>
<td>filter (4 h)</td>
<td>33 (±11$^{+}_{5}$)</td>
<td>0.11 (±0.12$^{+}_{0.05}$)</td>
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<tr>
<td>filter (6 h)</td>
<td>42 (±14$^{+}_{11}$)</td>
<td>0.16 (±0.10$^{+}_{0.07}$)</td>
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<tr>
<td><strong>TMB with HONO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tinfoil (10 h)</td>
<td>30 (±10$^{+}_{8}$)</td>
<td>0.012 (±0.0065$^{+}_{0.0036}$)</td>
</tr>
<tr>
<td>filter (10 h)</td>
<td>30 (±10$^{+}_{8}$)</td>
<td>0.016 (±0.0092$^{+}_{0.0050}$)</td>
</tr>
<tr>
<td>filter (18 h)</td>
<td>54 (±18$^{+}_{15}$)</td>
<td>0.030 (±0.025$^{+}_{0.0114}$)</td>
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<tr>
<td>filter (22 h)</td>
<td>80 (±26$^{+}_{22}$)</td>
<td>0.038 (±0.038$^{+}_{0.0161}$)</td>
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</table>
400-500 TgC/year (IPCC, 2007), indicating that between 0.048 and 0.8 TgC of the aerosol is from CH$_4$. The global SOA budget was determined to be between 80 and 225 TgC/year (Hallquist et al., 2009), resulting in a CH$_4$ contribution maximally 1%.

### 7.3.2 Subsequent experiments

Due to the daily dilutions and the need to replenish the suspended particle phase on the following days, an effective steady state was reached (in terms of $^{13}$C atom fraction) in the particle ($x_{SOA/blank}^{E}$) as well as in the gas phase ($^{13}$CO). The measured $x_{SOA/blank}^{E}$ in the aerosol remains between $1\times10^{-4}$ and $1.5\times10^{-4}$. It is remarkable that this $x_{E}$ level is reached already immediately after the ozonolysis of the freshly added α-pinene (with lights off) and that it cannot be enhanced by further photochemical oxidation. This result seemed to be independent of the inorganic seed used, the NO or HONO addition and the amount of α-pinene injected (40 or 80 ppb). Thus — from the second day on, when the OH exposure of the gas phase exceeds approximately $8\times10^{-7}$ cm$^{-3}$ h$^{-1}$ — it is meaningless to scale the methane yield to the amount of $^{13}$CH$_4$ reacted, as the (wall loss corrected) yield would always be highest after the ozonolysis and decrease with further $^{13}$CH$_4$ oxidation until the particles are lost to the walls.

In order to make the lab experiments applicable to atmospheric processes, scaling the methane yield to the methane reacted is unavoidable. The methane itself does not interfere with the chemical processes in the chamber. Only after oxidation by OH and subsequent radical production does it play a role, upon which it may be able to react with some available VOCs to form compounds of low enough volatility to partition into the particulate phase. The problematic nature of the subsequent days is apparent from Equation 7.1: the $x_{SOA/blank}^{E}$ (corresponding to $f$ in percent) measured by IR-MS stays constant from the second experimental day on (unless the smog chamber is diluted substantially and $^{13}$CH$_4$ not refilled), whereas the carbon mass of methane reacted ($\Delta M_{CH_4-reacted}$) in the nominator increases every day over the course of photochemical oxidation, thus the yield decreases from day to day. One method of solving this problem partly would be to sum up all the organic carbon masses from the previous days, as is done with the methane reacted. This would then result in yields similar to the one determined from the first experiment. However, having a constant $x_{SOA/blank}^{E}$ from a certain OH exposure onwards, the yield right after the α-pinene ozonolysis would always be higher than after a further photochemical oxidation time where methane reacted increases and the wlc SOA carbon mass stays almost constant. In addition new open questions arise — such as how to deal with the daily “dilutions” (compensating for the sample flows) and to what extent the wall lost particles are affected by these dilutions. A further reason, for reporting yields based on the first 24 hours of an experimental series is that the questionable atmospheric relevance of wall loss corrected, summed up, organic carbon mass concentrations of a few thousands of $\mu$g/m$^3$.

