Doctoral Thesis

Analysis of the chemical composition of secondary organic aerosol

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Analysis of the Chemical Composition of Secondary Organic Aerosol

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY (ETH) ZÜRICH

for the degree of
DOCTOR OF NATURAL SCIENCES

presented by

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2005
Parts of this thesis have been published


Parts of this thesis have been presented as a poster


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Summary

Aerosols in the atmosphere are of interest for the climate, because they act as cloud condensation nuclei and scatter and absorb solar radiation; they can affect human health when inhaled into the respiratory tract and can increase cardiovascular morbidity and mortality.

Secondary organic aerosol (SOA) is formed in the atmosphere when the oxidation of gas phase organic compounds leads to the formation of low-volatility reaction products, that partition into the particle phase. SOA can comprise a major part of ambient aerosols with various gaseous biogenic and anthropogenic precursors. The chemistry of these precursors in the atmosphere when reacting with hydroxyl radical, ozone, nitric oxides and light to form products that nucleate and/or condensate to form aerosol is complex and apart from the initial reaction steps not well understood.

The chemical composition of SOA is not fully resolved, yet. On a molecular level considerable efforts have been made to account for the total mass, but a significant part remains unclear. The polarity of many compounds makes the analysis on a molecular level, e.g. with gas chromatography, difficult. Therefore the focus of this work is not on accounting for the total mass of SOA, but on the analysis of the overall concentration of functional groups, such as carbonyls, alcohols, carboxylic acids or organonitrates and their concentration changes over several hours.

To investigate aerosol composition and reaction mechanisms leading to aerosols a reaction chamber was built at the Paul Scherrer Institut to study SOA in a controlled atmosphere with selected gaseous precursors. The “smog” chamber is a 27m³ Teflon bag in a wooden housing equipped with lights to simulate natural sunlight for photo-oxidation experiments. SOA from 1,3,5-trimethylbenzene (TMB) as an example for an anthropogenic precursor and α-pinene as a biogenic precursor was studied under pre-defined conditions in a mix of NO, NO₂, H₂O, and propene.

In a collaborative study with the Laboratory of Atmospheric Chemistry at Paul Scherrer Institut organic acids present in TMB-SOA were investigated with gas chromatography – mass spectrometry (GC-MS) and ion chromatography – mass spectrometry (IC-MS). 20 acids were found with MS of which 12 were identified and quantified based on IC data; the idenfication was confirmed with GC-MS. The sum of
the acids was 20-45% of the total aerosol mass at the maximum aerosol concentration and increased for about 5h after start of the irradiation.

With Fourier Transform Infrared (FT-IR) spectroscopy the development of the carbonyl, alcohol, carboxylic acids and organonitrate functional groups in SOA (from TMB and α-pinene) was monitored; the time resolution was about one hour for experiments up to 22h. FT-IR is a sensitive analysis method, which does not require any sample work up. However, only qualitative results can be obtained. A continuous increase of carbonyl, alcohol and carboxylic acid functional groups could be observed over the full duration of the experiments, which is in agreement with previous IC studies (for TMB) and with the theory that compounds in the particle phase undergo continuous reactions (oxidation) even if the growth of the aerosol mass slows down considerably.

GC-MS was used to analyze carbonyl and hydroxyl groups quantitatively. The time resolution and duration of experiments is comparable to FT-IR, but for GC-MS direct analysis of the sample is not possible; derivatization techniques for the functional groups have to be applied. By titrating a functional group with its specific derivatization agent, the total amount of this group could be determined. But we encountered several problems resulting in large statistical errors, so that no results within reasonable error limits could be obtained.

Recently, the concept of “organic macromolecules” or “oligomers” in SOA has gained much attention in the aerosol community and promises to resolve most of the unexplained mass of organic aerosols. Oligomerization of organic compounds generated from the irradiation of 1,3,5-trimethylbenzene in the smog chamber was investigated with Laser Desorption/Ionization MS for a qualitative identification of the SOA. We found that the molecular weight of the oligomers increases linearly with time to up to 1000Da.
Zusammenfassung

Aerosolpartikel in der Atmosphäre sind von Interesse für das Klima, da sie als Wolkenbildungskeime fungieren und Sonnenstrahlung streuen und absorbieren; sie können die Gesundheit des Menschen beeinflussen, indem sie bis tief in die Lunge eingeatmet werden, und somit können sie vermehrt zu Herz-Kreislauf-Beschwerden führen bis hin zu höherer Sterblichkeit.

In der Atmosphäre entstehen sekundäre organische Aerosole (SOA) wenn die Oxidation von organischen Gasphasenverbindungen zu schwererflüchtigen Substanzen führt, die daraufhin in die Partikelphase übergehen. SOA kann einen Großteil des Aerosols in der Umgebungsluft ausmachen, ausgehend von verschiedenen gasförmigen anthropogenen und biogenen Vorläufersubstanzen. Diese Vorläufersubstanzen bilden nach Reaktion mit Ozon, Stickoxiden und Sonnenlicht verschiedene Produkte in der Atmosphäre, die zu Aerosolen nukleieren und/oder auf bestehenden Aerosolen kondensieren können; diese Chemie ist komplex und abgesehen von den anfänglichen Schritten noch nicht gut verstanden.


Für die Untersuchung von Aerosolen und Reaktionsmechanismen, die zur Aerosolbildung beitragen, wurde eine Reaktionskammer am Paul-Scherrer-Institut gebaut, um SOA von ausgewählten Vorläufersubstanzen in einer kontrollierten Umgebung untersuchen zu können. Die “Smog”-kammer ist ein Teflonsack mit einem Volumen von 27m³, der, in einem geschlossenen Gehäuse hängend, mit Licht bestrahlt werden kann, um natürliches Sonnenlicht für Photooxidationsexperimente zu
simulieren. 1,3,5-Trimethylbenzol (TMB) als Beispiel für einen anthropogenen Vorläufer und α–Pinen als biogenen Vorläufer wurden unter definierten Bedingungen in einem Mix aus NO, NO₂, H₂O and Propen untersucht.

In einem Projekt zusammen mit dem Labor für Atmosphärechemie am Paul-Scherrer-Institut wurden organische Säuren im TMB-SOA mit Hilfe von Gaschromatographie gekoppelt mit Massenspektrometrie (GC-MS) und Ionenchromatographie gekoppelt mit Massenspektrometrie (IC-MS) untersucht. Mit MS wurden 20 Säuren gefunden, von denen 12 aufgrund von IC Daten identifiziert und quantifiziert werden konnten; die Identifizierung konnte mit GC-MS bestätigt werden. Die Summe aller Säuren betrug bei maximaler Aerosolkonzentration 20-45% der Aerosolmasse und nahm über einen Zeitraum von ca. 5h nach Start der Photooxidation zu.

Mit Fourier-Transform-Infrarot-Spektroskopie (FT-IR) konnte die Entwicklung der funktionellen Gruppen von Carbonylen, Alkoholen, Carbonsäuren und Organonitraten im SOA (von TMB) verfolgt werden; die Zeitauflösung war ca. 1h für Experimente mit einer Dauer von ca. 22h. FT-IR ist eine empfindliche Analysemethode, die keinerlei Probenaufbereitung erfordert. Allerdings können damit nur qualitative Resultate erhalten werden. Eine ständige Zunahme der funktionellen Gruppen von Carbonylen, Alkoholen und Carbonsäuren über die gesamte Dauer der Experimente konnte beobachtet werden, was sowohl mit vorher durchgeführten IC Analysen (für TMB) übereinstimmte als auch mit der Theorie, dass Substanzen in der Partikelphase selbst dann kontinuierlich weiterreagieren (oxidieren), wenn sich das Wachstum der Aerosolmasse schon beträchtlich verlangsamt hat.

Mit GC-MS wurden die Carbonyl- und Hydroxylgruppen quantitativ analysiert. Die Zeitauflösung und Experimentsdauer ist vergleichbar mit FT-IR, aber eine direkte Analyse der Proben ist mit GC-MS nicht möglich; für die funktionellen Gruppen mussten verschiedene Derivatisierungsmethoden angewendet werden. Die Menge einer funktionellen Gruppe wurde bestimmt, indem sie mit dem für diese Gruppe spezifischen Derivatisierungsreagenz titriert wurde. Allerdings stiessen wir auf verschiedene Probleme, die zu grossen statistischen Fehlern führten, so dass keine Resultate innerhalb vernünftiger Fehlerschranken erhalten werden konnten.

Seit kurzer Zeit gewinnt die Idee von “organischen Makromolekülen” oder “Oligomeren” im SOA mehr und mehr an Bedeutung in der Aerosol-Community; diese Idee verspricht eine Erklärung für den Grossteil der bisher unbekannten Masse.
### Abbreviations

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<tr>
<td>AcN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>APIN</td>
<td>α-pinene</td>
</tr>
<tr>
<td>BSTFA</td>
<td>N,O-Bis(trimethylsilyl)trifluoroacetamide</td>
</tr>
<tr>
<td>CPC</td>
<td>condensation particle counter</td>
</tr>
<tr>
<td>C=O</td>
<td>carbonyl</td>
</tr>
<tr>
<td>COOH</td>
<td>carboxylic acid</td>
</tr>
<tr>
<td>DFB</td>
<td>decafluorobiphenyl</td>
</tr>
<tr>
<td>dimeBAcid</td>
<td>3,5-dimethylbenzoic acid</td>
</tr>
<tr>
<td>ECD</td>
<td>electron capture detector</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>EP</td>
<td>equivalence point</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionization detector</td>
</tr>
<tr>
<td>FT-ICR</td>
<td>Fourier transform – ion cyclotron resonance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform - Infrared spectroscopy</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatography - mass spectrometry</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>IC-MS</td>
<td>ion chromatography - mass spectrometry</td>
</tr>
<tr>
<td>IS</td>
<td>internal standard</td>
</tr>
<tr>
<td>KCl</td>
<td>potassium chloride</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption/ ionization</td>
</tr>
<tr>
<td>MTBSTFA</td>
<td>N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide</td>
</tr>
<tr>
<td>OH</td>
<td>hydroxyl</td>
</tr>
<tr>
<td>PFBHA</td>
<td>O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SIM</td>
<td>single ion monitoring</td>
</tr>
<tr>
<td>SMPS</td>
<td>scanning mobility particle sizer</td>
</tr>
<tr>
<td>TBDMS</td>
<td>tert-butyldimethylsilyl</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMB</td>
<td>1,3,5-trimethylbenzene</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TOF MS</td>
<td>time-of-flight mass spectrometry</td>
</tr>
<tr>
<td>VTDMA</td>
<td>volatility tandem differential mobility analyzer</td>
</tr>
<tr>
<td>WEDD/AC</td>
<td>wet effluent diffusion denuder/aerosol collector</td>
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Chapter 1

Introduction
1.1 Overview of aerosols in the atmosphere

Aerosols are solid or liquid particles suspended in a gas. Aerosols can be of primary or secondary origin. Primary means that the aerosols are directly emitted into the atmosphere from various sources. Examples would be suspended matter including dust, sand, smoke or (sea) spray. Secondary aerosol is generated by condensation or nucleation of gas-phase compounds. This gas-to-particle conversion forms very small particles (<< 1µm) in the atmosphere. The gaseous precursors are both from anthropogenic and biogenic sources.

Aerosol particles in the atmosphere have important effects on human health, on regional air quality and on the global climate.

The pulmonary toxicity of ultrafine particles (smaller than 0.1µm) has been demonstrated in controlled laboratory experiments (Nemmar et al., 2001). Also, aerosols smaller than 2.5µm are linked to cause respiratory irritation and reduced lung function among other severe adverse health effects (Brauer et al., 2001). Aerosols affect the climate in two ways: the direct effect, meaning they absorb and scatter the incoming solar radiation and therefore provide a warming or cooling radiative forcing of the climate (IPCC, 2001). On a regional and local scale, they degrade visibility. Aerosols can also act as cloud condensation nuclei and alter the cloud albedo (fraction of solar energy that is reflected back to space); this is called the indirect effect. Particles also participate in heterogeneous reactions, thereby altering the chemistry of the atmosphere.

Figure 1-1 gives an overview over the various effects that influence radiative forcing and their change since 1750. Aerosols contribute to both, the warming and cooling effect of the climate, but this is still speculative. The x-axis denotes the level of scientific understanding, which is very low for most of the aerosol related effects.
Figure 1-1: Factors that force climate change: These radiative forcings arise from changes in the atmospheric composition, alteration of surface reflectance by land use, and variation in the output of the sun. Except for solar variation, some form of human activity is linked to each radiative forcing. The rectangular bars represent estimates of the contributions of these forcings - some of which yield warming, and some cooling. The vertical line above the rectangular bars indicates a range of estimates. Some of the forcings possess a much greater degree of certainty than others. A vertical line without a rectangular bar denotes a forcing for which no best estimate can be given owing to large uncertainties. The overall level of scientific understanding for each forcing varies considerably, as noted (adapted from IPCC (2001)).

Aerosols consist of an organic and an inorganic fraction. In brief, the inorganic fraction is composed of inorganic salts (e.g. ammonium sulfate, ammonium nitrate, sodium chloride), mineral dust, soot, metals (minor fraction) and water – depending on the relative humidity.

Although organic aerosols are a significant fraction of the ambient aerosol (up to 50% of the mass) (Seinfeld and Pandis, 1998), only little is known about their formation, composition and reactivity due to the complexity of their composition and the small concentration usually available for analysis.
1.2 Atmospheric chemistry

This chapter gives a brief overview over atmospheric chemistry in the troposphere (lowest layer of the atmosphere up to 10-15km altitude) during daytime. The gas phase of organic molecules chemistry in the troposphere involves the photo-oxidation in the presence of nitrogen oxides. Important reactions would be with OH•, ozone, or direct photolysis reactions. The oxidation proceeds via chains of free radical reactions with solar radiation acting as driving force of the radical reactions.

1.2.1 The photostationary state relation

Ozone can be considered as the principal product of tropospheric chemistry. It is formed in the atmosphere exclusively via the reaction of molecular oxygen with an oxygen atom.

\[
O_2 + O + M \xrightarrow{k_{(1-1)}} O_3 + M
\]

Equation 1-1

M represents a third molecule like N₂ or O₂ that takes up the excess vibrational energy. In the troposphere, atomic oxygen is produced by the photolysis of nitrogen dioxide, NO₂, at wavelengths λ< 424nm:

\[
NO_2 + h\nu \xrightarrow{j_{(1-2)}} NO + O
\]

Equation 1-2

Nitrogen monoxide, NO, reacts quickly with ozone to regenerate NO₂:

\[
NO + O_3 \xrightarrow{k_{(1-3)}} NO_2 + O_2
\]

Equation 1-3

Adding Eq. 1-1 to 1-3 results in a zero cycle that produces no net ozone. The oxygen atom is so reactive that it disappears by the reaction in Equation 1-1 basically as fast as it is formed by the reaction in Equation 1-2. Therefore, the rate determining
reaction for the ozone production is the generation of the atomic oxygen. Assuming steady state (ss) conditions the O₃ concentration can be calculated:

\[
[O₃]_{ss} = \frac{j_{(1-2)}[NO_2]}{k_{(1-3)}[NO]}
\]

Equation 1-4

This is the photostationary state relation. The ozone concentration depends only on the ratio of NO₂ to NO. But the mixing ratios of ozone in urban and regional atmospheres are often greater than those in the sample calculation. Other reactions than 1-1 to 1-3 are important in the atmosphere and therefore in the relation described in Equation 1-4. The photostationary state relation depends not only on NO, NO₂ and ozone. This will be discussed in the next section.

1.2.2 Reactions in the troposphere

A major class of compounds in the troposphere are the carbon-containing species and water (vapour). Water is present in the lower troposphere at mixing ratios up to 10⁴ ppm. It can react with the excited singlet oxygen atom -produced in the photolysis of ozone-

\[
O_3 + h\nu \overset{\lambda < 310nm}{\rightarrow} O(^1D) + O_2
\]

Equation 1-5

to produce the hydroxyl radical (OH•):

\[
O(^1D) + H_2O \rightarrow 2OH •
\]

Equation 1-6

This radical is unreactive towards oxygen and, as a result, survives and can react with most atmospheric trace species. The reactions of OH• are the key to understand tropospheric chemistry; it is the most important oxidation reagent in the atmosphere.
Carbon monoxide will react with the hydroxyl radical to form CO$_2$ and H\textbullet{}, with H\textbullet{} reacting so quickly with O$_2$ that the formation of the hydroperoxy radical (HO$_2$\textbullet{}) can be described as

$$\text{CO} + \text{OH}\cdot \xrightarrow{\text{O}_2} \text{CO}_2 + \text{HO}_2\cdot$$

Equation 1-7

The most important atmospheric reaction of HO$_2$\textbullet{} in polluted regions is the reaction with NO to form NO$_2$ and the hydroxyl radical. The reaction depends on the level of NO available; in the smog chamber the levels are higher than in polluted areas, therefore Equation 1-8 is valid.

$$\text{HO}_2\cdot + \text{NO} \rightarrow \text{NO}_2 + \text{OH}\cdot$$

Equation 1-8

Figure 1-2 gives an overview over reactions in the gas phase during the day including the NO-NO$_2$ cycle and volatile organic compound (VOC) degradation.
As mentioned before, the ozone concentration is higher than can be explained with the photostationary state relation. The net formation of ozone is due to other precursors, like methane, carbon monoxide and reactive organic gases (ROG). They form the RO\textsubscript{x} radical chain reaction, with photochemical start reactions, the RO\textsubscript{x} radical chain and termination reactions. The start reactions are the photolysis of ozone and the formation of the OH radical (Equation 1-5 and Equation 1-6) as well as photolysis of carbonyls to form the HO\textsubscript{2} radical (Equation 1-7) or RO\textsubscript{x} radicals.

The OH radical starts the radical chain by abstracting H from saturated VOCs or by adding to double bonds of unsaturated VOCs (see chapter 1.2.3.1 and 1.2.3.2).

The HO\textsubscript{2} radicals react according to Equation 1-8. This forms the hydroxyl radical again, and the chain is closed (the radical is also formed via reaction of ozone with HO\textsubscript{2}•).

This oxidation mechanism changes the NO\textsubscript{2} to NO ratio (see also Equation 1-9) to higher values and therefore is responsible for a net ozone production (photolysis of NO\textsubscript{2} and then Equation 1-1).

The termination reactions are e.g. the formation of nitric acid (OH• + NO\textsubscript{2}) under conditions with high NO\textsubscript{2} concentrations, the formation of hydrogen peroxide (•HO\textsubscript{2}...
and the formation of organic hydroperoxides \((\cdot \text{HO}_2 + \text{RCH}_2\text{OO}\cdot)\) at low NO\textsubscript{2} concentrations.

The tropospheric reactions of biogenic and anthropogenic VOCs are much more versatile than described so far. The presence of many different VOCs of various classes, – alkanes, alkenes, aromatic hydrocarbons etc. - adds to the complexity in the chemistry of these organic species (see chapter 1.2.3). The degradation process for most species starts with the OH radical reaction; the other main oxidation reagents are ozone (addition to doublebonds) or NO\textsubscript{3} radicals, which become important during nighttime.

### 1.2.3 Formation of SOA: reactions of the precursors in the gas phase (chemical reactions)

SOA is generally only formed from the atmospheric oxidation of hydrocarbons containing six or more carbon atoms (Seinfeld and Pankow, 2003) because the reaction products, e.g. oxygenated compounds, must be sufficiently nonvolatile to be able to transfer from the gas phase into the particle phase. The gas phase degradation of C\textsubscript{6} or more carbon compounds means that there are multiple reaction sites in the molecule for the attack of a radical to start the radical reaction and therefore the mechanisms are complex and the number of reaction products large (Johnson \textit{et al.}, 2005).

#### 1.2.3.1 Alkanes

Under tropospheric conditions (see chapter 1.2.2), alkanes react with OH and NO\textsubscript{3} radicals, but reaction with NO\textsubscript{3}\cdot accounts only for about 10% of the atmospheric loss during daytime (Seinfeld and Pandis, 1998). Basically, any H-atom in the alkane is susceptible to OH\cdot attack to abstract the H-atom, producing the alkyl radical. OH\cdot attack on a tertiary H-atom is faster than on a secondary atom and slowest on a primary H-atom.

The resulting alkyl radical \((\text{R}\cdot)\) reacts rapidly with O\textsubscript{2} to form RO\textsubscript{2}\cdot, the alkyl peroxy radical. This can react as follows:
Under urban conditions, reaction with NO is the dominant reaction pathway for RO\textsubscript{2} radicals. The formed RO radicals react via a variety of processes: unimolecular decomposition, unimolecular isomerization (only molecules with 5 or more carbon atoms), or reaction with O\textsubscript{2}: 

\[ RO_2 \cdot + O_2 \rightarrow RCHO + HO_2 \cdot \]  

Equation 1-10

Unimolecular decomposition produces an alkyl radical and a carbonyl compound. The subsequent reactions of RO\textsuperscript{•} determine to a large extent the products from the atmospheric oxidation of the VOCs.