Methane oxidation products are hardly capable of forming particles on their own and their yield might strongly depend on the amount, and composition of, the available seed aerosol and other VOCs in the gas phase. If the pseudo-ideal mixing assumption is valid and SOA from methane oxidation products and from α-pinene form a single solution (the ideal-mixing case), the SOA yields of methane should be a function of the total organic aerosol concentration in the system, and the SOA yields of α-pinene should be a function of the total suspended organic aerosol concentration, consistent with equilibrium partitioning (Hildebrandt et al., 2011).

To uncover the effect of α-pinene SOA mass on the determined methane yield, five α-pinene ozonolysis were performed in a row: by injecting each time 30 ppb of α-pinene into
the chamber which contained mainly methane oxidation products, wall lost particles as well as aged α-pinene ozonolysis products. The lights were switched off during the course of these ozonolysis experiments. Figure 7.3 shows the measured organic carbon mass (green line), the methane reacted (gray line) as well as the sampling periods (red lines) of an experiment that was conducted on the third day of the experimental series 2a. This late stage in the series is the reason for the high amount of methane reacted. For the time period of α-pinene ozonolysis, the methane reacted was calculated based on the modeled OH concentration. The dilutions — caused by the slow α-pinene injections — were neglected.

Figure 7.3 Five α-pinene (30 ppb each) ozonolysis in a row: The chamber contained 500 ppb ozone, a mixture of ozonolyzed and aged α-pinene, an inorganic seed as well as more than 170 ppb methane reacted (in total). All lights were off.

The first samples (filter and tinfoil), collecting the aerosols from the previous day, did not contain enough carbon mass (less than 1 µg/m³) to determine a proper isotopic ratio. The same was the case for the tinfoil sample after the first ozonolysis of (30 ppb) α-pinene. Figure 7.4 shows the determined $x^E(13C)(SOA/\text{blank})$ in the aerosols. The generally decreasing trend can be explained by the fact that more and more unlabeled α-pinene is injected into the smog chamber, while the available methane reacted in the gas phase is decreasing with each ozonolysis. The marginal dilutions caused by the α-pinene injections, might also contribute to this decreasing trend of $x^E(13C)(SOA/\text{blank})$.

Despite the decreasing $x^E(13C)(SOA/\text{blank})$ in the aerosols, the yields do increase with every further α-pinene injection (Fig. 7.5). This might be due to the partitioning: The aerosol yield of a semi volatile organic compound is dependent on the available organic material in a system. This yield dependence on the organic seed is not very surprising and has already been discussed before.

For these reasons it is presumable that the atmospheric relevance of our findings might be even lower. However the methane carbon contribution of 1 % to SOA mass might be considered as an upper limit, especially since it was determined at SOA mass concentrations which are clearly above the atmospherically relevant levels.

A last point that has to be discussed in this context of atmospheric relevance is the unrealistic high $^{13}$CH$_4$ concentration used: 75 ppm is more than 37 times higher than the mean concentration in the atmosphere. However as methane is very inert, its presence does not affect the experiment until the point where it undergoes H-abstraction by the OH. Recent field results, mostly from anthropogenic pollution, suggest that SOA formation occurs in a
Figure 7.4 The excess atom fraction of $^{13}$C ($x^{E^{(13)C}}_{\text{SOA/blank}}$) measured by IR-MS generally decreases with additional α-pinene. The fraction of $^{12}$C is increasing with every addition of fresh, unlabeled α-pinene.