1.2.3.2 Alkenes

The reactions of alkenes are of great importance in tropospheric chemistry, because not only anthropogenic emissions consist of alkenes, also the most important biogenic compounds isoprene and various monoterpenes are part of this class of substances. The atmospheric reactions of alkenes are more complex than of alkanes, because alkenes react not only with OH\textsuperscript{•} and the nitrate radical, but also ozone adds to the double bond (Atkinson, 1997).
Reaction with OH•

Alkenes react with the OH radical, which attacks at the double bond (85%), while the abstraction of an H-atom is of minor importance. The attack of OH• leads to a β-hydroxy alkyl radical \( R_1R_2C(OH)•-CR_3R_4 \) and \( R_1R_2C•-C(OH)R_3R_4 \) (double bond was between \( R_2 \) and \( R_3 \)). This reacts quickly with \( O_2 \) to form the β-hydroxy alkylperoxy radical \( R_1R_2C(OH)-C(O_2•)R_3R_4 \) and isomer analog to Equation 1-9(1). These peroxy radicals can react with NO and NO\(_2\), to form a β-hydroxy alkoxy radical \( R_1R_2C(OH)-C(O•)R_3R_4 \) and isomer. These alkoxy radicals can react further as described with the alkanes.

Reaction with NO\(_3\)

The reaction with the nitrate radical plays an important role only in nighttime chemistry. This will not be considered here, because the focus is on photo-oxidation of gaseous compounds.

Reaction with ozone

The reaction of ozone with alkenes leads to formation of OH•, sometimes close to a unit yield (1 molecule of OH per 1 molecule of alkene reacted) (Atkinson and Aschmann, 1993).

The ozone-alkene reactions proceeds via initial ozone addition to the double bond. This is followed by rapid decomposition of the resulting primary ozonide (molozonide) into a carbonyl compound and the energy-rich Criegee biradical (Seinfeld and Pandis, 1998). The biradical can be collisionally stabilized or can undergo unimolecular decomposition:

\[
\begin{align*}
[R_1CH_2C•(R_2)OO•] & \rightarrow R_1CH_2C•(R_2)OO• \quad (1) \\
& \rightarrow [R_1CH_2C(O)OR_2] \rightarrow \text{decomposition} \quad (2) \\
& \rightarrow [R_1CH = C(OOH)R_2] \rightarrow R_1C•HC(O)R_2 + OH• \quad (3)
\end{align*}
\]

Equation 1-11
The stabilized biradical (reaction 1) can react with a number of species: $\text{H}_2\text{O}$, NO, NO$_2$, SO$_2$, CO to form e.g. acids (with water) and aldehydes (with NO and NO$_2$). It appears that the reaction of the stabilized biradical with H$_2$O will predominate under tropospheric conditions (Atkinson, 1994).

1.2.3.3 Aromatic Hydrocarbons

Aromatic hydrocarbons are of great interest in the chemistry of the urban atmosphere because of their abundance in e.g. motor vehicle emissions. In the polluted urban environment the photo-oxidation of not only aromatics has been estimated to contribute up to 30% or so of photochemically produced ozone in the boundary layer over Europe (Derwent et al., 1998). In smog episodes in California 40-80% of the particulate organic carbon has been estimated to be secondary in origin (Turpin and Huntzicker, 1995). Aromatics are believed to play a dominant role in SOA formation (Forstner et al., 1997a; Odum et al., 1997).

Aromatics sum up to about 19% of the total non-methane hydrocarbons (Calvert et al., 2002) in urban air. They tend to have high reaction rates and high yields of radicals and reactive products that contribute to ozone formation (Calvert et al., 2002).

The gas-phase oxidation of aromatic compounds is initiated by reaction with OH•, which adds to the aromatic ring (=major pathway, ca. 90%, depending on the aromatic hydrocarbon) or abstracts an H-atom from alkyl-substituted aromatics (ca. 10%). Adding of OH• forms a hydroxycyclohexadienyl type radical. This reacts with O$_2$ to form a bicyclic peroxy radical, which subsequently reacts with NO to form a bicyclic oxy radical and NO$_2$. The following ring opening step is via $\beta$-scission. The structures of all of the reaction products due to hydroxyl addition to the aromatic ring are not well known, but representative structures as the dicarbonyls shown in Figure 1-3 can be assumed. In Figure 1-3 the addition of OH• leads for 1,3,5-trimethylbenzene (TMB) to the formation of methylglyoxal and 2-methyl-4-oxo-2-pentenal (APT1=aerosol precursor in reaction path A), both stable oxidation products that were observed in laboratory experiments.
Figure 1-3: Reaction pathway for OH addition to 1,3,5-trimethylbenzene (A) and reaction pathways for aerosol precursors (B), adapted from Dechapanya et al. (2003).

Reaction pathway B in Figure 1-3 shows the further reactions of APT1 with OH• to form products that can partition into the particle phase e.g. TPM1 and TPM2 due to their low vapour pressure (Dechapanya et al., 2003). In general, the more (alkyl-) substituted the ring the greater the importance of ring fragmentation. A large variety of reaction products is formed, with varying molecular weight and polarity depending on the functional groups and degree of substitution. Many of these species are expected to be more reactive than the parent hydrocarbon and therefore can be further
oxidized rapidly. This results in a large and complex number of semi- and non-volatile reaction products which partition between aerosol and gas phase.
In comparison to the alkanes and alkenes, the degradation mechanisms for the (photo-) oxidation of aromatic hydrocarbons are relatively poorly understood.

## 1.3 Secondary Organic Aerosol in atmospheric chemistry

### 1.3.1 Gas/Particle Partitioning and Aerosol Yield

Secondary organic aerosol (SOA) is aerosol that is chemically formed in the atmosphere, unlike primary aerosol. Chapter 1.2.2 describes the photochemical oxidation processes of VOCs. The vapor pressure decreases upon oxidation and the water solubility increases compared to the precursor compound; this process is responsible for the gas-particle partitioning (Griffin et al., 2003). Pankow (1994b) suggested that even products whose gas phase concentration is below their saturation concentration will partition into the particle phase. Pankow (1994a; 1994b) developed an absorptive gas-particle partitioning model, where the partitioning is assumed to be governed by equilibrium partitioning into an absorptive liquid organic matter phase.

For each compound that partitions into the organic matter (om) phase, Pankow has defined an absorption equilibrium constant $K_{p,i}$:

$$K_{p,i} = \frac{F_{i,om}}{A_i \cdot TSP} = \frac{760 \cdot RTf_{om}}{MW_{om} \cdot 10^6 \zeta_i P_{L,i}^o}$$

Equation 1-12

$A_i$ is the gas phase concentration (ng/m$^3$) of compound i, $F_{i,om}$ is the concentration of compound i (ng/m$^3$) in the absorbing organic matter phase, TSP the total suspended particulate concentration (µg/m$^3$). R is the ideal gas constant (8.206*10$^{-5}$ m$^3$ atm mol$^{-1}$ K$^{-1}$), T is temperature (K), $f_{om}$ is the mass fraction of the TSP that is the absorbing om phase, $MW_{om}$ is the mean molecular weight of the absorbing om (g/mol), $\zeta_i$ is the activity coefficient of compound i in the om phase, and $p_{L,i}^o$ is the vapor pressure (Torr) of the absorbing compound as a liquid (subcooled, if necessary).
Starting from that model, Odum et al. (1996) developed an expression for the aerosol yield $Y$, which relates how much particulate matter is produced when a certain amount of parent gaseous VOC is oxidized:

$$ Y = \frac{M_o}{\Delta VOC} $$

Equation 1-13

where $M_o$ ($\mu g \text{ m}^{-3}$) is the mass concentration of SOA produced from the reaction of $\Delta VOC$ ($\mu g \text{ m}^{-3}$). The organic particulate mass directly affects the gas/particle partitioning by acting as the medium into which the oxidation products can be absorbed. Therefore, products with relatively high vapor pressure may be absorbed into the particle phase even though the products are present at concentrations below their saturation point (Song et al., 2005).

The classical view of gas-particle partitioning assumes only physical absorption according to the thermodynamic equilibrium in Equation 1-12 and neglects any chemical reactions. But it has been shown recently that reactions within the SOA occur, e.g. oligomerization, therefore the model has to be adapted to the fact of heterogenous chemical reactions. The publication by Kroll and Seinfeld (2005) takes this into account and is recommended for further reading.

### 1.3.2 Size distribution

The general introduction described the effects of aerosols on climate and health, and for health effects and also cloud formation and light scattering, the size of the aerosol is important. The aerosol particles of the atmosphere is characterized by the the size distribution, plotted either as particle density, surface density or volume (mass density) per diameter interval (e.g. $dM/d\log D$ vs. $\log D$). The diameter $D$ is often assumed to be the equivalent diameter of a sphere. Respective plots are often on a logarithmic scale, because diameters of aerosols vary by many orders of magnitude. Figure 1-4 shows the difference in number (N)-, surface (S)- and volume (V) distribution of outdoor aerosol measurements. The plot number vs. the size of the particles shows that the smallest particles ($D < 0.1 \mu m$) are the biggest fraction in number. Surface vs. size shows a maximum between 0.02-0.04 $\mu m$, and volume vs.
size shows a bimodal distribution with maxima between 0.2-0.3µm and dominates at diameters > 1µm. The plot shown here is not the size distribution one would expect in typical urban areas in Switzerland. The number distribution would be mostly between 10 and 100nm; the surface with a maximum between 100nm and 1µm and the volume distribution would be mostly below 1µm. This is contrary to the figure shown where the bimodal distribution is dominant above 1µm.

Figure 1-4: Normalized number-, surface- and volume distribution of aerosol particles - measured October 1971 in Denver (originally from Seinfeld (1986), adapted by Staehelin (2003)).

In tropospheric chemistry, aerosol particles are generally divided in coarse (D > 1-2µm) and fine (D < 1-2µm) particles (see Figure 1-5). Mechanically generated aerosols are usually the biggest aerosols, the size is above 1-2 µm. The fine particles, smaller than 1-2µm, are generated differently, they consist of both primary (combustion) particles and secondary aerosols in the range from 0.001 to ca. 0.1µm (Aitken nuclei range). The accumulation range (0.1-2µm) consists mostly of secondary aerosols formed via gas-particle conversion and transfer from the nuclei range via condensation and coagulation.

Figure 1-5 shows the idealized size distribution which arises from different mechanisms of aerosol generation. The volume vs. number plot of Figure 1-4 (real data) shows the bimodal distribution that is displayed in Figure 1-5 (idealized figure).
In aerosol formation simulations under controlled laboratory conditions nucleation without any previous aerosol present (without “seed” aerosol) starts as cluster of molecules and particles grow up to 800-900nm via the above-mentioned mechanisms.

### 1.4 Characterization methods of SOA used

Considerable effort has been done to gain a detailed understanding of the formation and growth of SOA in the troposphere, and this remains still an area of great interest as it consists of difficulties in identifying the individual chemical components of SOA. Even a single precursor, e.g. TMB yields a large number of products in the gas and aerosol phase, most of them not identified yet. The chemistry following the initial oxidation of the gas phase precursor VOC and its role in SOA formation is not quite clear at present. For example, SOA formed in the photo-oxidation of aromatic hydrocarbons (e.g. TMB) includes compounds such as organic acids, cyclic anhydrides, polycarboxyls (Edney et al., 2001; Forstner et al., 1997a; Jang and...
Kamens, 2001; Yu et al., 1997), all highly oxidized compounds, which are probably not produced directly in the initial reaction of the hydrocarbon. They are more likely formed by photolysis or gas-phase reactions of first generation products. This chemistry (see Chapter 1.2.3) is so far not well understood, neither is their contribution to SOA. Among all anthropogenically emitted VOCs, aromatic compounds have the highest aerosol formation potential. In previous studies, which analyzed SOA-composition from aromatic photo-oxidation (Forstner et al., 1997a; Yu et al., 1997) only 10-20% of the mass could be attributed to specific compounds.

Ambient aerosol is often sampled on filters (Teflon or quartz fibers), or collected with impactors. When sampling with filters, care has to be taken to correct for sampling artifacts that occur when gas and aerosol phase are not separated. Often denuders (Gundel et al., 1995; Gundel and Lane, 1999) or polyurethane foams (Sax et al., 2003 + references therein) are used to remove the gas phase; see Chapter 3 for more details. Most of the sampling methods require off-line work-up and analysis with e.g. gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-MS (LC-MS). An advantage of LC-MS over GC-MS is that aerosol bound compounds that are often more oxidized and therefore more polar than their more volatile precursors can be easily analyzed. A wide range of separation columns and types of mass spectrometers have been used, such as quadrupole and ion trap MS, Time-of-flight (TOF) or combined systems. Atmospheric pressure chemical ionization (APCI) as well as electrospray ionization (ESI) are the typical interfaces in use for LC-MS. As in GC-MS a single separation is often not sufficient to resolve the highly complex mixture samples. Two-dimensional methods (Lewis et al., 1997) with LC-GC-Ultraviolet-MS have been developed. A way to obtain more information from MS measurements is to perform MS/MS (or MSn) experiments. In this technique, often performed in ion trap mass spectrometers or with a combination of quadrupole and ion trap or TOF instruments, a specific peak detected in the first mass separation is selected, all other masses are removed/ejected, and a second MS analysis is performed by fragmenting this selected ion.

GC-MS is still the most extensively used method in the last years for single compound analysis (Fraser et al., 2003; Rogge et al., 1993; Rogge et al., 1998; Schauer et al., 1999a; Schauer et al., 1999b; Schauer et al., 2002). A general problem with GC-MS remains the collection of atmospheric samples. The low concentration of the species of interest in the ambient air requires sample volumes of tens to hundreds
of m³ air in order to get a detectable signal. This can enhance sampling artifacts, and also limits the time resolution for sampling.

The polarity of some compound classes hinders identification and quantification by conventional analytical techniques, because the compounds are easily lost to the surfaces of injectors and columns. (Multistep) derivatization techniques have long been used to detect and identify compounds with multiple functional groups such as carbonyl, carboxyl, and hydroxyl-groups (Yu et al. (1998) + references therein).

On-line analysis for individual organic compounds is difficult because of the low quantities available. On-line analysis can be performed with e.g. an Aerosol Mass Spectrometer (AMS) but this gives mostly fragments of the organic compounds that have to be appointed to certain possible functional groups and not individual compounds. MS spectra of complex mixtures are usually also complex and difficult to interpret.

There is a wide range of other MS methods for atmospheric samples. For emissions from combustion sources, which is one of the most important anthropogenic emissions, a wide variety has been used (Kalberer et. al., 2004b). Among the new developments for MS are ESI-MS or matrix assisted laser desorption ionization (MALDI) MS to analyze SOA (see Chapter 7), but use of these techniques has just started recently (Gao et al., 2004; Iinuma et al., 2004; Tolocka et al., 2004).

Infrared spectroscopy has been used on-line and off-line, but this technique gives no information on single compounds but only on functional groups. More details on IR methods and applications are described in Chapter 8.

Many studies focus on single gaseous precursors to form SOA. This is done under controlled conditions in big bags made of Teflon, so-called smog chambers. The chambers can be outdoor or indoor. Gaseous precursors are injected into the chamber and then, depending on the reaction to be studied, mixed with ozone, NO, NO₂, and for photo oxidation experiments the bag is irradiated with natural sunlight or lamps to mimic the spectrum of the sun at the earth’s surface. The chamber used for studies described in this thesis is explained in full detail in Chapter 4.
1.5 Recent developments

Organic aerosols have been studied in both rural and urban atmospheres (Blando et al., 1998; Kaplan and Gordon, 1994; Polissar et al., 2001; Rogge et al., 1993). Up to 90% of the organic aerosol mass in urban areas can be secondary organic aerosol (Lim and Turpin, 2002). Many studies have focussed on toluene and other aromatic hydrocarbons (Forstner et al., 1997a; Izumi and Fukuyama, 1990), styrenes (Izumi and Fukuyama, 1990), cyclic olefins (Hatakeyama et al., 1985; Hatakeyama et al., 1987) and also alkenes (Forstner et al., 1997b; Grosjean, 1984; McMurry and Grosjean, 1985; Wang et al., 1992). The major precursors of SOA are, however, biogenic VOCs, with isoprene and the monoterpenes α- and β-pinene, sabinene and limonene as the most abundant ones. The aerosol forming potential of biogenic hydrocarbons has been investigated in a series of controlled chamber experiments (Hoffmann et al., 1998; Kamens et al., 1981; Pandis et al., 1991; Zhang et al., 1992). It has been found that isoprene does not contribute to SOA formation, although very recent studies indicate that isoprene might be involved in SOA formation (Claeys et al., 2004; Czoschke et al., 2003). The pinenes contribute significantly to SOA production. The oxidation chemistry of α-pinene (APIN) has been studied for two decades and remarkable progress has been made in identifying products and reaction pathways (Griffin et al., 1999; Hoffmann et al., 1998; Yu et al., 1999).

Summaries of the gas-phase kinetics of the monoterpane reactions with OH and NO3 radicals and ozone, products of these reactions and the pathways leading to their formation can be found in several review articles and books, e.g. (Atkinson, 1990; Calvert et al., 2000). Seinfeld and Pankow (2003) have summarized laboratory studies of SOA formation performed over the last decade. As a result of ever increasing information on the nature of the gas-phase products and the composition of the resulting aerosol from the oxidation of monoterpenes much effort is now being spent in developing combined gas-phase kinetics and aerosol partitioning models to represent secondary organic aerosol formation in ambient models (Griffin et al., 2002a; Griffin et al., 2002b; Kamens et al., 1999; Kamens and Jaoui, 2001; Pankow et al., 2001; Pun et al., 2002; Seinfeld et al., 2001). Most of the studies mentioned have been performed in smog chambers. But the translation of these results to the real...
atmosphere still requires thorough interpretation and further analysis and understanding of the chemical mechanisms. What remained unclear until recently, was the presence of species in SOA whose vapour pressures are far too high to support significant partitioning into the aerosol phase (Forstner et al., 1997a; Yu et al., 1998; Yu et al., 1999). Oligomer and/or polymer formation in biogenic and anthropogenic VOC degradation SOA has been found and might be responsible for an important fraction of the SOA chemical build up in the troposphere (Gao et al., 2004; Kalberer et al., 2004a; Tolocka et al., 2004). These recent discoveries provide a new point of view for SOA formation experimental studies and modelling. The exact mechanisms of the oligomer and/or polymer formation and their significance for the chemical formation and properties of the secondary organic aerosol remain to be determined.

1.6 Objective of this thesis

The main goal of this thesis is the analysis of the chemical composition of SOA from anthropogenic and biogenic precursors. Single component analysis has been done extensively and still cannot account for a large amount of the total aerosol mass. Current models do not support the formation of high molecular weight compounds, which were observed in smog chamber experiments and ambient aerosol measurements. For more accurate models more information is needed about the chemical reactions that might take place in the aerosol and to what extent oxidation processes continue after formation.

Experiments done under controlled conditions are important for reproducibility and for interpretation. The new smog chamber at the Paul Scherrer Institut (PSI) provides the ideal set-up for this kind of experiments. The chamber was built during the time of this thesis and instruments had to be set up there before beginning experiments. All described experiments are conducted there.

This thesis focuses on the analysis of functional groups and development of the SOA on a time dependent scale. A problem with analysis of single oxidation products in SOA is the small amount available and also the high degree of oxidation and the high molecular weight. This makes it difficult for conventional methods, like GC-MS, even with derivatization methods. For functional groups the amount is not so crucial.
MALDI and IR techniques were used, MALDI for high molecular weight compounds and IR for the functional group analysis of the SOA.

Single compounds will still be analyzed, not in order to find more reaction products, but to see the timely behaviour of certain oxidation products. GC-MS is the technique for off-line analysis and will be used for derivatization experiments also for functional group analysis.

A biogenic precursor, APIN and an anthropogenic SOA precursor, 1,3,5-trimethylbenzene (TMB), were chosen as model compounds (Figure 1-6). Both are well known compounds in the ambient atmosphere and extensively studied, also with respect to single compound analysis.

![Molecular Structure of APIN and TMB](image)

**Figure 1-6: Molecular Structure of APIN and TMB**

### 1.7 Outline of the thesis

A brief introduction into the world of atmospheric chemistry with respect to aerosol formation is given in Chapter 1. The methods used in this thesis are explained in Chapter 2.

A system for particle sampling and separation from the gas phase is examined and characterized in Chapter 3. The idea was to account for the different compounds in the gas and particle phase. But the idea of single compound analysis was not pursued further and the sampling for the other projects was done without gas phase separation and with another method to account for gas phase adsorption on the filter, respectively.

The reaction chamber, or smog chamber, for production of the SOA was newly built at the PSI between summer 2001 and fall 2002. The full characterization and instrumentation available up to spring 2005 is described in Chapter 4.

The focus of this thesis is on the aerosol phase, but the characterization of the gas phase is an important field and will be discussed in Chapter 5 with examples of TMB experiments at the smog chamber.
Chapter 1

Introduction

The identification of the SOA with various methods is the topic of Chapters 6 to 10. Chapter 6 focuses on carboxylic acids and Chapter 7 on the overall polymer content. The finding of high molecular weight compounds (up to 1000Da) in the SOA is a hot topic now in the scientific community and only at the beginning of understanding and interpretation.

Chapter 8 describes the use of infrared spectroscopy to analyze qualitatively the functional group content of SOA on a time resolved basis. Chapter 9 and 10 finally deal with the derivatization methods used for GC-MS, but not for single compound analysis but for the overall content of oxidized compounds, that is carbonyl and hydroxyl functional groups.

Chapter 11 summarizes the results and gives an outlook into further possible research.

1.8 References


Chapter 2

Instrumental
2.1 Gas chromatography – mass spectrometry

2.1.1 Gas chromatography

Gas chromatography (GC) is a widely used technique for the analysis of sufficiently volatile compounds in complex mixtures. Since the 1950s GC became a standard separation method. The separation results from the interaction of the gaseous analyte mixture with the stationary phase in the column. The differential partitioning into the stationary phase allows the compounds to be separated in time. The mobile phase is a gas (e.g. helium) and transports the analyte from the injector to the detector. In principle, analysis with GC is possible for all compounds that have sufficient vapor pressure in the temperature range of the GC system. But even compounds that do not fulfill this condition can be analyzed with GC, e.g. by derivatizing the molecule to change the vapor pressure. Figure 2-1 shows the necessary components of a GC system:

![Diagram of GC system]

The carrier gas (usually helium, hydrogen or nitrogen) serves as mobile phase and moves the gaseous samples through the column. The carrier gas flow can be quantified by the volumetric flow rate, expressed in ml/min, or by the linear velocity, expressed in cm/s. The volumetric flow rate is dependent on the column diameter, the linear velocity is not.
The injector is a heated glass cylinder which serves as the interface between the column and the GC user. The syringe with the analyte solution punctures the gas tight septum of the injection liner and introduces the sample onto the column. The temperature of the injector is controlled so that all components in the sample will be vaporized. Different injection techniques are established, which will be briefly mentioned. “Splitless injection” means that the total of the injected sample volume will be transferred onto the column whereas with “split injection” the carrier gas flow is split and only a small amount of the analyte is flushed onto the column. “On-column-injection” works without heated injector; the sample is introduced directly into the column with a thin steel- or quartz capillary. Finally, for solid samples the “pyrolysis-GC” method has been proven useful; the sample is heated in the injector until decomposition and the low molecular compounds are flushed on the column.

The GC column is the heart of the system. Column properties influencing the separation of a mixture are composition and thickness of the stationary phase, the diameter and the length of the column. The standard columns are fused-silica capillary columns coated with a stationary phase, a typical example being polysiloxanes or polyethylene glycol with 0.1-2.5µm film thickness. The typical length of a capillary column is between 15 and 60m, typical inner diameters are between 0.25 and 0.32mm. The column is placed in an oven, where the temperature can be controlled and ramped very accurately.

2.1.2 Mass Spectrometry

There are various types of detectors for GC separation, but the focus here is on the mass selective detector. Since the early 1960s, gas chromatography coupled with mass spectrometry (GC-MS) instruments equipped with quadrupoles or ion traps have been commercially available and have become standard analytical tools. The advantages of MS are the high sensitivity and the ability to function as an universal or (mass)selective detector (MSD). Many GC-MS instruments use electron impact (EI) as the ionization method, although soft ionization by chemical ionization (CI) is sometimes preferred. EI conditions lead to strong fragmentation of the analytes. This is desired for pure compounds, because fragments give structural information and are useful for identification of unknown compounds.
In this work, EI was employed as ionization method. The EI method uses a tungsten or rhenium filament, which is heated to emit electrons with a kinetic energy of 70-100eV. The electrons are accelerated, the neutral molecules (M) that enter the MSD from the chromatography column are impacted with electrons to generate radical cations (M⁺) in the so-called ion source:

\[
M(\text{g}) + e^- \rightarrow M^+(\text{g}) + 2e^-
\]

Equation 2-1

The electron beam has enough energy to fragment the molecule. Fragmentation depends on molecular structure, electron energy and temperature of the ion source. Characteristic fragments provide important structural information about the parent ions and may help to identify the compound.

The positive fragments are accelerated in vacuum through an electric field and are focused into the mass separating system. In this work, quadrupole MS was employed as detection method. Quadrupole filters consist of four concentric rods that have fixed DC and alternating RF potentials applied to them (Figure 2-2).

![Figure 2-2: Schematic drawing of a quadrupole mass analyzer.](image)

Ions produced in the source are focussed and move along the middle of the quadrupoles. The motion of the ions depends on the electric fields. Only ions of a particular mass-to-charge (m/z) ratio will be in resonance and pass through to the
detector. The RF is varied with time allowing ions with different \( m/z \) to reach the detector thus building up a mass spectrum.

As mentioned above not all compounds are suitable for GC, e.g. compounds which are not volatile enough or too polar. In complex environmental samples there are many compounds with carbonyl and/or carboxylic acid and/or hydroxyl groups. The resolution on the GC column is difficult and identification of unknowns impossible. Chemical derivatization of functional groups prior to analysis can change the volatility and polarity. Most of the samples measured with GC-MS in this work were derivatized to enable detection on the column. Another advantage of this method is the identification of functional groups in the mass spectrum: e.g. a derivatization agent for carbonyl groups used in this study yields a characteristic ion of the product with \( m/z \) 181. This has proven useful in complex samples, e.g. environmental samples, because every peak in the chromatogram with the 181 ion in the MS could be identified as carbonyl compound.

In this thesis a GC-MS system was used for identification and quantification of reference samples (Chapter 3), for identification of unknowns (Chapter 6) and for quantification of derivatization agents to measure overall functional group concentrations (Chapter 9 and 10). The instrument used (HP model 5890 Series II with a 5971A MS detector) is a very old one, but GC-MS is a well established method with the column as most important part of the system and the instrumental part is of robust nature that does not need much maintenance.

### 2.2 Infrared Spectroscopy

Molecule vibrations and rotations are excited by absorption of radiation in the infrared (IR) region (12500-10\,cm\(^{-1}\) or 0.8-1000\,µm). Wavenumbers \( \bar{v} \) and wavelength \( \lambda \) and speed of light are connected as follows:

\[
\bar{v} = \frac{1}{\lambda} \quad \text{and} \quad \lambda = \frac{c}{\bar{v}}
\]

Equation 2-2
IR spectroscopy in the mid IR range is of the greatest practical use for organic compounds, therefore referring to IR spectroscopy usually means working in the range between 400-4000cm\(^{-1}\).

In IR-spectroscopy organic molecules are exposed to IR radiation. When the radiant energy matches the energy of a molecular vibration, absorption occurs. The wavenumbers at which absorption occurs give valuable information on functional groups in the molecule.

The theory behind this will be briefly discussed:

### 2.2.1 Molecular vibrations

There are two types of molecular vibrations: stretching and bending. A molecule with \(n\) atoms has a total of \(3n\) degrees of freedom. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational, in a linear molecule, 2 degrees are rotational and 3 are translational. The remaining degrees correspond to fundamental vibrations. The degrees of freedom (net number of fundamental vibrations) for linear molecules, e.g. CO\(_2\), are therefore \(3n-5\), and for a nonlinear molecule, e.g. H\(_2\)O, they are \(3n-6\). Figure 2-3 shows the fundamental vibrations for water.

![Symmetrical stretching, asymmetrical stretching, scissoring (bending)](image)

Figure 2-3: Stretching and bending vibrational modes for H\(_2\)O.

Carbon dioxide has four fundamental vibrations, in addition to the ones shown for water, it has two bending vibrations (out of plane). The asymmetrical stretch of CO\(_2\) is present in many IR spectra as a strong band at 2350cm\(^{-1}\), since CO\(_2\) is present in the air, and many spectra recorded under atmospheric conditions contain therefore the CO\(_2\) band interfering with the spectra of the respective compound. Luckily, at 2350cm\(^{-1}\), no other functional group shows absorption. The two bending modes of CO\(_2\) are equivalent and therefore have the same frequency and one band at 666cm\(^{-1}\). The symmetrical stretch of CO\(_2\) is inactive in the IR, because this vibration produces
Chapter 2
Instrumental

no change in the dipole moment. IR radiation is only absorbed when there is interaction between the dipole moment and the electrical vector of light, i.e. a vibration must cause a change in the dipole moment of the molecule.

2.2.2 Stretching vibrations

For diatomic molecules, a good model often used is the model of two masses (atoms) joined by a spring (bond), described by Hooke’s law, where the frequency of the vibration \( \nu \) of the spring is related to the mass \( m \) and the force constant of the spring, \( k \). (see Equation 2-3)

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}
\]

Equation 2-3

The energy curve of the vibrations is described by the model of a harmonic oscillator. The energy of the harmonic oscillator, \( E=0.5*kx^2=\hbar \nu \) (\( x=\)displacement of the spring) depends on \( x \), therefore the molecule could absorb energy of any wavelength. But vibrational motion follows the rules of quantum mechanics and only transitions that follow Equation 2-4 are allowed; the levels are quantized. Only transitions to the next level are allowed, but transitions to higher levels occasionally occur.

\[
E = (n + 1/2) \hbar \nu
\]

\( n = \) quantum number (0,1,2,3..)
\( \nu = \) frequency of vibration

Equation 2-4

But molecules are not masses connected by a spring, and bonds between atoms can break, therefore the vibrations are better described by an anharmonic oscillator. The energy curve of the anharmonic oscillator is asymmetric and the vibrational levels are not equidistant anymore (Figure 2-4).
Figure 2-4: Energy curve for an anharmonic oscillator, showing vibrational levels for a vibrating bond (adapted from University of Colorado (2005)).

With increasing interatomic distance the energy reaches a maximum. The distance between the energy levels decreases with increasing interatomic distance; the allowed transitions become smaller in energy.

Equation 2-5, derived from Hooke’s law, shows the relationship between bond strength, atomic mass and wavenumber at which a molecule will absorb IR radiation.

\[
\nu = \frac{1}{2\pi c} \sqrt{\frac{f (m_1 + m_2)}{m_1 m_2}}
\]

\(\nu\) is the vibrational frequency
m1, m2 are the mass of atom 1 and 2, respectively
c is the speed of light
f is the force constant of the bond

Equation 2-5

When the force constant f (=k for the force constant in a spring) increases, i.e. a stronger bond between the atoms, the wavenumber also increases; when the mass of the atom increases, the wavenumber decreases. This is a useful approximation for interpreting spectra.
2.2.2 Fourier Transform Infrared Spectroscopy

The classical IR spectroscopy used before the Fourier method was developed works with continuous radiation from the light source. The beam is split in two beams of the same intensity, one goes through the sample, one is the reference beam, e.g. going through the pure solvent. The radiation measured at the detector is equilibrated and the monochromator (prism or grating) divides the resulting radiation. The optical signals are detected, converted into electrical signals and plotted by the recorder. The IR diagram is usually plotted as transmittance versus wavenumbers.

The Fourier Transform (FT) IR spectrometer obtains IR spectra by collecting an interferogram of a sample signal with an interferometer that measures all IR frequencies simultaneously. An interferometer uses a beamsplitter to split the incoming IR beam into two optical beams. One beam reflects off of a flat immobile mirror. Another beam reflects off of a flat mirror which travels some distance (i.e. a few millimeters) away from the beamsplitter (mobile mirror). The two beams reflect off of their respective mirrors and are recombined when they meet together at the beamsplitter. The recombined signal results in an interference of the 2 beams. The resulting signal is called interferogram. When the interferogram signal is transmitted through or reflected off of the sample surface, the specific frequencies of energy are absorbed by the sample due to the excited vibration of functional groups in molecules. The infrared signal after interaction with the sample is uniquely characteristic of the sample. The beam finally arrives at the detector and its intensity is measured by the detector. The detected interferogram cannot be directly interpreted. The interferogram undergoes Fourier transformation, meaning it is resolved into the frequencies of the individual vibrations. A background spectrum must always be run when analyzing samples by FTIR. A simple scheme of a FT-IR interferometer is shown in Figure 2-5.
The light source is usually a hot wire, emitting polychromatic light. Advantages of FT-IR over dispersive IR are high sensitivity, fast acquisition and accuracy in wavenumbers.

2.2.3 Measuring IR spectra

IR spectra can be taken from gaseous, liquid or solid samples or dissolved in a suitable solvent. Liquid samples are simply pressed between two plates that are IR transmittend, e.g. sodium chloride (NaCl) or zinc selenide (ZnSe) plates, and brought into the light beam. Solutions are pipetted into a sodium chloride cell and then exposed to the beam. Solid samples can be either suspended in Nujol (paraffin oil) or pressed with potassium bromide (KBr) to a thin pellet. Gaseous samples are measured in a cell, capped on both ends with NaCl plates.

By using FT-IR a reference sample is not necessary, because there is only one beam. A background spectrum must always be run when analyzing samples with FT-IR.

IR spectroscopy is a useful tool in analyzing functional groups. The vibrations of the molecule are localized to the functional group and do not affect the rest of the molecule.

IR-spectra are divided into two regions:
above 1500cm\(^{-1}\): Absorption bands here can be assigned to the individual functional groups of the molecule; 
below 1500cm\(^{-1}\): This region is called fingerprint-region, because it characterizes the molecule as a whole.

Usually with a first glimpse at the spectrum it is possible to say what kind of functional group is absorbing. By taking a closer look at the exact wavenumber and intensity more details are revealed, e.g. is the aromatic ring substituted once or several times, is it a carboxylic acid, ester, amide, etc. But of course with complex mixtures the details become less clear and the fingerprint-region of the spectra is not useful anymore. Functional groups above 1500cm\(^{-1}\) become then the important feature of the spectrum of e.g. an aerosol sample. In this thesis the main focus of the IR spectra are prominent functional groups, such as carbonyl, carboxylic acid or hydroxyl groups. Also the organonitrate group is a functional group that shows dominant peaks even in complex mixtures. To reveal more details about compounds present in the mix than these functional groups stretches the ability of interpreting IR spectra. But as will be shown in Chapter 7, time dependent changes in samples can be followed and qualitatively interpreted with IR spectroscopy.

### 2.3 (Matrix-assisted) Laser Desorption Ionization (MALDI)

#### 2.3.1 Principle of MALDI-MS

General introduction

One way to ionize the sample for mass spectrometry is via EI as described in 2.1.2. This method leads to strong fragmentation of the molecule and often the parent ion cannot be identified. For complex mixtures a method is desirable that allows desorption and ionization without fragmentation (“soft”). Two soft ionization methods are used nowadays: electrospray ionization (ESI) and Matrix-Assisted Laser Desorption Ionization (MALDI).

In MALDI-MS, the analytes are incorporated into a matrix which assists their desorption and ionization during irradiation with laser pulses. The most preferred
laser is the nitrogen laser at 337nm for UV-MALDI. Two slightly different MALDI methods were invented simultaneously by Karas and Hillenkamp (1988) and Tanaka et al. (1988). Karas and Hillenkamp used small organic molecules to assist desorption and ionization, Tanaka et al. used fine metal powders and glycerol.

![Figure 2-6: Principle of the MALDI process](image_url)

Figure 2-6 shows the MALDI process: The non-volatile molecules (analyte) are co-crystallized with an excess of matrix that can absorb laser photons. The absorption of laser energy by the matrix molecules leads to a fast evaporation process, followed by liberation of the intact analyte molecule into the gas phase (Karas et al., 1987). A small fraction of the desorbed molecules is ionized during the process. Ionization can be protonation/deprotonation of the analyte molecules by the matrix or metal ion or organic matrix ion adduct formation. The major amount of analyte molecules is not ionized, therefore neutral and not accelerated towards the detector.

**Ion formation**

The ionization process can be divided into two steps: primary and secondary ionization (Zenobi and Knochenmuss, 1998). The laser generates charged species in the primary ionization process. This can occur via multiphoton ionization, energy
pooling, disproportionation reactions, excited state proton transfer, thermal ionization, desorption of preformed ions, and the break up of the sample into charged chunks and clusters. Thermal ionization may have particular significance in particle-assisted MALDI (see 2.3.2). Examples are given for (m=matrix molecule):

Multiphoton ionization: \[ m \rightarrow m^{n \ h \ \nu} + n \ e^{-} \]

Thermal ionization: \[ m + m \rightarrow m^{*} + m^{*} \]

After laser desorption, the MALDI plume is formed by an almost explosive solid-to-gas-phase transition (Zhang, 2003). There is a relatively high residual collision rate and the density of the neutral molecules has been measured to be about $10^{-4}$ atmospheres (Puretzky and Geohegan, 1998). These are good conditions for ion-molecule reactions. In these secondary ionization processes, the initial charged species can be neutralized or neutrals can be converted to ions which are then finally detected. In this process, proton transfer, charge transfer and cation attachment or transfer are involved (m=matrix, A=analyte, Cat=cation):

Proton transfer: \[ [m + H]^{+} + A \rightarrow m + [A + H]^{+} \]

Charge transfer (electron): \[ m^{+*} + A \rightarrow m + A^{+*} \]

Cation transfer: \[ [m + Cat]^{+} + A \rightarrow m + [A + Cat]^{+} \]

The complex processes in the plume, primary and secondary reactions between matrix and analytes are still not completely understood, although much progress has been made in the recent years (Karas and Kruger, 2003; Knochenmuss, 2003; Knochenmuss and Zenobi, 2003; Zenobi and Knochenmuss, 1998).

Matrices

The matrix has the following functions: it absorbs the laser energy, it transfers the analyte molecule into the gas phase by its own evaporation without decomposition and it assists the ionization of the analyte molecule. Therefore the choice of matrix is crucial. An overview of the matrices found to be useful for different compound
classes is given in Zenobi and Knochenmuss (1998). Examples of matrices are 2,5-dihydroxybenzoic acid, p-nitroaniline or sinapinic acid. Furthermore, an important issue is the sample preparation. The sample should be evenly distributed and cocrystallized with the matrix. Inhomogenities in the mixture, a problem that occurs when using solid matrices, can lead to the so-called “hot spot” phenomenon: the signal intensity fluctuates depending on the spot irradiated with the laser (good signal=hot spot). Therefore, MALDI is not suited for quantitative studies.

If the sample itself contains molecules that are similar to matrix molecules, e.g. molecules that contain a conjugated π-system, the addition of matrix is not necessarily required. In experiments with TMB and its oxidation products good signal intensities were observed without any added matrix.

### 2.3.2 Particle-assisted LDI-MS

A variation of MALDI is the use of small particles (with diameter in the low nanometer to micrometer range) instead of an organic matrix. The particles serve as the matrix, basically, but there are two phases on the sample plate. The small particles absorb the laser energy and heat the sample. The heating is very fast due to the large surface of the particles and desorption is achieved without excessive heating of the sample. Sometimes liquid matrices are added to improve the reproducability of the spectra because inhomogeneities due to crystallization are avoided.

Materials for the particles range from cobalt (Tanaka et al., 1988), silicon (Dale, R. et al., 1997), titanium nitride (Schurenberg et al., 1999) to graphite (Dale, M. J. et al., 1996). In the aerosol analyzing studies described here, graphite was used as assisting particle, therefore the method is referred to as GALDI-MS (Dale, M. J. et al., 1996). Figure 2-7 shows the set-up for the analysis performed with aerosol samples described in Chapter 7.
Figure 2-7: Principle of GALDI-MS: The (aerosol) sample is deposited with graphite powder (1-2µm diameter) on a sample (impactor) plate. Sodium and potassium salts are abundant in the atmosphere and are always found in MALDI samples. The laser irradiates the sample and desorbs the analyte. The adducts formed with sodium or potassium are accelerated into the mass analyzer, e.g. time-of-flight-MS (reproduced with permission from Dietemann (2003)).

2.3.3 Time-of-flight mass spectrometry

The mass analyzer commonly used in combination with MALDI is the time-of-flight mass spectrometer (TOF-MS).

After desorption of the ions, they are extracted out of the ion source and accelerated by the acceleration voltage U. They fly through a field free drift tube from the ion source to the detector. The flight distance d can be 1m, for instance.

The kinetic energy, $E_{kin}$, depends only on the acceleration voltage U, therefore it is the same for all ions with mass m and with the same charge $e \cdot z = q$ ($e =$ elementary charge, $z =$ number of charges, $q =$total charge): $v$ is the velocity of the ion.

$$E_{kin} = \frac{mv^2}{2} = e \cdot z \cdot U$$

Equation 2-6
The time $t$ for flying the distance $d$ is $t = \frac{d}{v}$. The separation in the drift tube is based on the mass-to-charge-ratio ($m/z$) of the ions. By measuring the flight time $t$, $m/z$ can be determined

$$\frac{m}{z} = \frac{2 \times U \times e}{d^2} \times t^2$$

Equation 2-7

### 2.4 References


Chapter 3

Sampling Gaseous Oxidation Products of Aromatic Compounds in Gas/Particle Separation Systems

Adapted from Mirjam Sax, Markus Kalberer and Renato Zenobi
3.1 Abstract

In this study we performed a direct comparison between two different ambient air samplers to characterize their performance in sampling oxidized gaseous organic compounds, known as oxidation products of aromatics. We investigated compounds with a variety of functional groups and vapor pressures. A polyurethane foam (PUF) adsorbent and an annular diffusion denuder sampler were operated along with particle filters. In both systems the sampling devices were liquid-extracted, followed by derivatization and analysis by GC-MS. The PUF system works very well for aromatic as well as non-aromatic compounds, whereas the denuder shows smaller collection efficiencies for highly volatile non-aromatic compounds. In addition, the sampling efficiencies in the PUF set-up are in good agreement with the calculated vapor pressures of the compounds and also the particle phase is not affected by most compounds.