Figure 7.5 Wall loss corrected carbon yield of methane when of α-pinene was added stepwise into the smog chamber (day 3 of series 2a). The chamber contained 500 ppb ozone, a mixture of ozonolyzed and aged α-pinene, an inorganic seed as well as more than 170 ppb methane reacted (in total). Lights were off during the whole period.

timescale of one day after emission of the precursors, while aging of the SOA is rapid at first and continues at a slower rate for at least a week. Indirect measurements of OH concentrations in the atmosphere have established that the annual
7.3 Results and discussion

The globally weighted average OH concentration in the troposphere is roughly \(10^6\) cm\(^{-3}\) (Prinn, 2001; Krol and Lelieveld, 2003). During the mean aerosol lifetime of about one week, the atmospheric aerosol and methane OH exposure is about \(168\cdot10^6\) cm\(^{-3}\) h. Within the 6 hours aerosol lifetime (used for the yield calculations) in our smog chamber the OH exposure is roughly five times lower. The amount of methane reacted during an aerosol life time is still few times higher in the smog chamber than in the atmosphere. Therefore it is inevitable to scale the methane yield to the parameter “methane reacted” — as this was done.

7.3.3 Further test experiments

Possible methane oxidation products that could be responsible for our findings are mainly the methyl peroxide or the formaldehyde. A MCMv3.1 model run for the “intermediate NO\(_x\) experiments” with 80 ppb \(\alpha\)-pinene reveals that the photo stationary steady state of the \(^{13}\)C-formaldehyde is between 30 and 40 ppb H\(^{13}\)CHO. In the “no-NO\(_x\)” experiments this is even lower. Performing an \(\alpha\)-pinene ozonolysis experiment that contains 40 ppb of H\(^{13}\)CHO as the only labeled gas, results in more than an order of magnitude lower \(x^{E}(^{13}\)C)(SOA/blank) in the aerosol than those produced by \(\alpha\)-pinene ozonolysis in an aged gas phase containing methane reacted. Not even an \(\alpha\)-pinene ozonolysis experiment in the chamber that contains over 800 ppb H\(^{13}\)CHO (which is exceeding the amount of methane reacted by far) as only labeled precursor, can reach the \(x^{E}(^{13}\)C)(SOA/blank) that one gets by \(\alpha\)-pinene ozonolysis in an aged gas phase containing methane reacted. Interestingly the \(x^{E}(^{13}\)C)(SOA/blank) can be significantly increased in the 40 ppb H\(^{13}\)CHO experiment by turning the lights on, whereas in the high H\(^{13}\)CHO experiment this is not the case. However this increase is clearly not enough, to explain the obtained \(x^{E}(^{13}\)C)(SOA/blank) in the aerosol. These findings are consistent with the result of Kroll et al. (2005) who studied the reactive uptake of simple carbonyl species onto inorganic aerosol and did not observe any growth for formaldehyde at 5 ppm. We also tested the formaldehyde uptake into the inorganic seed aerosol. Even though we sampled for more than twice as long as during the \(^{13}\)CH\(_4\) experiments, we did not obtain enough carbon mass on the filters and tinfoils when samples were taken from the humidified chamber (RH=85 %) containing only the inorganic seed (ammonium bisulfate) and H\(^{13}\)CHO. All these findings suggest that peroxides might be mainly responsible for the \(^{13}\)C uptake and the resulting \(x^{E}(^{13}\)C)(SOA/blank) in the aerosol. This is at least true within the first 24 hours of an experimental series — before refilling the chamber.

Based on MCMv3.1 model runs, the increase in the amount of peroxides (especially the labeled methyl peroxide) between the intermediate- and the “no-NO\(_x\)” experiments is marginal. This might be the reason why we did not observe a clear difference between the two NO\(_x\) conditions in the suspended particle phase. Interestingly we observed a clear difference regarding the \(^{13}\)CO atom fraction between the intermediate NO\(_x\) and the no-NO\(_x\) experiments. The \(^{13}\)CO atom fraction in the latter case was about half as much (20 %) as in the intermediate NO\(_x\) case (40 %).

For the ozonolysis of \(\alpha\)-pinene in an aged gas phase, it seems that more than one oxidation product of methane is able to get into the aerosol — among others also formaldehyde (as found in the H\(^{13}\)CHO experiments). The enhanced \(^{13}\)C amount in the aerosol right after the ozonolysis of \(\alpha\)-pinene was uncovered already in a pre-study, where the conditions were similar to those of series 1, but without inorganic seed and at a lower relative humidity (RH=55 %). However, the resulting \(x^{E}(^{13}\)C)(SOA/blank) was slightly lower compared to the ones presented here.

A model run with MCMv3.1 reveals that the measured \(x^{E}(^{13}\)C)(SOA/blank) could be explained if a small fraction (a few percent) of the methane reacted reacts with the (non-excited) stable criegee intermediate (sCI) to form products of low enough volatility to partition into
the particle phase of SOA. This holds with the assumption of a relatively slow kinetic reaction rate of $7 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the methane oxidation product with the criegge intermediate. This kinetic reaction rate corresponds to the one of $\text{SO}_2 + \text{sCI}$ in the MCM. However recent theoretical quantum mechanical studies [Jiang et al., 2010] [Kurten et al., 2011], as well as laboratory experiments [Welz et al., 2012], have found the $\text{SO}_2 + \text{sCI}$ reaction to be significantly faster than previously thought. Thus by assuming a collision limited reaction rate, the involved part of methane reacted could be even several orders of magnitude less.

Recently [Mauldin III et al., 2012] observed in field and laboratory measurements strong evidence of the existence of a previously unknown oxidant X, probably a stabilized Criegee intermediate or its derivative, which has a significant capacity to oxidize sulfur dioxide and potentially other trace gases. They report that the production of OH from ozonolysis of branch emissions during this experiment was minor in comparison to production of X. However, as in our case, the mechanism is not yet clear, even though the atmospheric methane oxidation chain is very well known. We note here that besides sCIs, other ozonolysis intermediates might also be responsible for the observed uptake of $^{13}\text{CH}_4$ oxidation products during the ozonolysis of $\alpha$-pinene.

For a future study it would be interesting to determine methane yields in a high NO$_x$ regime, where all the methyl peroxy radicals react with NO and — after a further oxidation of the methoxy radical step with O$_2$ — form formaldehyde. This might decrease the methane yield significantly and would provide strong evidence that the path via methyl peroxide has to be the main reaction pathway into the suspended particle phase.

### 7.4 Summary and conclusion

By labeling methane with $^{13}\text{C}$, a stable isotope of carbon atoms, we could show that its oxidation products can subsequently be found in preexisting organic seed aerosols (1,3,5-TMB or $\alpha$-pinene). The atmospheric relevance of these findings are small and the global methane contribution has been determined to be maximally 1% of the atmospheric aerosol carbon mass. However, the mechanism remains unclear. Experiments with labeled formaldehyde explain the findings only partly. Therefore we hypothesize that organic peroxides might be mainly responsible for the reported methane yields. The effect of seed aerosol composition on the methane yield is unknown and merits further study.

For the first time we have shown in laboratory experiments that oxidation products of the fairly inert and very volatile methane can be found in the condensed phase. This squares with the partitioning theory. Based on these findings, we conclude that there is strong evidence that every existing VOC must be able to contribute, at least to some extent, to the global burden of particulate matter.
Conclusion and outlook

8.1 OH clock

Regarding the OH clock I believe that this seems to be almost a closed chapter. The need of linking the laboratory results with the atmosphere by using a chemical time dimension is undoubted. Whether the presented 9 fold deuterated butanol (butanol-d9) is also for other smog chambers a suitable hydroxyl radical tracer — where the ranges of OH exposures might be quite different — has to be confirmed as well as the reported kinetic reaction rate (see also Chapter 4). One aspect that we were afraid of was the contribution of butanol-d9 to the produced total SOA amount in the smog chamber — especially for experiments with atmospherically relevant, low [VOC] precursor concentrations and low (near-ambient) organic mass concentrations.