3.2 Introduction

Hydrocarbons, aromatic and non-aromatic, are abundant organic compounds in the polluted atmosphere, but they are also detected in almost every compartment of the environment. The atmosphere is a well known pathway for transport and also deposition of organic compounds (Bidleman, 1988). Several polycyclic aromatic hydrocarbons (PAHs), important constituents of the organic matter in the atmosphere, have been identified as carcinogens (Bostrom et al., 2002; Finlayson-Pitts and Pitts Jr., 2000) or mutagens (Finlayson-Pitts and Pitts Jr., 2000). The environmental fate of volatile organic compounds (VOC) is phase dependent because atmospheric reactions, transport and deposition processes differ for gas and particle phase species (Bidleman, 1988). Information about phase distribution is required, for example, for strategies to control volatile organic pollutants. Low volatility compounds produced by oxidation reactions of aromatics in the atmosphere - mostly emitted by anthropogenic activities - are among the most important contributors to secondary organic aerosol (SOA) mass (Odum et al., 1997). Many of these reaction products are distributed between the gas and the particle phase. Particles in the atmosphere have important effects on human health (Pope et al., 1995), regional air quality (Tanner and Parkhurst, 2000) and climate forcing (Griffin et al., 1999; Hansen and Sato, 2001; Heintzenberg, 1999).

Separation and sampling of gas and particulate organic compounds in the atmosphere require an efficient separation of the two phases. Most phase distribution measurements have been made by determining the concentrations of particulate phase organics on filters and the analysis of gas phase species trapped by adsorbents. Gundel et al., (1995) used an annular denuder coated with the adsorbent resin XAD-4, which adsorbs organic gas phase species from the air stream before collecting the particles on a filter. Some publications (Cui et al., 1998; Eatough, 1999) also used several diffusion denuders to provide the determination of gas and particulate phase VOCs. Another standard method for monitoring VOCs uses samplers equipped with polyurethane foam (PUF) adsorbents. In these types of samplers, air is drawn through a filter to retain the particle phase and then through the PUF to adsorb the gas phase compounds. They have been employed extensively to study VOCs in the atmosphere (Baker and Eisenreich, 1990; Hawthorne et al., 1989; Pankow, 1989; Simcik et al.,
The advantages of PUFs over denuders are easy handling, storage, and transportation, as well as the low cost of the material. PUFs are in general Soxhlet extracted overnight (Maddalena et al., 1998). Maddalena et al. (1998) described also another method where the PUF is compressed to minimize the ratio of mobile phase to specific surface area. The adsorbed compounds are eluted with a solvent to remove the analyte.

All of the currently available separation systems suffer from artifacts by under- or overestimating the gas/particle partitioning. A main sampling artifact is that the gaseous compounds adsorb to particle filters and therefore lead to an overestimation of the particle phase. Mader and Pankow (2001; 2002) as well as Kirchstetter et al. (2001) described positive gas adsorption artifacts when using Teflon membrane filters and quartz fiber filters.

We directly compare two common sampling set-ups used for semi-volatile oxidized compounds. The sampling setup with the best collection efficiencies will be later used to characterize smog chamber experiments. In our lab studies are currently underway to determine the SOA and gas phase compounds generated via photooxidation pathways from aromatic compounds. The sampling efficiency is a crucial parameter for determining the compounds in both phases. In this study we performed experiments with a filter/PUF setup and a denuder/filter setup for collecting aromatic and non-aromatic gas phase compounds known to be reaction products of aromatic oxidation. The collection efficiency and the handling of both systems are compared in detail. We show that collecting gas phase compounds works well, without measurable adsorption onto the filters for most of these compounds.

### 3.3 Experimental

#### 3.3.1 Materials and Chemicals

The PUFs, the annular denuders as well as the round glass containers for the PUF sampling line were purchased from University Research Glassware (URG, Chapel Hill, NC, USA). The Teflon™ coated quartz fiber filters (TQFF), PALLFLEX Membrane Filters, were from PALL Gelman (Ann Arbor, MI, USA). Chemicals used as standard compounds were either from Sigma-Aldrich or Fluka, solvents (HPLC-
grade) as well as tetradecane used as internal standard were from Fluka. All experiments were carried out at room temperature.

### 3.3.2 Instrumentation

Samples were analyzed using a HP model 5890 Series II Gas Chromatograph interfaced to a HP Model 5971A quadrupole mass selective detector (MSD). The GC was equipped with a split/splitless injector. The injector was run in the splitless mode and the pressure was set to 54 kPa. The GC was equipped with an Optima δ-6 capillary column (30 m x 0.25 mm, 0.25 μm film thickness) from Machery-Nagel (Oensingen, Switzerland). The mobile phase was He with a flow velocity of 34.4 cm/s. The temperature program of the column was isothermal at 50° for 0.1 min, 12°/min ramp to 190°, 5°/min to 250°, 15°/min to 300° and isothermal at 300° for 1 min. The injector and detector temperatures were 250° and 300°, respectively, and the injection volume was 1 μl. The MSD was run in selective ion monitoring (SIM) mode (Table 3-1) for quantifying analytes, and total ion current for qualitative identification.
### Chapter 3

Gas/Particle Separation System

#### Table 3-1: Identification Parameters for Analysis by GC-MS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Molecular weight of derivative&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mass for SIM [m/z]</th>
<th>Ion for SIM</th>
<th>Retention Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>glyoxal</td>
<td>58.04</td>
<td>448.22</td>
<td>448.22</td>
<td>M</td>
<td>18.94</td>
</tr>
<tr>
<td>methylglyoxal</td>
<td>72.06</td>
<td>462.24</td>
<td>265.16</td>
<td>M-197</td>
<td>19.25</td>
</tr>
<tr>
<td>glyoxylic acid</td>
<td>74.04</td>
<td>383.38</td>
<td>326.27</td>
<td>M-57</td>
<td>14.09</td>
</tr>
<tr>
<td>pyruvic acid</td>
<td>88.06</td>
<td>397.65</td>
<td>340.54</td>
<td>M-57</td>
<td>15.10</td>
</tr>
<tr>
<td>2,5-dimethylbenzaldehyde</td>
<td>134.18</td>
<td>329.27</td>
<td>329.27</td>
<td>M</td>
<td>18.27</td>
</tr>
<tr>
<td>2,6-dimethylbenzoquinone</td>
<td>136.15</td>
<td>331.24</td>
<td>331.24</td>
<td>M</td>
<td>18.72</td>
</tr>
<tr>
<td>6-nitro-m-cresol</td>
<td>153.14</td>
<td>267.39</td>
<td>210.28</td>
<td>M-57</td>
<td>16.10</td>
</tr>
<tr>
<td>3,5-dimethylbenzoic acid</td>
<td>150.17</td>
<td>264.42</td>
<td>207.31</td>
<td>M-57</td>
<td>14.70</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molecular weight for derivative is for full derivatization of all functional groups in the molecule. Of the two carbonyl groups in 2,6-dimethylbenzoquinone only one is derivatized with PFBHA.

### 3.3.3 Procedures

Filters, denuders and PUFs were cleaned before use as follows: The TQFFs (15 mm diameter) were sonicated in toluene for 15 min, air dried in the hood and stored in a glass vial with a Teflon<sup>TM</sup> cap until use. Each PUF (7.5 cm x 2.5 cm) was rinsed twice with deionized water, then sonicated for 15 min with methanol (2x) followed by dichloromethane (2x), then allowed to air dry in a fume hood, and stored in a glass beaker covered with aluminum foil in the dark until use. The denuders are 40 cm long and consist of 5 annular channels with 2 mm spacing. They were cleaned with organic solvents and the sandblasted walls were coated with ground Amberlite XAD-4 (40 µm grain size) using the procedure described by Gundel et al. (1995). XAD-4 was chosen because it is widely used, because of its good adsorption characteristics for volatile organic compounds, and because of its high surface area (725 m<sup>2</sup>/g) (Gundel et al., 1995).

The compounds used (Figure 3-1) are known oxidation products of aromatic hydrocarbons, e.g. of 1,3,5-trimethylbenzene (Cocker et al., 2001; Holes et al., 1997;
Yu et al., 1997) m-xylene (Cocker et al., 2001; Yu et al., 1997) or toluene (Yu et al., 1997).

They cover a range of volatility from highly volatile to less volatile over several orders of magnitude. The vapor pressure is a critical parameter governing the partitioning of VOCs between the two phases (Pankow, 1994a; Pankow, 1994b). Vapor pressure estimates are therefore a useful proxy for gas/particle partitioning. We estimated the vapor pressures at 298 K (Figure 3-1) according to Myrdal and Yalkowsky (1997). The compounds cover the range from 1.6*10^-8 atm for 3,5-dimethylbenzoic acid to 0.39 atm for glyoxal. Compounds with a vapor pressure below 10^-4 atm are considered semi-volatile (Mader and Pankow, 2000). Boiling points – if required – were calculated according to Walters et al. (1995) from the available melting points. For pyruvic acid the estimated vapor pressure compares well
with literature values (Lemmon et al., March 2003) (NIST: \(1.7\times10^{-3}\) atm, estimation: \(1.2\times10^{-3}\) atm for pyruvic acid). The vapor pressure of glyoxalic acid was not calculated, because neither the boiling point nor the melting point was available in the literature. It is likely to be slightly higher than the vapor pressure of pyruvic acid. Both aromatic and non-aromatic compounds are represented in the selection, which includes aldehydes, ketones, carboxylic acids and nitro-compounds, covering a variety of functional groups. Prior to the experiment, test runs were performed for all compounds with the GC-MS to standardize the analysis and to validate the mass selection in the SIM mode.

### 3.3.4 Sampling Experiments

A first set of experiments was performed with only gas phase compounds present in the sampling system. For the experiments with the two sampling setups (Figure 3-2)a \(= 0.1\ m^3\) bag made of FEP-Teflon™ was used, a so-called pillow bag.

![Figure 3-2: Sample setup for experiments with two polyurethane foams (top) and three denuders (bottom). a: mass flow controller, b: 3-way-valve, TQFF: Teflon™ coated quartz fiber filter.](image)

The bag was cleaned by filling it with N\(_2\) and evacuating it with a pump for at least two times before use. A mixture of eight compounds (see Figure 3-1) in acetonitrile was injected into the pillow bag injection port and flushed into the bag with N\(_2\). The concentration for all compounds was the same \((100\ \mu g/m^3)\), except for 2,5-dimethylbenzaldehyde, which was added at half the concentration, because of its high ionisation efficiency in the MS. The gas volume of the filled pillow bag was drawn through one of the sampling systems with a flow rate of 6.5 l/min, controlled by a mass flow controller. The PUF arrangement consisted of a TQFF followed by two
PUFs. The second PUF collects “blow-off” of gas phase products from the first PUF, which might be expected for highly volatile compounds. The denuder system consisted of two 5-channel annular denuders followed by a TQFF and a third backup denuder. A laminar flow of $\text{N}_2$ through the denuders efficiently prevented deposition of particles on the denuder walls. The residence time in the denuder is approximately 0.7 s, i.e. fairly long, to assure enough time for interaction between the gas phase compounds and the XAD-4 cover of the denuder. The first two denuders adsorb gas phase compounds and the third denuder collects compounds released from the filter. Although no particles were present in these experiments, filters were present in both systems and also analysed in order to detect possible adsorption artifacts of gaseous compounds, which would adsorb to the filter surface.

Filters from both systems were extracted by sonication in 1 ml acetonitrile for 15 min. For extracting the PUF, it was loaded into a glass column (3.3 cm x 12.5 cm) with the sample face down to minimize the distance the analyte has to travel through the matrix. The PUFs were compressed to 10-15% of their original volume and extracted with 50 ml acetonitrile (Maddalena et al., 1998). The extraction efficiency of the PUFs was found to be $\geq 85\%$. It was tested by extracting the PUF spiked with the mixture and extracting it a second time. Denuders were extracted by manual shaking 5 times in a 30 ml mixture of 47% dichloromethane, 40% acetonitrile and 13% hexane; this procedure is similar to that described by Gundel et al. (1995).

Derivatization reactions for carbonyl, carboxyl and hydroxyl groups were performed with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) and N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA), respectively. A tenfold excess of both derivatization reagents was added. These reagents convert polar into less polar compounds suitable for GC, i.e., carbonyl groups react with PFBHA to form oxime derivatives (Yu et al., 1998) and carboxyl and hydroxyl groups react with MTBSTFA to form N-tert-butyldimethylsilyl derivatives. MTBSTFA silylates the compounds in an analogous way to N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) as described by Yu et al. (1998). MTBSTFA was used because it is less sensitive to hydrolysis. Tetradecane was used as internal standard and added to the PUF and the denuder immediately after sampling and to the filter together with the acetonitrile before sonication.

The extracts were allowed to react with PFBHA overnight (16-20 h) at room temperature. The next day the volume of the solutions was minimized by using a
rotary evaporator and then almost blown to dryness in an N<sub>2</sub>-stream. MTBSTFA was added and after ca. 1 h of reaction time at room temperature the solutions were ready for the GC-MS measurement. For integration of the peaks in SIM mode the most significant fragment ions were used as listed in Table 3-1. Derivatization with PFBHA for carbonyls leads to a fragment of the PFBHA derivatisation agent [CH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>] at m/z = 181, which makes it easy to identify. For compounds with carbonyl groups the fragment M-197, which results from loss of [OCH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>], was also used for identification. Molecules derivatized with MTBSTFA generally produce fragments at M-57 due to the loss of [C(CH<sub>3</sub>)]<sub>3</sub>. 2,5-Dimethylbenzoquinone was derivatized with PFBHA only once, although it carries two carbonyl functionalities.
3.4 Results and Discussion

Figure 3-3 shows the distribution of the gaseous compounds in percent between TQFF and two PUFs (A) and three denuders (B), respectively.

Figure 3-3: Distribution in percent of 8 compounds (see Figure 3-1) after sampling and analysis with GC-MS. The solid bars denote the mean values, the error bars the standard deviation. 3A: results from the PUF-line, 3B: results from the denuder-line. Sorted from left to right with decreasing vapor pressures.
Five experiments for each sample line were performed and the averages with the standard deviations are shown. 6-nitro-m-cresol was only measurable in 3 experiments. For the quantitative analysis the ratio of the peak areas of the compounds and the internal standard was calculated. The total amount recovered in the system was set to 100% for each compound. We did not measure the absolute recoveries for the compounds sampled on a PUF or denuder, because the main focus of this study is on the distribution of the compounds chosen between the sampling devices, not possible losses (e.g., to the wall) due to the use of the pillow bag. All compounds are gaseous and are expected to adsorb mostly on the first PUF or denuder, unless undesired adsorption to the filter material occurs. In the filter/PUF experiment PUF 1 clearly adsorbs most of the gaseous phase of all compounds. 89-100% of pyruvic acid and all four aromatic compounds are found on PUF 1, whereas on PUF 2 only negligible amounts were measurable (Figure 3-3A). The most volatile compounds (e.g. glyoxal, methylglyoxal and glyoxylic acid) are also found on PUF 2, assuming that glyoxylic acid has a vapor pressure value between methylglyoxal and pyruvic acid as estimated from the structure. For all components only small amounts (0-2.2%) were found on the filter, except for glyoxal and 3,5-dimethylbenzoic acid (9.5% and 10.5%, respectively), showing that adsorption for most of these compounds to the filter material is negligible. The filters were cleaned prior to use, i.e. there was no organic phase into which these compounds might have partitioned, which could result in a positive sampling artifact. Therefore adsorption to the TQFF surface seems to be the most likely reason. The volatility of glyoxal and 3,5-dimethylbenzoic acid is very different (estimated 0.39 atm and 1.6*10^{-8} atm, respectively), which excludes the possibility of adsorption to the filter due to similar vapor pressures. At standard conditions glyoxal exists as a mixture of different oligomers (Whipple, 1970) thus lowering significantly the vapor pressure as calculated for the monomer, which could explain the adsorption on the filter. The low volatility of 3,5-dimethylbenzoic acid is likely the reason for its adsorption on the filter. The total amount found on the filters was very low for all compounds, producing only small peaks in the chromatograms, which in turn resulted in a lower signal-to-noise ratio than for the PUF samples. In addition, in the PUF samples the response for compounds 1, 2 and 3 was small (up to 200x smaller) compared to all others. This is the reason for the higher standard deviations for 1, 2 and 3.
Figure 3-3B shows the distribution between three denuders and a TQFF. It is expected that most of the compounds are adsorbed by D1 and significantly less on D2; TQFF and D3 are expected to be empty, if no sampling artifacts occur. Basically, the same observation as for the PUF system also applies here. Note the appearance of 1, 2 and 3 on all the three denuders as well as 1 and 2 on the filter. The collection efficiency of the denuders is noticeably better for aromatic (91%) than for non-aromatic compounds (43%) used in this study. This is possibly due to the lower vapor pressures of the aromatic compounds used here. In addition, the coating for the denuders (XAD-4) is an apolar, hydrophobic polystyrene granulate, improving the affinity of the aromatics to the coating. In contrast, the non-aromatic compounds (1-4) are retained much less by the denuders and therefore also found on D2 and D3 in significant amounts.

D3, used as a back-up denuder, is not expected to show any signal, but due to high volatility of some compounds, breakthrough after D1, D2 and TQFF may occur. This was indeed found for glyoxal (12.3%), methylglyoxal (20.9%) and glyoxylic acid (6.0%), the three most volatile compounds. All four aromatic compounds showed no signal on D3 as expected.

Comparing Figure 3-3A and B, both systems are able to collect the aromatic compounds and pyruvic acid with high efficiencies. However, the non-aromatic, more volatile compounds, glyoxal, methylglyoxal and glyoxylic acid are clearly retained better by the PUF system. Whereas for the PUF system a clear difference from PUF 1 to PUF 2 is observed, this is not true for D1 and D2 for these three compounds. Therefore the PUF system can be recommended as the preferred system to collect gas phase oxidation products of aromatic compounds.

In an additional set of experiments it was investigated whether particle filters loaded with organics would cause a change of the separation efficiency of the PUF/filter system for gaseous compounds. The particle filters were coated with ≈ 1 mg of either sebacic acid (C\textsubscript{10}H\textsubscript{18}O\textsubscript{4}), a long-chain dicarboxylic acid, or benzo(e)pyrene (C\textsubscript{20}H\textsubscript{12}), respectively, as surrogates of polar and apolar aerosol components. None of the 8 compounds could be detected on the coated filters. Therefore we can conclude that there is no sampling artifact, i.e., even high filter loadings will not affect the gas/particle separation of aromatic oxidation products due to additional gas adsorption to the collected organic aerosol when using a filter/PUF system.
3.5 Conclusions

Two air-sampling systems (denuder-filter and PUF-filter) were compared for collection efficiency of oxidized compounds. We could show that the PUF system is preferable to the denuder set-up for compounds with vapor pressures over the range of \(1.6 \times 10^{-8}\) atm to 0.39 atm. For the semi-volatile compounds both systems were comparable, but the most volatile compounds were better retained on the PUFs than on the denuders. An advantage is also the easy handling and the lower cost of polyurethane foams. In addition, the adsorption to the TQFF placed before the PUFs is negligible for most of the investigated compounds.

3.6 Acknowledgements

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3.7 References


Eatough, D. J., 1999: BOSS, the Brigham Young University Organic Sampling System: Determination of Particulate Carbonaceous Material Using Diffusion


Chapter 4

A new reaction chamber
Chapter 4
Secondary organic aerosol formation by irradiation of 1,3,5 trimethylbenzene-NO$_x$-H$_2$O in a new reaction chamber for atmospheric chemistry and physics

adapted from
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Chapter 4  A new reaction chamber

4.1 Abstract

A new environmental reaction (smog) chamber was built to simulate particle formation and growth similar of that expected in the atmosphere. The organic material is formed from nucleation of photooxidized organic compounds. The chamber is a 27m$^3$ fluorinated ethylene propylene (FEP) bag suspended in a temperature controlled enclosure. Four xenon arc lamps (16 kW total) are used to irradiate primary gas components for experiments lasting up to 24 hours. Experiments using irradiations of 1,3,5-trimethylbenzene-NO$_x$-H$_2$O at similar input concentrations without seed particles were used to determine particle number and volume concentration wall loss rates of 0.209 ± 0.018 hr$^{-1}$ and 0.139 ± 0.070 hr$^{-1}$, respectively. The particle formation was compared with and without propene.
4.2 Introduction

Environmental reaction chambers around the globe have proven to be indispensable tools in the study of atmospheric chemistry and physics (Akimoto et al., 1979a; Karl et al., 2004; Kleindienst et al., 1999; Odum et al., 1996; Takekawa et al., 2003). The reaction chambers are often used in the investigation of secondary organic aerosol (SOA). SOA forms from oxidation reactions of primary anthropogenic and biogenic gaseous precursors (for example, automobiles and vegetation, respectively). The chemical pathways involved in SOA formation include a large number of compounds, most of which are highly oxidized at low concentrations. Environmental reaction chambers provide controlled and repeatable conditions to study and characterize these complex systems and also to test novel analytical instrumentation.

A new environmental reaction (smog) chamber was built to study the gas and particle phase products which lead to secondary organic aerosol (SOA) formation in the atmosphere. Photochemical gas phase reactions are initiated with a xenon arc light source similar to the atmospheric light spectrum. These reactions lead to condensable species, which can condense homogeneously and heterogeneously to form particles, and then partition between the gas and particle phases. A small chamber surface area to volume ratio (2 m$^{-1}$) was chosen to reduce the effects of wall losses. A suite of online instrumentation for the analysis of the gas phase as well the chemical and physical characterization of the aerosol phase was used to capture the highly dynamic changes of the oxidation processes. In addition, samples were taken for detailed offline analysis of the gas as well as the aerosol phases.

4.3 Systems and Procedures

The reaction chamber is suspended in a temperature controlled wooden enclosure having dimension 4×5×4 m (L×W×H). The walls and ceiling of the enclosure are covered with reflective aluminum foil to maximize the light intensity and increase light diffusion. The aluminum foil has greater than 80% reflection for spectra greater than 300 nm. The housing floor is covered with less reflective but more durable aluminum sheets. A plan view of the chamber and enclosure is shown in Figure 4-1.
The chamber temperature is controlled by two cooling units (total capacity 19.5 kW), allowing for temperature stabilization of ±1°C within the range of 15 to 30°C. The cooling units are placed on opposite sides of the chamber. The cool air supply is distributed along the bottom perimeter of the chamber housing through 50 cm diameter ducting. Air is returned to the cooling units through air ducts in the enclosure ceiling. One thermocouple is placed between the enclosure and chamber walls. Three more thermocouples measure the gas temperature inside the chamber at approximately 0.5, 1.0, and 1.5 m from the chamber wall (Figure 4-1).

Figure 4-2 shows light transmission of DuPont™ Tedlar® polyvinyl fluoride (PVF, TST20SG4 and TUT10BG3) and fluorinated ethylene propylene (FEP) transparent films measured with a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrophotometer. The FEP film shows >90% light transmission in the relevant region of 290-800 nm which compares well with total solar transmission value of 96% reported by the manufacturer (method ASTM E-424) (DuPont™, 1996). The PVF film TST20SG4 shows favorable transmission cutoff at the lower wavelengths, however the ultraviolet (UV) absorbing additives in the Tedlar® films are not permanent (DuPont™, 1995). Similar to the FEP films, additional light filtering of the lower wavelengths (<290 nm) would still be necessary. In addition, a study raised objections to the use of PVF material for chamber studies. It was concluded that the release of organic compounds from PVF film created a total hydrocarbon (HC) interference (van Ham, 1978).
on the characteristic depletion of the UV blocking properties of Tedlar® over time, difficulties in manufacturing a PVF film chamber of the requested dimensions, and objection to its use, the FEP film was chosen.

The chamber is a $27\text{m}^3$ ($3\times3\times3$ m) flexible bag made of 125 µm (5 mil) DuPont™ Teflon® fluorocarbon film (FEP, type 500A, Foiltec GmbH, Germany). Collapsible environmental chambers made of FEP films are found to have the most favorable radical source magnitude and are generally accepted materials in environmental chamber design (Carter, 2002). Conditioning of the films is necessary to remove contaminants from the manufacturing process and to reduce surface destruction of reactive species (Finlayson-Pitts and Pitts Jr., 2000). Conditioning includes long term (days) flushing with pure air (see description of pure air below) and long term (days) irradiation with chamber light sources. Other advantages of such films include low rates of HC off-gassing and high transmission of light in the region of 290-800 nm (Finlayson-Pitts and Pitts Jr., 2000).

The disadvantage of using fluorocarbon film in collapsible chamber design is the buildup of electrostatic charge on the film surface. The local electric field created at the surface strongly influences wall deposition rates for particles smaller than 0.5 µm.
A new reaction chamber

(McMurry, 1985). For example, McMurry and Rader (1985) demonstrated that the wall loss rates for a singly charged 0.1 µm particle were 100 times greater than for a neutral particle of the same size. Usually sample volumes were restricted to <10 m³ to avoid underpressure in the bag. Occasionally experiments required longer sample times and larger sample volumes, possibly resulting in higher wall-loss rates as chamber surfaces tended towards the center during experiments.

The chamber is suspended in the enclosure from above using a rectangular frame of cylindrical aluminum tubes. Another rectangular aluminum frame suspends the chamber approximately 0.5 m above the enclosure floor. Two manifolds (inlet and outlet) made of stainless steel and Teflon® allow for easy installation of additional inputs and sampling lines. Particle samples are taken from the center of the chamber using stainless steel lines. Exceptions to sampling at the chamber center include Teflon® gas sampling lines which are not rigid enough to reach the center of the chamber.

Four xenon arc lamps (4 kW rated power, 1.55*10⁵ lumens each, XBO® 4000 W/HS, OSRAM) are used to simulate the solar light spectrum and to mimic natural photochemistry. One lamp is placed at each corner of the housing (Figure 4-1). Calculations or numerical models were not used to optimize lamp placement. The chamber is illuminated using indirect light, where the lamps are oriented towards the reflective aluminum walls. Indirect light was chosen over direct light (lamps focused directly towards the chamber) to increase light homogeneity, thus decreasing possible “hot spots” of photochemical activity. The lamps are directed alongside the bag walls. A series of coatings were tested to optimize the reflected radiation from the original parabolic lamp reflectors. Cone-shaped reflectors were constructed and coated with the reflective aluminum (same as walls) and provided the highest reflectance of all reflector/coating combinations.

Sunlight at the earth’s surface includes UV in the wavelength range of 290 to 400 nm. The amount of UV light reaching the earth’s surface is dependent upon the distance the light must travel through the earth’s atmosphere; hence the amount of UV light arriving at any point on the earth’s surface fluctuates. The light spectrum was designed to mimic ground level sunlight with clear sky conditions. Xenon arc lamps with spectral filters were chosen over sources such as blacklights or UV-A lights because they produce the most atmospherically representative spectrum from 300 nm
to 800 nm (Carter et al., 1995). Blacklights and UV-A lights are a suitable short wavelength source however they do not emit in the longer wavelength regions (> 400nm) which are responsible for photolysis of organics such as methylglyoxal (Cocker et al., 2001a).

The unfiltered spectral distribution of the light source alone provides too much actinic UV below the wavelength of 300 nm. Therefore spectral filtering is needed, and is accomplished by using filters made of 3 mm thick (50 cm wide by 50 cm high) borosilicate glass plates (Finlayson-Pitts and Pitts Jr., 2000; Winer et al., 1979). Two different types of borosilicate glass, “borofloat 33” and “selected white floatglass” (BF33, SWF, Praezisions Glas & Optik GmbH, Germany), were tested. Figure 4-3A shows the percent transmission and spectral distributions of the filter samples. The unfiltered and filtered light spectra were measured with a fiber optic spectrometer (USB2000 UV-VIS, Ocean Optics, Inc., USA) combined with a cosine-corrected irradiance probe (CC-3-UV) to make spectroradiometric measurements. The measurements were made directly in front of a lamp and outside of the bag at a distance of 3 meters from the spectral filter. Figure 4-3B compares the unfiltered and filtered spectra. The SWF glass was chosen over BF33, having 50% transmission at 310 nm and 297 nm, respectively.

Figure 4-3B also shows the spectrum using the SWF filter after more than 500 hours of irradiation. There is no apparent shift of the filtering characteristics for the irradiated filter. Figure 4-3C compares the SWF spectra inside and outside of chamber bag. The chamber bag contributes slightly to the filtering of light below 300 nm.

The photolysis rate of nitrogen dioxide (NO₂) is determined from the photostationary state relation

$$O_3 = \frac{J_{NO_2}[NO_2]}{k[NO]}$$

Equation 4-1

where $k$ is the rate constant of nitric oxide (NO) and ozone (O₃) reaction (Seinfeld and Pandis, 1998). A mixture of NO₂ (~200 ppb) and AADCO pure air (no water) was irradiated. The resulting steady-state mixing ratios of NO, NO₂ and O₃ are measured. The measurements are then corrected for dark O₃ plus NO reaction in the sampling line. After applying this method, an NO₂ photolysis rate of $J_{NO_2} = 0.12 \text{min}^{-1}$ was obtained.
Purified air is supplied by an AADCO (737-250 series, AADCO Instruments, Inc., USA) pure air generation system. This unit has been used in other reaction chambers and laboratories (Carter, 2002; McMurry and Stolzenburg, 1989). The purification reactors (AADCO type-A and methane reactors) deliver pure air with ambient concentrations of carbon dioxide (CO$_2$) and oxygen (O$_2$). The manufacturer’s purity specifications include <1 ppb ozone, methane and non-methane HCs, oxides of nitrogen (NO/NO$_x$), hydrogen sulfide (H$_2$S), sulfur dioxide (SO$_2$), carbonyl sulfide (COS), carbon monoxide (CO), sulfur hexafluoride (SF$_6$), and fluorocarbons.

The primary component injection system is shown in Figure 4-4. Gaseous components (NO, NO$_2$, and C$_3$H$_6$) are supplied to the smog chamber through a mass-flow controlled system (model 5850S, control unit Model 0154, Brooks Instruments) and Teflon® lines. One mass flow controller (MFC, 0-10 l min$^{-1}$) is used to input NO, NO$_2$, and propene (C$_3$H$_6$) from gas bottles. The gases are selected at a bank of four on/off valves with one valve supplying pure air to insure that each gas is flushed through the system. An ozone generator is provided by irradiation of pure air in quartz tubes with UV lamps. The generator can operate with 1 to 3 lamps and various flow
rates, providing ozone of ppb to ppm concentrations in the chamber. A second MFC (0-10 \text{ l min}^{-1}) is used to control the ozone input.

Liquid parent HC (for example, 1,3,5-trimethylbenzene or TMB) is evaporated in a 500 ml glass sampling bulb. The sampling bulb is wrapped in a silicon heater (80°C) and flushed with 10-15 \text{ l min}^{-1} of AADCO pure air. In addition, transport lines to the chamber downstream of the glass bulb are wrapped in silicon heaters (80°C) to prevent high boiling point compounds from condensing on transport line walls. Hexafluorobenzene (C$_6$F$_6$), which is used as a tracer compound for GC-FID measurements and leak detection of the bag, is also flushed in using this system. Depending upon the rate of sample volume removed from the chamber, no significant reduction of C$_6$F$_6$ is observed with the PTR-MS during the first 8 to 12 h of an experiment.

Figure 4-4: Primary component injection system.
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The humidification system uses commercial clothes steamer (J-4000 series, Jiffy® Steamer Company, LLC, USA). The steamer has a stainless steel boiler tank, site glass, and a 1500 watt corrosion resistant inconel (heat resisting alloy) heating element. Water is purified using a Milli-Q® Academic ultrapure water system (18.2 MΩ•cm @ 25°C; 5-10 ppb total organic carbon, Millipore, USA). The steamer converts water to steam at a rate approximately 32 ml min⁻¹. The steam exits and mixes with pure air before entering a 1.5 m long, 35.5 mm i.d. (38 mm o.d.) stainless steel tube. The tube is situated at an angle of 45° to allow condensed water to drain back into the steamer. Since visible water droplets are not yet in the vapor phase, it is important to either evaporate these droplets or condense them out before entering the chamber. This design facilitates droplet removal by giving droplets sufficient time to evaporate, settle out, or condense onto the cooler tube walls.

A particle generation system is available for seed particle experiments. Particles are generated using a TSI 3076 type nebulizer. A schematic diagram of the particle generation system is shown in Figure 4-5. ADDCO pure air enters the nebulizer at a gauge pressure of approximately 275 kPa and expands to nearly atmospheric pressure inside of the nebulizer. A check valve immediately downstream of the nebulizer is used as a safety precaution to prevent the nebulizer from being pressurized. The particle laden air leaves the nebulizer at nearly 100% relative humidity (RH) and enters the ejector pump (model TD260HSS, Air-Vac Engineering Co., USA). Directly upstream of the ejector is a valve used to control dilution. The ejector pump is supplied with AADCO pure air at the high pressure inlet (35 to 172 kPa). The ejector pump serves three purposes in the system: (1) to provide mixing and dilution, (2) to increase total aerosol flow and (3) to enhance initial evaporation of water molecules from the droplets. A bypass flow is placed directly downstream of the check valve to ensure nearly atmospheric pressure inside of the nebulizer. A second bypass is placed directly downstream of the ejector pump to bleed excess flow before the diffusion drier. HEPA cartridge filters are placed at the bypasses for clean-air venting into the laboratory. A silica gel diffusion dryer is placed after the ejector pump. This allows water molecules to further diffuse out of the air stream and adsorb onto the silica gel surface. Sufficient drying is achieved in the ejector pump (<10% RH), however, the diffusion driers are used for smaller aerosol flows when very dry particles are essential. The particles pass through a Krypton-85 (Kr-85) neutralizer to bring them to
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a bipolar charge equilibrium using a cloud of bipolar ions. Finally, the seed particles are transported to the reaction chamber input manifold.

An in-line blower (model 30480, 75mm, Jabsco GmbH, Germany) at the exit of the chamber (Figure 4-1) increases the exchange rate of the chamber volume by allowing for higher pure air flush flows (maximum 250 l min\(^{-1}\)). The bag is kept “plump” but not tight or stressed. This allows a slight over-pressure in the bag to reduce backflow of external contaminants. Flushing starts at the end of experiments to minimize transport of products to the walls. Additionally, high concentrations of ozone (>2 ppm) are flushed into the chamber to facilitate cleaning of the bag walls. The high ozone concentration is maintained for at least 12 h. This cleaning procedure has been used by other facilities to “deactivate” and condition the chamber walls (Akimoto et al., 1979b; Grosjean, 1985; Kelly, 1982). The cleaning usually occurs without irradiation. Typically, the chamber is flushed for at least 24 hours between experiments giving final background particle concentrations of less than 0.1 cm\(^{-3}\) and 20 cm\(^{-3}\) before and after humidification, respectively.

As mentioned previously, smog chamber facilities using collapsible chambers have found that the chambers must be initially “conditioned”. This was also the case for this chamber. During the conditioning phase the chamber was “baked” using the xenon arc lamps. The chamber was flushed continuously for one week with pure air and high levels of ozone (>2 ppm) to react away HCs. In addition, leaks were found in the chamber at stress points due to the bag’s own weight. Suspect stress points were reinforced with fluoropolymer (ETFE) tape obtained from the bag manufacturer (Hostafion® ET 6235, Foiltec GmbH, Germany).

Figure 4-5: Seed particle generation system.

As mentioned previously, smog chamber facilities using collapsible chambers have found that the chambers must be initially “conditioned”. This was also the case for this chamber. During the conditioning phase the chamber was “baked” using the xenon arc lamps. The chamber was flushed continuously for one week with pure air and high levels of ozone (>2 ppm) to react away HCs. In addition, leaks were found in the chamber at stress points due to the bag’s own weight. Suspect stress points were reinforced with fluoropolymer (ETFE) tape obtained from the bag manufacturer (Hostafion® ET 6235, Foiltec GmbH, Germany).
4.4 Instrumentation

Various instruments are used to monitor the gas and particle phases during an experiment. Table 4-1 gives an overview of the available instrumentation and some of the instrument specific parameters. Full-time instrumentation includes instruments such as particle counters and standard gas analyzers.

Table 4-1: Overview of available instrumentation.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Monitored parameter</th>
<th>Lower limit/range</th>
<th>Time resolution</th>
<th>Accuracy</th>
<th>Flow rate (1 min⁻¹)</th>
<th>Full-time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean Optics USB2000</td>
<td>light spectrum</td>
<td>250–800 nm</td>
<td>User selectable</td>
<td>NA</td>
<td>NA</td>
<td>no</td>
</tr>
<tr>
<td>UV/VIS spectrometer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotronic Hygro Clip SC05</td>
<td>% relative humidity (RH), temperature</td>
<td>0–100%</td>
<td>&lt;10 sec</td>
<td>±1.5%</td>
<td>NA</td>
<td>yes</td>
</tr>
<tr>
<td>humidity sensor</td>
<td>-40–</td>
<td>RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+100°C</td>
<td>±0.3°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermocouple type K</td>
<td>chamber temperatures</td>
<td>0–1200°C</td>
<td>1 sec</td>
<td>± 1°C</td>
<td>NA</td>
<td>yes</td>
</tr>
<tr>
<td>Vaisala PTA 427 pressure transmitter</td>
<td>ambient pressure</td>
<td>80–106 kPa</td>
<td>2 sec</td>
<td>± 0.03 kPa</td>
<td>NA</td>
<td>yes</td>
</tr>
<tr>
<td>Aero Laser 5002 carbon monoxide monitor</td>
<td>CO</td>
<td>1–10⁶ ppb</td>
<td>10 sec</td>
<td>± 2%² ± 10%³</td>
<td>0.1</td>
<td>yes</td>
</tr>
</tbody>
</table>

1 NA = not applicable
2 precision of standard measurements
3 accuracy considering the uncertainty of the standard
<table>
<thead>
<tr>
<th>Instrument</th>
<th>Species</th>
<th>Concentration Range</th>
<th>Time</th>
<th>Precision</th>
<th>Resolution</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environics S300 ozone analyzer</td>
<td>O$_3$</td>
<td>0–1000 ppb</td>
<td>1 min</td>
<td>3%</td>
<td>1.1</td>
<td>yes</td>
</tr>
<tr>
<td>Monitor Labs 9841A NO$_x$ analyzer</td>
<td>NO and NO$_x$ – NO</td>
<td>0–2000 ppb</td>
<td>1 min</td>
<td>± 10%$^3$</td>
<td>0.6</td>
<td>yes</td>
</tr>
<tr>
<td>Monitor Labs 8810 ozone analyzer</td>
<td>O$_3$</td>
<td>0–10$^5$ ppb</td>
<td>1 min</td>
<td>5%</td>
<td>0.6</td>
<td>yes</td>
</tr>
<tr>
<td>Proton Transfer MS (PTR-MS)</td>
<td>VOCs</td>
<td>0.1–5000 ppb</td>
<td>1–5 min</td>
<td>± (5–30%)</td>
<td>0.5</td>
<td>no</td>
</tr>
<tr>
<td>Thermo Environmental Instruments 42C trace level NO$_x$ analyzer</td>
<td>NO and NO$_x$-NO</td>
<td>0–200 ppb</td>
<td>1 min</td>
<td>± 10%$^3$</td>
<td>1.3</td>
<td>yes</td>
</tr>
<tr>
<td>Varian 3400 GC-FID parent HC (ROG)</td>
<td>parent HC</td>
<td>10 ppb</td>
<td>15 min</td>
<td>± 5%</td>
<td>0.1</td>
<td>yes</td>
</tr>
<tr>
<td>Varian 3400 GC-MS organic compounds</td>
<td>Sub ppb</td>
<td>Samples taken every 1–8 h; then offline analysis</td>
<td>5–40%$^4$</td>
<td>25–30</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Varian 3400 GC-MS Impactor for LDI-MS and FTIR</td>
<td>organic compounds</td>
<td>NA</td>
<td>1–5 h</td>
<td>NA</td>
<td>8</td>
<td>no</td>
</tr>
</tbody>
</table>

$^4$ based on sampling, sample work-up, and measurement
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<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measurement</th>
<th>Range</th>
<th>Time</th>
<th>Error</th>
<th>Degree</th>
<th>Measurement Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMPS (TSI 3071 and 3010 CPC)</td>
<td>number weighted particle size</td>
<td>0.01 cm$^3$</td>
<td>2 min</td>
<td>± 10%</td>
<td>1.0</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>distribution</td>
<td>7–316 nm</td>
<td></td>
<td>± 3 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSI 3022 Condensation Particle Counter (CPC)</td>
<td>total particle number concentration</td>
<td>7–&gt;1000 nm</td>
<td>1 sec</td>
<td>± 10%</td>
<td>1.5</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>0.01–10^5 cm$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Effluent Denuder/Aerosol Collector (WEDD/AC)</td>
<td>organic acids when coupled with ion chromatography-MS (IC-MS)</td>
<td>100 ppt–5 ppb</td>
<td>30 min</td>
<td>10–60%</td>
<td>1.5</td>
<td>no</td>
</tr>
<tr>
<td>TSI 3025 CPC</td>
<td>total particle number concentration</td>
<td>3–&gt;1000 nm</td>
<td>1 sec</td>
<td>± 10%</td>
<td>1.5</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>0.01–10^7 cm$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VTDMA</td>
<td>particle volatility</td>
<td>15–300 nm</td>
<td>2 min</td>
<td>± 2%$^6$</td>
<td>1.0</td>
<td>no</td>
</tr>
</tbody>
</table>

A gas chromatograph-flame ionization detector (GC-FID) is used to quantitatively monitor the decay of the reactant parent HC. The GC-FID is calibrated before each experiment. Calibration solutions containing varying amounts of parent HC and a constant amount of the internal standard ($C_6F_6$) are flushed into a 30 l FEP bag. An aliquot of 2ml of the FEP bag volume is introduced into the GC using a gas valve. Quantitative calibration curves are obtained by normalizing the parent HC signal to the internal standard, which are then used to quantify the amount of parent HC present in the smog chamber. The GC-FID (Varian 3400) is equipped with an Optima-5 column (Macherey-Nagel, Switzerland) and is run with 2ml min$^{-1}$ of helium as mobile phase. The temperature of the GC-FID is first held for 2 min at 40°C, and then increased at a rate of 25°C min$^{-1}$ to 200°C.