To ensure that the organic mass formed during the experiments is not significantly influenced by background contamination in the smog chamber, several blank experiments were carried out: During two blank experiments (performed in May 2012) at RH 50% with neither HONO nor seed aerosol present, the maximum mass concentration was below 0.04 µg·m⁻³ after 5 h and 8 h exposure to UV and xenon lights. These very low background values (the background aerosol mass could be reduced by two orders of magnitude compared to earlier blanks) could be achieved with a newly defined cleaning procedure at high relative humidity and thanks to the new UV lights underneath the smog chamber bag. After this active cleaning period, a flushing period with pure, humidified air at 30°C for at least 20 hours is following. Despite the mentioned ameliorations, a blank experiment with ammonium sulfate seed, HONO as an OH source and a relative humidity of 85% revealed a peak organic mass concentration of 1.7±0.1 µg·m⁻³ 30 minutes after lights on. A third kind of “blank experiment” was performed which was similar to the one at 85% RH and with HONO plus inorganic seed respectively. This time we injected additionally butanol-d9, as only extra added [VOC]. It is remarkable, that the OH concentration in this butanol-d9 blank experiment was about twice as high compared to experiments with about 40 ppb α-pinene and 50% RH. This was the reason why the ~14.5 ppb of butanol-d9 was depleted within 10 hours after lights on. Fortunately the peak organic mass concentration did not exceed the value of 1.7±0.1 µg·m⁻³, which was the measured maximum during the blank experiment without the butanol-d9 injection. However the organic mass peak was reached several hours later than without the
butanol-d9 addition. This indicates that there might be a small contribution to SOA mass from the OH tracer. And this is confirming the findings from the $^{13}$C labeled methane campaign: Every VOC is able to contribute to SOA mass of an existing aerosol. However this contribution is so small that with the HR-TOF-AMS it is not distinguishable from other (similar) blank experiments — but without butanol-d9.

8.2 Yield determination of small carbonyls and methane

Concerning the yield determination of small carbonyls and methane by using $^{13}$C labeled precursors I do believe that this is a great path to go. Apart of the mentioned good sensitivity (see also Chapter [7]), it is crucial to perform experiments under near-ambient conditions (as shown e.g. in Chapter [6] Section [6.3]). As seen during the methane campaign (Chapter [7]) unfortunately this is not always possible as desired. Another advantage is that generally the $^{13}$C labeled VOCs do not exert such a strong kinetic isotope effect (KIE) as many-fold deuterated compounds — as shown for butanol-d9 (Chapter [4]) where the KIE was determined to be 2.5.

Apart of the technical advantages that one has, when using $^{13}$C labeled precursors for aerosol yields determination, the Laboratory of Atmospheric Chemistry at PSI has probably the unique opportunity to have an “stable isotope group” within a lab for atmospheric chemistry integrated. The “Ecosystem Fluxes Group” (this is the official name) does mainly stable isotope analysis for the study of environmental changes. Thus they provide the instrumentation and the know how to conduct experiments such as the $^{13}$C labeled methane experiments (described in Chapter [7]). Fortunately they also consist of helpful people willing to work with us in another research field. This made many things easier, which was very convenient — especially since these kind of experiments were very elaborative and time-consuming.

Probably the main drawbacks of the use of $^{13}$C labeled VOC precursors for aerosol yield determinations are the rather high costs of the labeled products together with the very time consuming and elaborate sampling and measurement technique. Another spot of bother was the over all low and varying sampling efficiency of the impactor and the resulting high amount of sampling volume. The theoretical sampling efficiency should have been more than by factor two higher. During the campaign in April/May 2012 we tested a prototype of a new impactor, which should have exhibit a more stable and in general higher efficiency than the previous one. This increase in performance should have been achieved on the cost of a moderately higher background signal by IR-MS. Unfortunately this hope was not fulfilled and the efficiency could not be increased. Another colleague tested the efficiency, depending on the distance between the critical orifice and the impactor plate. The maximally achieved efficiency was below 50%. This could also be achieved on our tinfoil — which exhibited a slightly varying distance to the critical orifice.