$^5$ for total number concentrations having Dp>50nm  
$^6$ measured accuracy of absolute particle size change
Ozone is measured by UV-absorption (Environics S300), CO with UV-vacuum fluorescence (AeroLaser AL 5002), and NO and NO₂ via gas-phase chemiluminescence detection (Monitor Labs 9841A). Prior to detection, NO₂ is converted to NO using a molybdenum converter. As this conversion is not only sensitive to NO₂, but also to other reactive nitrogen species such as peroxyacetyl nitrates (PAN), the measurements of substantially aged air masses (as it is the case in the reaction chamber experiments after several hours) can be ill-defined and are only of minor information. A photolytic converter (Droplet Measurement Technologies, USA) which usually shows negligible interferences of other nitrogen species is now implemented in a chemiluminescence trace level NO-NO₂-NOₓ analyzer (42C, Thermo Environmental Instruments Inc, USA). Prior to the gas component input, the NOₓ analyzer is calibrated with gas bottle standards (1 to 10 ppm, Carbagas, Switzerland). The CO instrument is automatically calibrated every two hours using a gas bottle standard (2 ppm, Carbagas). The O₃ analyzer is cross-calibrated every year with a NIST-traceable ozone calibrator.

A proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria) is used to monitor the parent HC and its oxygenated oxidation products. The measurement method is based on proton transfer reactions that cause a soft ionization with only little fragmentation and a subsequent detection of the product ions in a quadrupole mass spectrometer (for details see Lindinger et al. (1998)). The reaction rate coefficients for exothermic proton transfer reactions are close to the collisional values predicted by the Langevin theory for non-polar reactants (Lindinger, 1986) and the capture rate theory (Chesnavich et al., 1980; Su and Chesnavich, 1982) in case of polar species. The dipole moment and the polarizability of the compounds are needed for the capture rate theories, therefore, the concentrations of VOCs with these known input parameters can be theoretically derived from the measurements without calibration. However, measurements are limited by the ± 20% uncertainty of these calculated reaction rate constants (Hansel et al., 1999).

An 8-component standard including TMB, propene, toluene, and few oxygenated VOCs (Apel & Riemer Environmental Inc., USA) is used to determine the sensitivity of the instrument. Since gas standards for some compounds are not available, mixing ratios of the oxidation products must be calculated using computed reaction rate constants and the calibrated mass dependent sensitivity.
Two condensation particle counters (CPC, models 3022 and 3025, TSI Inc., USA) are used to monitor total particle concentrations (see Table 4-1). Number weighted particle size distributions are obtained with a Scanning Mobility Particle Sizer (SMPS) (Wang and Flagan, 1990). Care is taken to obtain the most accurate particle size distributions with the available instrumentation. The SMPS system in Figure 4-6 consists of a long column differential mobility analyzer (model 3071, TSI Inc., USA) operating at aerosol and sheath flow rates of 1 and 10 l min\(^{-1}\), respectively. These flow settings allow for a sampling range from 7 to 316 nm. The system uses a temperature adjusted TSI 3010 CPC and the data inversion method of Wang and Flagan (1990). It has been observed that differences in the dew point of the chamber contents and SMPS sheath air have contributed to growth or evaporation of sampled particles, thus altering the size distribution (Izumi et al., 1988). Therefore, the SMPS system is placed inside the chamber enclosure to reduce temperature related sampling effects (Figure 4-1).

The closed-loop sheath air flow system consists of a sealed regenerative DC blower which produces pulsation-free air flow. Since the blower does work on the air, a finned-tube heat exchanger is needed to remove the excess heat. Two thermocouples, one located at the aerosol sample inlet and a second at the sheath air exit, are used to monitor the system temperatures (not shown). A laminar flow element (LFE) produces a pressure drop which is linearly proportional to the volumetric flow rate. A
pressure transducer is then used to generate a proportional signal which is fed back to a proportional-integral-differential (PID) controller. The LFE is calibrated before each experiment with a primary flow standard (Gilibrator-2, Sensidyne, Inc., USA). Finally, a high efficiency pure air (HEPA) capsule filter placed in-line cleans the return air. This system produces stable sheath air flows and maintains the gas temperature and gas composition of that in the reaction chamber.

The detection efficiency of the CPC 3010 can be improved by increasing the temperature difference (ΔT) between the saturator and condenser. A larger ΔT allows activation of smaller particles by increasing the supersaturation of the air stream in the condenser. Although there is a possibility that such an increase in ΔT may result in homogeneous nucleation of the working fluid (butanol) vapor, no problems were encountered during operation. The CPC ΔT is programmatically changed (code available from TSI) from the default upper limit of 17 to 25°C. This change lowers the 50% detection limit from 10.5 to 5.7 nm. Figure 4-7 compares the old efficiency curve (ΔT = 17°C) and the new efficiency curve (ΔT = 25°C) obtained from the analytical formula of Mertes et al. (1995).

![CPC efficiency curves](image)

Figure 4-7: 3010 CPC efficiency curves for ΔT = 17°C (TSI data) and 25°C (calculated according to Mertes et al., (1995)) and transport line penetration efficiency used to correct for diffusion losses.

Particles undergoing Brownian diffusion will diffuse from higher to lower concentrations. Within transport lines, the inner wall will ideally have a zero particle concentration; therefore, the sampling line surface will act as a sink for particle
deposition. SMPS particle size distributions are corrected for diffusional losses in the transport lines. The transport efficiency of particles due to diffusion in a circular tube under laminar flow conditions (Reynolds number, $Re < 2300$), $\eta_{\text{diff, lam}}$ is predicted by the formulation of Gormley and Kennedy (1949) where

$$\eta_{\text{diff, lam}} = 1 - 2.56 \xi^{2/3} + 1.2 \xi + 0.178 \xi^{4/3} \quad \text{for } \xi < 0.02$$

Equation 4-2

or

$$\eta_{\text{diff, lam}} = 0.819 \exp(-3.65 \xi) + 0.0975 \exp(-22.3 \xi) + 0.0325 \exp(-57.0 \xi) + 0.0154 \exp(-108 \xi) \quad \text{for } \xi > 0.02$$

Equation 4-3

where

$$\xi = \frac{\pi DL}{Q}$$

Equation 4-4

is the dimensionless deposition parameter, $D$ is the particle diffusion coefficient, $L$ is the length of the transport line, and $Q$ is the flow rate. Note that the laminar flow transport efficiency is not dependent on the transport line diameter. Furthermore, to reduce transport line losses in laminar flow, one should reduce $L$ or increase $Q$. Figure 4-7 includes the efficiency curve used to correct chamber particle size distributions using $L = 2.62$ m and $Q = 1.01$ min$^{-1}$ ($Re \sim 280$).

Transport efficiency corrections are only made for particle transport lines. The SMPS inversion technique used here does not take into account transfer functions for diffusing particles (Stolzenburg, 1988). Transfer functions for diffusing particles must be included in the data inversion before transport efficiency corrections for the SMPS can be made. For example, Reineking and Porstendorfer (1986) made transport efficiency corrections by matching peak response to theory, which would overestimate losses for small particles if the data inversion technique used transfer functions for non-diffusing particles (Reineking and Porstendorfer, 1986; Stolzenburg, 1988).

A Volatility Tandem Differential Mobility Analyzer (VTDMA) (Liu et al., 1978; Orsini et al., 1999; Rader and McMurry, 1986) is employed to quantify the particle volume fraction remaining (Kalberer et al., 2004). This technique characterizes...
particles based on their electrical mobility and thermodynamic behavior. The VTDMA system shown in Figure 4-6 includes the first DMA (TSI 3071 type) as a classifier, an aerosol heater (conditioner), and the SMPS system described above. The classifying DMA operates at the same flow conditions and uses the same flow system design as the SMPS. The first of the two DMAs in series allows selection of a specific narrow size channel from the chamber particle size distribution. The size selected aerosol is subsequently heated in heaters having wall temperatures of 100, 150, and 200°C. The heaters are made from 30 cm of 0.5 cm i.d. coiled stainless steel tubing. Any size reduction of the particles due to evaporation is detected downstream using the SMPS, which measures the conditioned number weighted particle size distribution. Details of the VTDMA and its application will be included in a forthcoming paper.

Samples for detailed chemical analysis of the particle and gas phase oxidation products are collected with a filter/PUF (polyurethane foam) sampling system and analyzed using gas chromatography-mass spectrometry (GC-MS) as described elsewhere (Sax et al., 2003). Sampling times range from 1-8 h (see Table 4-1). Samples are analyzed for oxygenated compounds such as acids, alcohols and carbonyls using derivatization techniques (Sax et al., 2003).

In addition, particles are collected for analysis with laser desorption ionization mass-spectroscopy (LDI-MS) using a multistage impactor (Maenhaut et al., 1996). LDI-MS is used to measure the molecular size distribution of the particle constituents with an emphasis on the oligomeric fraction and its evolution with time. Samples are collected on steel plates and analyzed without further sample preparation using LDI-MS as described in Kalberer et al. (2004).

Similarly, particle samples for Fourier transform infrared spectroscopy (FTIR) analysis are impacted on ZnSe discs, which are transparent to infrared (IR) light. IR-spectra are obtained directly from the samples without further treatment, minimizing sample preparation artifacts. The FTIR-spectra are analyzed for functional groups, which were compared to spectra of synthetic standards and evaluated for their relative change with time (Kalberer et al., 2004).

Gaseous and particulate organic acids were determined on-line with a wet effluent diffusion denuder/aerosol collector (WEDD/AC). The WEDD/AC consists of a glass denuder gas phase sampling and aerosol mixing chamber for the aerosol. To sample water soluble gases, water is continuously pumped to the inner surface of the denuder.
in counter flow to the air sample. The aerosol is then sampled by supplying steam into a chamber, transforming virtually all aerosol particles into cloud droplets, which are then easily separated from the gas stream by impaction. The effluents of both the denuder and the aerosol collector are then concentrated on a concentrator column, followed by alternating analysis with ion chromatography. Time resolution for a single sample is 30 minutes. In some cases, the effluent behind the conductivity detector was sampled with a fraction collector for off-line analysis with ion chromatography – mass spectrometry. Further details are given in Fisseha et al. (2004).

The data acquisition is provided by a 16 bit, 200 kHz, PCI data acquisition board (DaqBoard/2000, Iotech, Inc., USA). One signal conditioning module provides 8 differential or 16 single-ended BNC connected analog inputs with programmable gains of x1, 10, 100, or 1000 (DBK1). A second signal conditioning module provides 14 thermocouple inputs including on-board-cold-junction and off-set-drift compensation (DBK52). Data is displayed and acquired using a program written with National Instruments’ Labview® software.

An experiment can begin when sufficient flushing has lowered gas and particle concentrations to the acceptable levels (a minimum of 10 chamber volumes). The air conditioners are turned on to cool the chamber to approximately 20°C. The chamber is then humidified to 50% nominal RH. Next, NO, NO₂, and propene are flushed in sequentially. A small amount (10-15 l min⁻¹) of AADCO pure air is flushed into the preheated glass bulb, which then passes into the chamber. The parent organic HC is then injected through a septum of the glass bulb using a microliter syringe. After the HC has completely vaporized, C₆F₆ is also injected into the bulb. Finally, the contents are left to mix for approximately 45 minutes before turning on the lamps.

### 4.5 Results

Seventeen experiments having similar initial input concentrations of 520 to 660 ppb of TMB (~2590-3280 µg m⁻³), ~150 ppb NO, ~150 ppb NO₂, ~300 ppb propene, and ~50% nominal RH (referred to as TMB-NOₓ from here on) were conducted. The average temperature for each run, based on 3 thermocouples placed at 50, 100, and 150 cm inside the chamber (see Figure 4-1), was 23.5 ± 1°C. During any one
experiment, an assortment of instruments was used to monitor the gas and particle phases. Although 17 experiments were conducted in total, difficulties sometimes arise during the experiments such that an instrument is taken off line. Therefore, depending upon the measured parameter, the number of available data sets for each experiment (and analysis) will vary. In addition, outliers of various data sets were determined and excluded according to Chauvenet's criterion.

4.5.1 Gas phase

After flushing, ozone mixing ratios were below the detection limit of the instruments (<1 ppb), as were NO/NO\(_x\) (<100 ppt) and CO (<6 ppb) mixing ratios. Background gas mixing ratios were checked with PTR-MS. The PTR-MS was zeroed with synthetic air (O\(_2\) 99.998%, N\(_2\) 99.999%). The AADCO pure air does not give an indication of impurities compared to this synthetic air. Figure 4-8A shows the difference of mass signals between AADCO pure air and synthetic air yielding an average over all masses of 3 ppt and a standard deviation of 60 ppt. The comparison of the dry chamber air with flushing AADCO zero air yields on average a slight positive offset of 30 ppt. Assuming that all signals above 180 ppt (3 times the standard deviation) are due to wall off-gassing there is approximately 4 ppb of VOCs available at the start of the experiment. The precursors TMB and pinene used in the chamber were at levels of 20 and 300 ppt, respectively. We assume that the background consists most probably of oxygenated species. Figure 8B is a PTR-MS mass trace taken after 2.5 hours of irradiation. During the course of the reaction a suite of different oxygenated compounds is formed up to a mass of 184 (m/z 186 is an internal standard).
Figure 4-8: (A) Mass signals from the PTR-MS showing the difference between AADCO pure air (+) and synthetic air (○). (B) PTR-MS mass trace taken after 2.5 hours of irradiation.

Figure 4-9 shows the average (± 1 standard deviation) measured gas mixing ratios of 10 different experiments with similar input concentrations. Initial NO mixing ratios of 150±12 ppb decrease rapidly to less than 5 ppb after 75 min (A). In the beginning, O₃ remains at a low level and starts to rise after about 40 min, reaching its maximum mixing ratio 150 min after lights-on (B). CO mixing ratios steadily increase throughout the experiments (C).
Figure 4-9: Average (± 1 standard deviation) gas mixing ratios (ppb) of 10 experiments during 6 hours of irradiation. Ozone (B) is shown with only one experiment for the first 60 min due to technical problems. TMB was calibrated with a gas standard (NPL). Methylglyoxal and dimethylbenzaldehyde rate constants of $2.05 \times 10^{-9}$ and $4.1 \times 10^{-9}$ cm$^3$mol$^{-1}$s$^{-1}$ were used to calculate mixing ratios.

Figure 4-9D-F show the time profiles of the masses m73, m121 and m135 measured with the PTR-MS. These masses are attributed to the parent HC TMB (m121) and the oxidation products methylglyoxal (m73) and dimethylbenzaldehyde (m135). The consumption of TMB shows a similar time profile for all experiments (Figure 4-9D). The ring opening route shown by others yields methylglyoxal as the dominant reaction pathway (Calvert et al., 2002). Additionally, the ring containing reaction of the OH radical with an alkyl group generating dimethylbenzaldehyde is only a few percent.

### 4.5.2 Particle phase

Time resolved number and volume weighted particle size distributions formed from one irradiation of TMB-NO$_x$-H$_2$O are shown in Figure 4-10A and B. After humidification, background particle concentrations are consistently less than 20 cm$^3$. 
(50% nominal RH). Figure 4-10A shows that particle formation is detectable by the SMPS after approximately 25 minutes of irradiation. A peak number concentration of $8.45 \times 10^4$ cm$^{-3}$ occurs after 53 minutes of irradiation and a peak mass concentration of 91.0 µg m$^{-3}$ (assumed density of unity) occurs after 4 h and 20 min of irradiation. The particle growth rates for this experiment were determined from the shift in the particle size distribution and range from $\sim$100 nm h$^{-1}$ within the first 30 minutes to $\sim$15 nm h$^{-1}$ towards the end of the experiment. See text below for a discussion of wall losses.

![Figure 4-10: Typical time resolved number (A) and volume (B) weighted size distributions from an irradiation of TMB-NOx. The wall loss accounted number (C) and volume (D) weighted distributions are also shown. Note: scales were changed to maintain contour color consistency.](image)

The repeatable generation of organic aerosol is important when comparing independent runs which use various analytical measurement techniques. The repeatability of 14 experiments was examined. Figure 4-11 shows the time resolved integrated number and volume concentrations and number weighted size distribution statistics for 14 independent experiments having the same input parameters. The particle growth was consistently described by a geometric standard deviation (GSD) of 1.23 after 3 hours of irradiation. Table 4-2 summarizes the average peak particle number, surface area, and volume concentrations of the experiments. The average peak mass concentration was 87.2 µg m$^{-3}$. Correspondingly, Table 4-3 summarizes the
average times at which the peak values were reached. The results shown from these 14 independent experiments demonstrate that the chamber performs consistently well.

Figure 4-11: Integrated number and volume concentrations and number weighted size distribution statistics for 14 independent experiments having the same input parameters (no account for wall losses). Error bars represent ± 1 standard deviation. Geometric number mean diameter = GMD and geometric standard deviation = GSD.
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Table 4-2: Peak integrated SMPS values obtained from 14 chamber runs having the same input parameters.

<table>
<thead>
<tr>
<th>Weighting</th>
<th>Average concentration</th>
<th>Standard deviation</th>
<th>Coefficient of variation</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number (cm(^{-3}))</td>
<td>6.65*10(^4)</td>
<td>1.12*10(^4)</td>
<td>17%</td>
<td>4.47*10(^4)</td>
<td>8.45*10(^4)</td>
</tr>
<tr>
<td>Surface (mm(^2) cm(^{-3}))</td>
<td>3.01*10(^3)</td>
<td>4.28*10(^2)</td>
<td>14%</td>
<td>2.36*10(^3)</td>
<td>3.90*10(^3)</td>
</tr>
<tr>
<td>Volume (mm(^3) cm(^{-3}))</td>
<td>87.2</td>
<td>13.2</td>
<td>15%</td>
<td>68.3</td>
<td>114</td>
</tr>
</tbody>
</table>

Table 4-3: Time to reach peak values of particle number, surface area, and volume concentrations.

<table>
<thead>
<tr>
<th>Weighting</th>
<th>Average time to max conc. (hours)</th>
<th>Standard deviation (hours)</th>
<th>Coefficient of variation</th>
<th>Minimum (hours)</th>
<th>Maximum (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>1.14</td>
<td>0.20</td>
<td>17%</td>
<td>0.83</td>
<td>1.52</td>
</tr>
<tr>
<td>Surface</td>
<td>3.81</td>
<td>0.25</td>
<td>7%</td>
<td>3.45</td>
<td>4.40</td>
</tr>
<tr>
<td>Volume</td>
<td>4.60</td>
<td>0.34</td>
<td>7%</td>
<td>3.93</td>
<td>5.08</td>
</tr>
</tbody>
</table>

Particles formed in the chamber are lost to the chamber walls primarily due to the mechanisms of diffusion and electrostatic deposition. As previously stated, a disadvantage to using collapsible Teflon\(^{®}\) chambers is the electrostatic buildup on the chamber surface which can significantly increase wall loss rates. The particle number weighted wall loss rate is described by

\[
\frac{dN(D_p,t)}{dt} = -\beta_N N(D_p,t)
\]

Equation 4-5

where \(\beta_N\) is the particle number concentration wall loss coefficient and \(N(D_p, t)\) represents particle number concentration at the core of the chamber as a function of particle diameter, \(D_p\), and time, \(t\) (Crump \textit{et al.}, 1983). The wall loss coefficients are determined by fitting the decrease of the integrated particle number concentrations over time to an exponential decay function. Equations for surface area and volume concentrations can be written analogous to Equation 4-5. Least-square fits are performed separately for loss coefficients of particle number, surface area (\(\beta_s\)), and volume (\(\beta_v\)) concentrations since different loss mechanisms
will dominate for various moments of the particle size distribution. Figure 4-10C and D show the time resolved size distributions after accounting for number and volume concentration wall losses ($\beta_n = 0.214 \text{ hr}^{-1}$ and $\beta_v = 0.125 \text{ hr}^{-1}$). Number concentration wall losses were accounted for 16 chamber runs having the same input parameters, where $\beta_n$ ranged from 0.182 to 0.240 hr$^{-1}$ with an average of 0.209 hr$^{-1}$ and coefficient of variation (CV) of 9%. Similarly, 14 chamber runs were accounted for volume concentration wall losses where $\beta_v$ was determined to range from 0.050 to 0.272 hr$^{-1}$ with an average of 0.139 hr$^{-1}$ and a CV of 50%. The large CV obtained from the volume concentration wall loss is due to the variation of the rate at which sample volumes were removed from the chamber. Higher sampling rates lead to a higher $\beta_v$ by allowing the chamber surfaces to tend toward the center earlier in an experiment.

Note that $\beta_n$, $\beta_s$, and $\beta_v$ are expected to be time dependent. This is because they are nonlinear functions of particle size. The particle size distribution is expected to change with time due to particle surface growth and reactions. In addition, the particle charge distribution may also change with time leading to changes in the coefficients. However, over the windows of time for which the number, surface area, and volume concentration decay is observed, the number, surface area, and volume geometric mean diameters vary from approximately 0.1 to 0.25 µm, which does not give rise to large fluctuations in $\beta$ as demonstrated in McMurry and Rader (1985).

Ideally one would calculate a loss coefficient for every measured size bin of the particle distribution as a function of time. Since the simpler approach used here produces physically reasonable results and results similar to published work (Cocker et al., 2001a; McMurry, 1985), such an extensive and exhaustive application of the theory was not carried out here.

One focus of reaction chamber studies is the aerosol yield. The aerosol yield is defined as

$$ Y = \frac{\Delta M_0}{\Delta ROG} $$

Equation 4-6

where $\Delta M_0$ (µg m$^{-3}$) is the organic aerosol mass concentration produced for a certain
amount of reacted organic gas, $\Delta$ROG ($\mu$g m$^{-3}$) (Seinfeld and Pandis, 1998). In this work the particle density is assumed to be unity. A challenge in comparing aerosol yield data is brought about by the various definitions used by authors to describe such yields (Izumi and Fukuyama, 1990). For example, Izumi and Fukuyama (1990) used a systematic approach of plotting the formed volume concentration (unaccounted for wall losses) against the consumed ROG concentration. A least-squares fit was then made to the linear portion to obtain a volume based aerosol yield per unit concentration of ROG, whereas Stern et al. (1987) calculated the yield based on the peak volume concentration (unaccounted for wall losses). Cocker et al. (2001b) report values for yield calculations were taken when a plateau of aerosol formation was maintained for 1 h and a decrease in the measurable parent HC was no longer detected Cocker et al. (2001b). An approach similar to Stern et al. (1987) is used in this work where the value and time of the peak volume concentration (unaccounted for wall losses) is used together with $\beta_V$ to determine the wall loss accounted and unaccounted aerosol yield.

Inside the chamber, the particle volume concentration rate of increase reaches zero at a point when the particle volume growth rate is equal to the particle volume wall loss rate. At this point, the average aerosol yield for 8 runs, unaccounted for losses, is then $4.7 \pm 0.7\%$ (consumed ROG concentration data were only available for 8 runs). The wall loss accounted aerosol yield is determined from the same time at which the volume concentration peak was reached for the unaccounted case. After accounting for losses, the average aerosol yield is then $7.7 \pm 2.1\%$. This value falls within the range of wall loss accounted yields reported by Cocker et al. (2001b) of 3.4-8.1% for experiments without seed particles having the same parent organic HC at similar input conditions. It is apparent that neglecting particle wall losses would substantially underestimate the aerosol yield. This may have accounted for part of the discrepancy between other reaction chambers when comparing aerosol yields using similar experimental conditions as mentioned in Odum et al. (1996).

Most experiments used propene, which is reported to be a photochemical initiator and to facilitate OH radical production (Cocker et al., 2001b; Griffin et al., 1999; Odum et al., 1996). However, two experiments performed without propene revealed a similar OH concentration profile (determined from the TMB consumption rate) and did not significantly change the particle formation. Figure 4-12 shows contour plots from two
TMB-NO$_x$-H$_2$O irradiations (640 ppb TMB, 150 ppb NO, 150 ppb NO$_2$, 50% RH) without propene addition. The contour is similar, although not identical, to the contour mentioned in Figure 4-10 A. Figure 4-12 also shows the integrated volume concentrations for the experiment along with the average from the 14 independent experiments using 300 ppb of propene. It is apparently not necessary to add propene to generate a sufficient amount (for subsequent analysis) of organic particulate mass at these primary component concentrations, which does not necessarily apply to experiments at lower primary input concentrations. Although it has been stated that the propene oxidation products (for example, formaldehyde and acetaldehyde) are not likely to partition into the particle phase (Kleindienst et al., 1999), questions stemming from the possible influence of the photooxidation products of propene are avoidable.

Figure 4-12: Number weighted size distributions of a an irradiation of TMB-NO$_x$-H$_2$O without propene addition (top) and integrated volume concentrations for the same run compared to the average from runs with propene addition (bottom).
In total, 20 organic acids were found in the WEDD/AC, 12 of which were identified. For example, the most abundant aerosol phase compounds identified were acetic acid, formic acid, lactic acid, and pyruvic acid. The sum of organic acids comprised 20 to 45% of the total aerosol mass. More information is given in Fisseha et al. (2004).

VTDMA measurements were made at the input conditions described above. At a wall temperature of 100°C, an increase of the volume fraction remaining from approximately 38% to 90% illustrated that approximately 50% of the initial particle mass participates in the oligomerization. Similar results were found for heater wall temperatures of 150 and 200°C. The observed decrease in volatility occurred over periods from 1 to 24 hours. In addition, experiments performed at atmospherically relevant concentrations showed a distinct difference compared to the oligomerization at higher concentrations. Namely, within the first nine hours a higher initial particle volume fraction remaining was found for the same irradiation time (Kalberer et al., 2004). Furthermore, chamber experiments using the biogenic precursor α-pinene (irradiations of α-pinene-NOₓ-H₂O-C₃H₆) showed a similar rate of decrease of the particle volatility with time inside the chamber (Paulsen et al., 2005).

Other reaction chamber groups have observed similar oligomer production with sulfuric acid catalyzed reactions on inorganic seed particles (Jang et al., 2002). Although the seed particle generation system is available for future experiments, additional acid or seed particles were not used for the data presented in this work. Hence, all acids were formed from the oxidation of organic compounds in the chamber. The VTDMA technique has been used to demonstrate the dynamic range and degree of this continuing process using three different heater temperatures (Kalberer et al., 2004). Application of a similar system to measure atmospherically generated aerosols will be necessary to demonstrate the extent of the process in the atmosphere.

There are implications relating to the oligomerizing behavior of organic aerosols. For instance, some oxidized (aged) compounds may be hygroscopic in the atmosphere, however, (oligomerizing) organic films may inhibit water uptake. This oligomerization will increase the lifetime of aerosols by reducing cloud droplet activation potential (Finlayson-Pitts and Pitts Jr., 2000; Folkers et al., 2003). Additionally, the dynamic behavior of the aerosols observed in the chamber inevitably influences surface photochemistry, surface reactivity, surface tension, optical
properties, sorption properties, and vapor pressure of the aerosols. Finally, future atmospheric models may need to account for the effects of oligomerization relative to such processes.

4.6 Acknowledgements

This work was supported by the Swiss National Science Foundation (No. 2169-061393), by ETHZ (No. TH-10./01-2), as well as by the European Commission (EUROCHAMP, No. FP6-505968) and the Swiss Bundesamt für Bildung und Wissenschaft (ACCENT, No. 03.0430-1; EU No. GOCE-CT-2004-505337). We thank the technical staff of the Paul Scherrer Institute, namely Erwin Scherrer and Josef Weiss for constructing the chamber housing. We also thank Robert Maag for his assistance in designing the cooling system and Markus Furger for his assistance with films and chamber lights.

4.7 References


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Chapter 5
Gas phase in the smog chamber
5.1 Introduction

The gas phase chemistry in the smog chamber as simulation of the troposphere involves the oxidation of the organic molecules (e.g. APIN and TMB) in the presence of oxides of nitrogen while irradiated by sunlight. VOCs and sunlight drive the NO/NO\textsubscript{2} circle which produces ozone. To understand the components of the SOA phase the gas phase components and their formation must be understood. The gas phase is analyzed with various instruments at the smog chamber (see Chapter 4); the instrumental focus of this chapter is only on the proton-transfer-reaction mass spectrometer (PTR-MS) and gas chromatography with flame ionization detector (GC-FID) which both monitor the parent hydrocarbon. The PTR-MS is also capable of detecting various oxidation products.

The most important gas phase reactands are nitric oxides, ozone and OH\textsuperscript{*}; their mixing ratios during experiments will be described in more detail in this chapter.

In this thesis, two precursors (APIN and TMB) were examined, but this chapter focuses on TMB only, for reasons of clarity. The course of the nitric oxides and ozone are the same, but for APIN only little PTR-MS data are available.

In the following sections the term “mixing ratio” is used. In tropospheric chemistry it is the most suitable term, because it is independent of temperature and pressure; ppb, ppm etc. is related to the number of parts (“volume mixing ratio”); 1ppm is 1 part in $10^6$ parts. Sometimes it is referred to as ppm(v/v) (=volume/volume) to avoid confusion.

5.2 NO, NO\textsubscript{2} and ozone mixing ratios during a TMB experiment

The main gas phase components are constantly monitored throughout the experiments. Standard gas analyzers for ozone, NO and NO\textsubscript{x} are used (instrumental details see Chapter 4).

Figure 5-1 shows the course of NO, ozone and NO\textsubscript{2} during a typical TMB (1300ppb input) experiment. The calculated, i.e. for 27m\textsuperscript{3} bag-volume, initial NO\textsubscript{x} (=NO+NO\textsubscript{2}) mixing ratio was 640ppb (320ppb each).
Figure 5-1: Mixing ratios of NO, NO\textsubscript{2} and ozone (ppb) during 6h of irradiation of TMB. The dashed vertical line indicates the beginning of the experiment (=turning on the lights).

The calculated mixing ratios of NO and NO\textsubscript{2} are higher than the actual measured ones. Depending on the total volume of the bag (27m\textsuperscript{3} \pm 1-2m\textsuperscript{3}), the measured values can change. Before turning the lights on there is no ozone; as soon as the lights are on, ozone formation starts within minutes, but at low mixing ratio (several ppb). At the beginning (with only NO, NO\textsubscript{2} and ozone present) the classical photostationary state relation is determining the NO\textsubscript{x} mixing ratios (see Equation 1-4). After 30min NO decreases, due to reactions with, e.g., hydroperoxyl radical to form OH\cdash{} (Equation 1-8), so NO\textsubscript{2} increases. Now more reactands are involved in the photostationary state relation, not only the abovementioned “classical” three compounds. The ozone mixing ratio increases (Equations 1-1, 1-2) after about 1h and the NO\textsubscript{2} mixing ratio increases further; now more and more peroxy radicals are formed which react with NO to form NO\textsubscript{2} and oxy radicals. After ca. 1.3h NO\textsubscript{2} reaches its maximum while the NO level is around 1ppb; then loss of NO\textsubscript{2} starts by reaction with OH\cdash{} to produce HNO\textsubscript{3}, and by photolysis to NO which now reacts with an increasing number of peroxy radicals to form, e.g., organonitrates.
After ca. 4h the NO$_2$ mixing ratio is at a low level together with NO. Then also ozone decreases slowly due to continuous photolysis and decreasing NO$_x$. NO$_x$ stays at a low level, but does not completely disappear, because now – at low NO$_x$ levels – peroxo acyl nitrate (PAN) releases NO$_2$ and a peroxo radical. PAN is a reservoir compound of NO$_2$ in polluted areas; it is a temperature-controlled equilibrium. NO$_2$ then photolyses to form NO and O to produce ozone, but at low NO$_x$ levels the ozone level cannot be as high as before and the ozone loss reactions start dominating.

### 5.3 PTR-MS and GC-FID

The PTR-MS instrument (IONICON Analytik GmbH, Innsbruck, Austria) at the PSI smog chamber is an essential tool for monitoring organic gas phase components during experiments. The technique has been described in detail elsewhere (Steinbacher (2004) and references therein). Just a very brief description will be given here: The method is based on proton transfer from H$_3$O$^+$ to compounds with a higher proton affinity than water and subsequent detection of the product ions in a quadrupole MS. Common components in the air, like O$_2$, N$_2$, CO$_2$, O$_3$ have a lower proton affinity than water and do not produce any signal. Most common (oxygenated) volatile organic compounds in the atmosphere have sufficient proton affinities (excluding alkanes and small alkenes/alkynes) to assure sufficient protonation. This makes the PTR-MS a useful and fast tool for measuring most of the common organic trace gases in the atmosphere.

The H$_3$O$^+$ ions are created by a hollow cathode discharge from water vapor. The ions enter a drift tube that is continuously flushed with the sample air. In the drift tube the VOCs are ionized according to:

$$ H_3O^+ + VOC \xrightarrow{k} VOCH^+ + H_2O $$

Therefore the masses measured in the PTR-MS are the protonated molecular ions.

The advantage of the PTR-MS is the low detection limit (around 0.1 ppb) and only little fragmentation due to soft chemical ionization.

For constant monitoring and quantifying the parent hydrocarbon a GC-FID was employed at the smog chamber. The instrument (Varian 3400) is equipped with a...
Optima-5-column (Macherey-Nagel, Switzerland) with helium as mobile phase. In the FID the transported organic compounds are ignited in a flame made of hydrogen and air. The compounds produce ions as they burn and the changing current within the flame is measured and sent to the computer to be seen as peaks in the chromatogram. The only parameter to identify compounds is the retention time, therefore the GC-FID is not suitable for identifying unknowns, but a useful, robust and general detector for analysis of organic compounds.

5.3.1 Monitoring of 1,3,5-Trimethylbenzene with PTR-MS and GC-FID

Both, PTR-MS and GC-FID were running at the smog chamber during the first two years of experiments. The PTR-MS was not always available. Therefore, and also for reasons of comparison, the GC-FID was running.

Both instruments monitor the parent hydrocarbon (only TMB experiments were performed in this time), whereas the PTR-MS additionally monitors the oxidation products. Calibration of the PTR-MS was done with standards if available, otherwise calculated mixing ratios had to be used (more details see also Chapter 4). Before each experiment, the GC-FID was calibrated with calibration solutions of TMB and hexafluorobenzene (5µl/ml methanol) as internal standard, both in methanol. 20µl of the solutions with varying amounts of TMB (10-1µl/ml methanol) are injected into a small Teflon bag (30l, filled with clean air). Based on the calibration curves, the amount of TMB present in the smog chamber is quantified. The addition of the internal standard (IS, into the calibration bag and into the smog chamber) also helps to detect leaks in the smog chamber bag by monitoring the IS, that should not change during an experiment due to the low reactivity of hexafluorobenzene with OH• and organics. A comparison of the two instruments, both measuring TMB is shown in Figure 5-2.
Figure 5-2: Gas mixing ratios (ppb) of TMB during 11h of irradiation measured by GC-FID and PTR-MS. Light was switched on at 0h (nominal initial conditions were 656ppb TMB, 160ppb NO, NO$_2$ each, 300ppb propene).

There is a good agreement between the two instruments. The time resolution of the PTR-MS is much better. The GC-FID values are constantly higher by about 10-12%. The slightly larger difference at the beginning (about 15%) can be explained by insufficient mixing in the bag, the constant difference afterwards seems to be a systematic or calibration error.
Figure 5-3: Correlation of the mixing ratios for TMB (ppb) measured with GC-FID and PTR-MS (nominal initial conditions: 656ppb TMB, 160ppb NO, NO\textsubscript{2} each, 300ppb propene).

The correlation shown in Figure 5-3 is also very good. The correlation coefficient for 16 experiments is always > 0.96.

These two figures show the good agreement of the two instruments; for some experiments only one of the two was available, but after many experiments with good correlation, we could rely on one of them independently. After 2 years the GC-FID was not used anymore, only the PTR-MS was employed. For some experiments neither of the two instruments was used due to technical problems; but the experience showed that the smog chamber performed very well in terms of repeatability and consistency (see also Chapter 4).
5.3.2 Organic gaseous products of TMB photo-oxidation measured with PTR-MS

Figure 5-4 shows the concentrations of selected PTR-MS masses for a typical TMB experiment as a function of time.

Figure 5-4: Gas mixing ratios (ppb) of a typical TMB experiment during 9h of irradiation. TMB (m121) and 6 (m113, m73, m47, m61, m135, m89) products are shown. Note the two different x-axis (nominal initial mixing ratio TMB 1300ppb, 320ppb NO, 320ppb NO\textsubscript{2}, 300ppb propene).

The traces shown are attributed to TMB (m121, note that the protonated species is shown) and selected gaseous oxidation products, namely methylglyoxal (m73), 3,5-dimethylbenzaldehyde (m135), pyruvic acid (m89), acetic acid (m61), formic acid (m47) and m113, which can be attributed to three different species that are all possible degradation products of TMB: 2-methyl-4-oxo-pentenal, 3-methyl-2,5-furandione or 3,5-dimethyl-5(2H)-2-furanone. 2-methyl-4-oxo-pentenal has been identified as a product in photo oxidation of TMB (Kleindienst et al., 1999), but the presence of the others cannot be excluded by the sole use of the PTR-MS.
It can be seen very nicely how TMB degrades and the product mixing ratios increase with time. The dominant reaction pathway of TMB oxidation is the ring opening route which yields methylglyoxal (m73) (Calvert et al., 2002). The route generating ring containing products is of minor importance, thus the amount of 3,5-dimethylbenzaldehyde is very low; so is pyruvic acid (m89). 3,5-dimethylbenzaldehyde, pyruvic acid and 2-methyl-4-oxo-pentenal increase for about 2-3h and then stay at a constant level but with pyruvic acid still increasing slowly, whereas methylglyoxal decreases after 3-4h. Mixing ratios of acetic and formic acid have a very similar course, they continuously increase to 170ppb and 150ppb, respectively.

Figure 5-5 illustrates nicely the correlation between the TMB (parent hydrocarbon) decrease and increase of the SOA mass from the nucleation and condensation of the gas phase oxidation products.

![Figure 5-5: Gas mixing ratio (ppb) of TMB during 5.5h of irradiation and volume concentration of TMB (nominal initial mixing ratio TMB 1300ppb, 320ppb NO, 320ppb NO$_2$, 300ppb propene).](image)

The observed particle nucleation starts after about 15-20min (diameter > 3nm measured with a CPC) and after about 25min particle formation is detectable by the SMPS, but the mass is very little. Only after about 1h the particles are in a size range
> 1µg (assumed density of 1g/cm³). The volume concentration reaches its maximum after about 4h, the decrease afterwards is due to wall losses. Although the PTR-MS allows for measuring many gaseous oxidation products it is not possible to determine the gaseous compounds responsible for the particle nucleation or growth just by comparing the time trends of the gaseous species with the volume concentration trends of the compounds. This is not the case, because for nucleation only small amounts are needed, and the change of concentration might be within measurement uncertainties. All compounds react further also in the gas phase. Therefore it is not possible to assign a decreasing mixing ratio to a loss to the particle phase or to a loss due to gas phase oxidation. A useful tool that is now being developed (Gascho et al., 2005) is the determination of aerosol species with the PTR-MS. During a smog chamber experiment the gas and aerosol phase can be monitored alternately and gas phase compounds can be attributed to partition into the SOA phase. Furthermore, a partitioning coefficient for gas-particle-partitioning of certain compounds can be determined.

5.4 References


Chapter 6

Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments

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6.1 Abstract

Organic acids in the gas and aerosol phase from photo-oxidation of 1,3,5-trimethylbenzene (TMB) in the presence of 300 ppb propene and 300ppb NOx in smog chamber experiments were determined using a wet effluent diffusion denuder/aerosol collector (WEDD/AC) coupled to ion chromatography (IC) with conductivity detection. Behind the IC, the samples were collected using a fraction collector, for identification of unresolved/unidentified organic acids with ion chromatography – mass spectrometry (IC-MS). In total, 20 organic acids were found with MS of which 10 were identified. The organic acids identified offline by IC-MS were then further quantified based on the on-line IC data. The identification was additionally confirmed with gas chromatography–mass spectrometry (GC-MS). At the maximum aerosol concentration, organic acids comprised 20-45% of the total aerosol mass. The method has a detection limit of 10 to 100ng/m³ for the identified carboxylic acids.
6.2 Introduction

Organic compounds contribute 10 to 70% of the fine atmospheric aerosol mass (Lim and Turpin, 2002). In general the organic fraction of aerosol is highly complex as it consists of a multitude of individual compounds, which have a variety of sources. These include primary emissions, mainly from combustion (Schauer and Cass, 2000) and biogenic sources (Kavouras et al., 1998), and secondary organic aerosol (SOA) resulting from the reaction of primary volatile organic compounds (VOC) in the atmosphere. The SOA fraction can contribute up to 80% to the total aerosol mass in smog events (Turpin and Huntzicker, 1995). The proportion of the primary emitted organic species vs. the secondary compounds is still far from being understood. A detailed knowledge on the formation and properties of SOA in the atmosphere is therefore essential to characterize the chemical composition of ambient organic aerosols and to incorporate such processes in air quality models. Chamber experiments are now widely used to study the possible mechanisms of SOA formation (Hoffmann et al., 1998; Hoppel et al., 2001) and to quantify the aerosol yield of organic precursors (Odum et al., 1996) in the atmosphere. Starting with aromatics or terpenes, a wide variety of compounds are produced (Forstner et al., 1997), with organic acids, aldehydes, and ketones being the major components both in the gas and aerosol phase. Recently, Kalberer et al. (2004) showed in chamber experiments that polymerization of some organic compounds occurs during SOA formation and that these polymers make up a large fraction of total SOA. Tolocka et al. (2004) also showed the formation of oligomers in secondary organic aerosol. Both authors indicated a substantial contribution by organic acids. Detailed information about the gas and aerosol phase concentration of these organic acids is therefore necessary to increase our understanding of SOA formation. However, the measurement of organic acids is a demanding task, as the analytical method must provide a high time resolution and low detection limits.