It is clear that the sampling system and the sampling method has to be improved for future campaigns. The plans for an improved impactor have already been designed. Another idea would be to use the OC-EC aerosol analyzer (an instrument from Sunset Laboratory, which is also available at the LAC) to do the aerosol sampling on a integrated quartz filter. As we are mainly interested in the total carbon amount, the distinction between elemental carbon (EC) and organic carbon (OC) — which is often a subject of concern since it is not trivial at all — is subordinate. By heating the filters in the OC-EC monitor, the previously collected aerosols get released and could be trapped in a cold trap. From there the aerosols could be injected directly into the inlet for IR-MS. The latter step could also be improved by using an automatized multi-valve system between several cold traps and the inlet for IR-MS.
With regard of the methane campaign and the completely unknown outcome of the results, the applied method was absolutely adequate. In addition we had to deal with several new and unknown parameters such as e.g. new UV lights. Also a new organic inlet system, based on capillary diffusion, was tested. In order to reduce the uncertainty of the outcome, we conducted a quite elaborate pre-study (in June/July 2010) which was not mentioned in this work, but which was the ground work of the results presented in Chapter 7. It might be worth to mention it here, since it can be quite useful for some experimental set-ups where the outcome is vague and one would like to test several input parameters within a short amount of time. For this purpose we used a small smog chamber with a volume of 15 liters that works in principle like a flow tube. The so called potential aerosol mass (PAM) chamber provides by definition the maximum aerosol mass that oxidation of precursor gases produce. The hypothesis behind the PAM chamber is that all possible precursors are rapidly oxidized and form SOA in a highly oxidizing environment. The PAM chamber is described more in detail by Kang et al. (2007). The PSI smog chamber was used as a reservoir of VOC and humid air, in order to provide stable concentrations for the PAM chamber. Figure 8.1 shows the experimental set-up of this campaign. This set-up allowed us to change the UV intensity and thus the oxidizing environment every 30 minutes and it helped to save the expensive $^{13}$C labeled methane. For a pre-study, where one needs to test several things within a narrow time period, this approach might be very convenient and recommendable.

![Figure 8.1](image.png)

**Figure 8.1** Experimental setup for the $^{13}$C methane campaign using the potential aerosol mass (PAM) chamber in combination with the PSI smog chamber.

Improving the sampling method, by increasing the sampling efficiency for the collected aerosols as well as reducing the time consumed for sampling and sample preparation, opens new doors for further experiments with $^{13}$C labeled compounds. The importance of small carbonyls has been mentioned in section 1.3.3. With labeled acetylene e.g., one could produce labeled glyoxal and determine its yield under various atmospherically relevant conditions. The fact that small carbonyls are able to contribute to SOA mass, has been shown now by several groups. However, providing reliable SOA yields of the most important (and most abundant) carbonyls for near-ambient conditions, in order to improve the atmospheric models, would be very valuable for the atmospheric research community.


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<tr>
<td>2-S</td>
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<tr>
<td>AMS</td>
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<td>LAC</td>
<td>Laboratory of Atmospheric Chemistry</td>
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<td>LIF</td>
<td>laser-induced fluorescence</td>
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<td>low-volatility oxygenated organic aerosol</td>
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<td>MCM</td>
<td>Master Chemical Mechanism</td>
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<td>MS</td>
<td>mass spectrometer</td>
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<td>MUCHACHAS</td>
<td>MUltiple CHamber Aerosol CHechemical Aging Study</td>
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<td>V/H-TDMA</td>
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<td>VOC</td>
<td>volatile organic compound</td>
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