Techniques often applied for the gas phase measurement of organic acids are gas chromatography (GC) (Odum et al., 1996), gas chromatography coupled to mass spectrometry (GC-MS) (Jaoui and Kamens, 2003), and proton transfer reaction mass spectrometry (PTR-MS) (Kalberer et al., 2004). The GC based methods provide
important data for most compounds formed in chamber experiments, however, due to their high polarity, organic acids cannot be measured online with these methods (Hamilton et al., 2003). Sampling with adsorption tubes (Hoffmann et al., 1998), impingers (Jaoui and Kamens, 2003) or cartridges (Van den Bergh et al., 2000) followed by extraction for the GC measurements is therefore necessary. These methods are labor intensive and prone to artifacts. PTR-MS, which has less shortcomings with respect to the polarity of the compounds, could be a better choice for the measurement of these compounds. However, it is difficult to get unbiased data for all compounds of interest since different compounds with the same mass appear as a single peak in the PTR-MS. In addition, fragmentation could also result in positive and negative bias in the quantification of some organic acids (Kuster et al., 2004).

Impactors (Cocker et al., 2001) and filters (Forstner et al., 1997; Hoffmann et al., 1998; Turpin et al., 2000) are the most commonly used aerosols sampling devices with subsequent extraction of the compound of interest for offline measurement. These methods are also vulnerable to artifacts (Kirchstetter et al., 2001; Turpin et al., 2000) during sampling and extraction processes. Online analysis of organic components in fine and ultrafine particles by photo ionization aerosol mass spectrometry has been recently described by Öktem et al. (2004) for ambient and smog chamber measurements. Although this method brings a significant progress in organic aerosol measurements, it still has not filled the gap for the identification and quantification of the compounds that contribute significantly to the formation of SOA.

Ion chromatography (IC) identifies compounds solely based on their retention time. When two or more compounds co-elute, identification of the compounds is hampered. With the coupling of a mass spectrometer to an ion chromatograph however, co-eluting compounds can be separated, provided they have different mass. We present here a pilot study for online analysis of gas and aerosol phase water-soluble organic acids in chamber experiments using a wet effluent diffusion denuder/aerosol collector (WEDD/AC) coupled to IC with conductivity detection followed by offline ion chromatography-mass spectrometry (IC-MS). Online measurement of inorganic gases and aerosol with a WEDD/AC coupled to IC has been discussed by Simon and Dasgupta (1995). Recently, Löflund et al. (2001) and Boring et al. (2002) also showed the use of such systems for atmospheric organic acid measurements. We demonstrate here that direct coupling of IC-MS to WEDD/AC is feasible and a suitable technique for the study of atmospheric chemistry.
6.3 Experimental section

6.3.1 The PSI smog chamber

The indoor smog chamber at the Paul Scherrer Institute (PSI) consists of a 27m³ transparent Teflon® bag suspended in a temperature controlled housing. Four xenon arc lamps (4 kW each) are used to simulate the solar light spectrum as closely as possible and to mimic tropospheric photochemistry. Primary gas components such as organics, oxides of nitrogen, purified air, and water vapor are flushed into the chamber where they diffuse and mix for 30-45 minutes before turning on the lights. For these experiments a mixture of 600ppb 1,3,5-trimethylbenzene (TMB), 300ppb propene and 300ppb NOₓ at a nominal relative humidity of 50% was irradiated. Particle size distributions from 7 to 316nm were measured with a scanning mobility particle sizer (SMPS) consisting of a TSI 3071 differential mobility analyzer (DMA) and a TSI model 3010 condensation particle counter (CPC). From these size distributions, integrated aerosol volume concentrations were calculated assuming spherical shape of the particles, and mass concentrations were determined using a density of 1.38g cm⁻³ as determined with a DMA and an Aerodyne aerosol mass spectrometer (R. Alfarra, University of Manchester, June 2004, personal communication). Gas phase measurements of organic compounds were performed using PTR-MS and a Varian 3400 GC. More details of the smog chamber facility and instrumentation are given by Paulsen et al. (2005).

6.3.2 Sampling and analysis

The aerosol from the PSI smog chamber was sampled using a 1-m Perfluoroalkoxy (PFA) tube at a flow rate of 1.5 l/min and passed through the WEDD/AC. The WEDD/AC is a custom-built instrument consisting of a glass denuder for gas phase sampling and an aerosol collector. The denuder is flattened in the middle and has dimensions of 35cm x 3.5cm x 3mm (H, L, W). The inner surface of the denuder is coated smoothly with sodium silicate. Ultra pure water (from Millipore Milli-Q water purification system) is continuously pumped using an ISMATEC peristaltic pump at a
flow rate of 1.5ml/min to the inner surface of the denuder in counter flow to the air sample.
The aerosol collector is a 300ml glass cylinder, which is connected at the top end of the denuder. There is a continuous supply of steam (0.6ml/min) at 100°C transforming virtually all aerosol particles into cloud droplets, which are then easily separated from the gas stream by impaction. The bottom of the aerosol collector is connected to a Peltier element in order to cool down the effluent. A detailed description of the instrument is given elsewhere (Dasgupta et al., 1997; Ferm, 1979; Simon et al., 1991; Zellweger et al., 1999).

The effluents from the denuder and aerosol collector were pumped each through a separate concentrator column to concentrate the anions. The presence of a concentrator column before the analytical column also helps to remove some non-acidic water-soluble compounds which otherwise would have been detected by the mass spectrometer. The analysis of the sample was made in a quasi-continuous fashion such that the concentrated sample from the denuder was analyzed while the effluent from the aerosol mixing chamber was concentrated, and vice versa. The total analysis time was 30min (24min analysis time and 6min equilibration time for the ion chromatograph), which enabled an hourly analysis of the gas and the aerosol phase. The effluent from the IC conductivity detector was directed to a fraction collector (ISCO Foxy 200), for separate collection of individual peaks. Alternatively, the whole sample was collected in one vial for further analysis by IC-MS and GC-MS. During the two days between sampling and analysis, the samples were kept in a refrigerator at 4°C. Blank samples were also prepared the same way as the samples for both the denuder and aerosol collector.

### 6.3.3 IC and IC-MS

A DX 600 system consisting of an EG-40 hydroxide eluent generator, an anion trap column (ATC-1) to clean the eluent, a CD-25 conductivity detector, an IP-25 isocratic pump, two trace anion concentrator columns (TAC-LP1) and an anion self regeneration suppressor (ASRS-ultra 4mm) in the external water mode (300mA) was used for sample analysis. The analysis of the concentrated ions switched between the two-concentrator columns using a Rheodyne valve, which was controlled by the
Chapter 6  Identification of organic acids in SOA and gas phase

Chromeleon software. An IonPac 4mm AS 17 column was used for the analysis of the anions. The IC system was calibrated using standard solutions of organic acids. The samples from the fraction collector were analyzed by an IC-MS, consisting of an IonPac AS11-HC (4-mm) column on the ion chromatograph and a standard mass spectrometer with a single quadrupole mass detector (Dionex, MSQ™). This mass spectrometer uses atmospheric pressure ionization (API), which allows positive and negative ions to be detected. The API source is based on electrospray ionization (ESI). The mass spectrometer was operated at the negative mode to detect deprotonated compounds with in a mass range of $m/z$ 50-2000.

6.3.4  GC-MS

To qualitatively confirm the IC-MS compound identification, samples taken with the fraction collector were also analyzed with GC-MS for both the gas and aerosol phase. The carboxylic acids were derivatized with N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) (Sax et al., 2003) using an estimated tenfold excess of MTBSTFA. MTBSTFA derivatizes carboxyl and hydroxyl groups to form silyl derivatives, which are less polar and thus suitable for GC. Since the products of the derivatization are sensitive to hydrolysis, it could not be directly used in the aqueous fractions from the IC. The fractions were therefore transferred to an aprotic solvent by extracting the acidified (with hydrochloric acid) IC fractions three times with chloroform. The volume of the united extracts was reduced to ca. 1ml by a gentle nitrogen stream and the samples were then analyzed by a HP model 5890 Series II Gas Chromatograph interfaced to a HP Model 5971A quadrupole mass selective detector (MSD).

Chemicals
All chemicals were analytical reagent grade. Ultra pure water (~0.054µS) was used throughout the experiment.
6.4 Results and discussion

6.4.1 Efficiency of the WEDD/AC

The sampling efficiency of the WEDD/AC was measured for both the gas and the aerosol phase. A mixture of acetic and formic acid from a permeation source was passed through the denuder, and the collection efficiency was calculated to be at least 85% and 75% for acetic and formic acids, respectively at a flow rate of 4 l/min. Losses on the surface of the sampling line and some uncertainty due to the ageing of the permeation source lowered the collection efficiency of the denuder. For the aerosol collector ammonium sulfate particles (particle diameter $D_p$ 10-220nm) were passed through the system and the collection efficiency was calculated to be 95%. Using a scanning mobility particle sizer (SMPS) less than 0.5% particle loss was observed in the denuder for particles greater than 50nm.

6.4.2 Identification of the organic acids

Using primary component concentrations of 600ppb TMB, 300ppb NO$_x$, and 300ppb propene, at 40-50% relative humidity and 20°C, particle formation ($D_p > 7$nm) is detected with the SMPS after approximately 25 minutes of irradiation, and the particle size increases to 150nm within ~2.5h. For chemical characterization, a number of experiments were carried out using IC coupled to the WEDD/AC. Several organic acids were measured in these experiments, however; there were some unidentified organic acids, which either co-eluted with known organic acids or were present as separate peaks. The large peak of carbon dioxide, which elutes from the anion column as carbonate, also hides some dicarboxylic organic acids. Four samples (two from the denuder and two from the aerosol collector during the same experiment) obtained with the fraction collector were additionally analyzed offline with IC-MS and GC-MS. Figure 6-1 shows the IC chromatogram (Panel 1A) as well as IC-MS mass chromatograms of selected masses of the aerosol sample (Panels 1B-1G).
Figure 6-1: IC-MS chromatograms. Panel A gives the chromatogram from the IC while panels B to G show chromatograms for various masses.
The MS peaks clearly indicate different masses of co-eluting acids and also confirm the mass of those organic acids that were already identified by IC alone. In addition, compounds with very low signal strength by IC were detected with a high signal to noise ratio by IC-MS. For quantification, the online data from the ion chromatograph was used using their respective standards, as the samples analyzed with IC-MS were too limited to provide a time evolution of the concentrations of the organic acids in the chamber. The identification was verified by injecting the standards into the IC-MS system. For the masses that were not structurally known, their respective concentrations were estimated based on the standard curve of a known acid with a similar retention time. The largest uncertainties (~ 50% error) were determined for succinic and malic acid, which elute within the broad peak of carbonate. However, this does not affect the total amount of organic acids measured in the system since their contribution to the total aerosol mass is less than 1%.

In Figure 6-1B, two peaks with a mass of 90 (actual mass =m/z +1) appear. One co-eluted with acetic acid at a retention time of 2.3min while the other one appeared at 9.6min. The early and late mass 90 compounds were identified as lactic and oxalic acid, respectively, based on their IC retention times. Interestingly, peaks with a higher mass were also detected by IC-MS. For example, an organic acid with a mass of 234 Dalton was found in the aerosol sample, but not in the gas phase. Based on its retention time, the peak was assigned to a dicarboxylic acid, but the exact structure is not yet known. However, its mass suggests that this may be a di-mer/tri-mer formed in the aerosol. Mixtures of standard solutions of the compounds identified in the sample were prepared and injected into the IC-MS instrument in order to check if these high mass organic acids could also be formed in the analytical column of the ion chromatograph. No new high mass compounds were detected in this case. Nitric acid (as nitrate) and nitrite were also measured. However, due to the presence of NO₂ gas and other nitrogen containing organic acids and peroxynitrates, the values may be biased (Boring et al., 2002). Therefore these two acids will not be discussed further.

The chloride and sulfate peaks are due to contamination.

The list of all organic acids detected both in the gas and aerosol phase is given in Table 6-1.
Table 6-1: Organic Acids identified in both the gas and aerosol phases at the maximum aerosol concentration (4:30h after lights on).

<table>
<thead>
<tr>
<th>Mass</th>
<th>Compound</th>
<th>Type (IC-MS)</th>
<th>Gas phase (IC-MS) c in µg/m³</th>
<th>Aerosol phase (IC-MS) c in µg/m³</th>
<th>Vol. ratio (IC-MS)</th>
<th>Identified with GC-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>Formic acid</td>
<td>Mono</td>
<td>75.2</td>
<td>15</td>
<td>0.07</td>
<td>g, a</td>
</tr>
<tr>
<td>60</td>
<td>Acetic acid</td>
<td>Mono</td>
<td>26.1</td>
<td>16</td>
<td>0.08</td>
<td>g, a</td>
</tr>
<tr>
<td>88</td>
<td>Pyruvic acid</td>
<td>Mono</td>
<td>29.2</td>
<td>11</td>
<td>0.05</td>
<td>g, a</td>
</tr>
<tr>
<td>90</td>
<td>Lactic acid</td>
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<td>44</td>
<td>0.21</td>
<td>g, a</td>
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<tr>
<td>90</td>
<td>Oxalic acid</td>
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<td>0.42</td>
<td>0.001</td>
<td>N.P.</td>
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<tr>
<td>104</td>
<td>Malonic acid</td>
<td>Di</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>g, a</td>
</tr>
<tr>
<td>114</td>
<td>N.I.</td>
<td>Di</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>118</td>
<td>Succinic acid</td>
<td>Di</td>
<td>0.54</td>
<td>0.49*</td>
<td>0.006</td>
<td>g, a</td>
</tr>
<tr>
<td>122</td>
<td>N.I.</td>
<td>Di</td>
<td>N.Q</td>
<td>N.P.</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>129</td>
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<td>-</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>130</td>
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<td>0.001</td>
<td>g</td>
</tr>
<tr>
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<td>Di</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>134</td>
<td>Malic acid</td>
<td>Di</td>
<td>0.4*</td>
<td>0.23*</td>
<td>0.001</td>
<td>N.P.</td>
</tr>
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<td>150</td>
<td>3,5-dimethylbenzoic acid</td>
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<td>N.P.</td>
<td>N.P</td>
<td>-</td>
<td>g, a</td>
</tr>
<tr>
<td>166</td>
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<td>Di</td>
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<td>0.10</td>
<td>0.0005</td>
<td>N.P.</td>
</tr>
<tr>
<td>171</td>
<td>N.I.</td>
<td>-</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>178</td>
<td>N.I.</td>
<td>Di</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>188</td>
<td>N.I.</td>
<td>Di</td>
<td>0.03</td>
<td>0.12</td>
<td>0.0005</td>
<td>N.P.</td>
</tr>
<tr>
<td>190</td>
<td>N.I.</td>
<td>Di</td>
<td>N.Q</td>
<td>N.Q</td>
<td>-</td>
<td>N.P.</td>
</tr>
<tr>
<td>192</td>
<td>Citric acid</td>
<td>Tri</td>
<td>0.03</td>
<td>0.03*</td>
<td>0.0003</td>
<td>N.P.</td>
</tr>
<tr>
<td>234</td>
<td>N.I.</td>
<td>Di</td>
<td>N.Q.</td>
<td>10.9</td>
<td>0.05</td>
<td>N.P.</td>
</tr>
</tbody>
</table>

g=gas phase, a=aerosol phase, (N.Q: not quantified; N.I: not identified; N.P.: not present)

* Present above detection limit only after the maximum aerosol concentration
In total, 20 organic acids were detected with IC-MS, namely 4 monocarboxylic, 13 dicarboxylic, and 1 tricarboxylic acid. Some of the dicarboxylic acids could also be dimers of monocarboxylic acids, indicating the first step of polymerization as discussed in Kalberer et al. (2004). Organic acids with odd masses were also identified from the mass spectra. These are believed to be acids with a nitrogen group. Some of the organic acids identified here were also mentioned by other authors. For example Cocker et al. (2001) reported C2 saturated dihydroxy carboxylic acids as well as pyruvic acid and C5-oxo-carboxylic acids. Smith et al. (1999) and Kleindienst et al. (1999) reported the presence of methyl maleic anhydride, which is the anhydride form of methyl maleic acid. Methyl maleic acid was detected in high concentrations in the denuder sample, which at least partially may be attributed to the hydrolysis of maleic anhydride in the denuder. Fragmentation of a carboxyl group was observed for one organic acid (original mass 166, fragment mass 122 Dalton). There is also an organic acid with an original mass of 122 Dalton, however, since the retention times of the acids are different, they are easily discriminated.

From the GC-MS measurements, acetic, formic, lactic, pyruvic, malonic, methyl maleic and succinic acid were also detected (see Table 6-1). 3,5-dimethylbenzoic acid was found with GC-MS but not with IC-MS. A standard solution of 3,5-dimethylbenzoic acid was injected into the ion chromatograph, but did not elute as a peak. Oxalic, malic and other high mass organic acids were not detected by GC-MS, due to the very low concentrations.
6.4.3 Gas and aerosol phase organic acid concentrations

Figure 6-2 shows temporal concentration evolutions of identified acids.

Figure 6-2: Organic acid concentrations for both the aerosol phase (left panel) and gas phase (right panel).

The concentrations of the organic acids increased significantly approximately 2h after the start of the irradiation. Most of the organic acids were observed in both the gas and aerosol phase (see Table 6-1), with the concentrations in the gas phase generally being higher than in the aerosol. The gas phase organic acid concentrations increased until the lights were turned off; whereas the aerosol concentrations decreased 4:30 hours after the lights were on. This decline was in good agreement with the evolution of the total aerosol mass concentration. The sum of the organic acid concentrations in the aerosol is highly correlated with the total aerosol mass concentration ($r= 0.93$), and at the maximum aerosol concentration the organic acids in the aerosol contributed
25% of the total organic acids formed in the chamber and 20-45% of the aerosol mass (Figure 6-3).

![Figure 6-3: Comparison of total aerosol mass concentration measured with the SMPS (●) with the sum of organic acids measured in the aerosol (◇).](image)

For both the gas and aerosol phase, monocarboxylic acids had higher concentrations than dicarboxylic acids. Formic acid showed the highest concentration throughout the measurement in the gas phase, while lactic acid had the highest concentration in the aerosol phase (Figure 6-2). The concentration of lactic acid may however be overestimated by ~20%, because the peak of lactic acid co-elutes with acetic acid in IC, which hampers an accurate quantification of both acids. Pyruvic acid, which was also found in higher concentrations in both the gas and aerosol phases, is believed to be one of the compounds involved in polymerization (Kalberer et al., 2004). The high fraction of the particulate organic acids fraction with respect to the total aerosol mass along with the high polymerized fraction (Kalberer et al., 2004) suggests that those organic acids participating in the polymerization are broken down to their monomers in the steam condensation chamber. The presented method would thus be sensitive for the individual building blocks but not generally for the polymers. A further discussion on the formation and transformation mechanism of organic acids in chamber experiments is however beyond the scope of this paper.
Chapter 6  Identification of organic acids in SOA and gas phase

6.5 Conclusions

The use of an online system for organic acid measurements in both the gas and aerosol phase reduces the sampling artifact and helps understanding of the time variation of the acids in chamber and field experiments. IC-MS enabled us to identify a suite of organic acids and to determine the molecular weight of a number of additional structurally unknown compounds. Here, the specificity of IC to organic acids and their different retention times made the analysis of the mass spectra easier by narrowing the list of possible compounds. The method has a very low detection limit for most of the organic acids. Due to the pilot study character of this work, online coupling of the sampling instrument with the IC-MS system was not possible. However we believe that online coupling of the MS to the ion chromatograph would even provide more data than we presented here. The number of acids detected with this system is also dependent on the type of column used in the ion chromatograph. Therefore the use of other anion columns could also be helpful to detect other organic acids in addition to the ones presented here.

6.6 Acknowledgement

This work was supported by the Swiss National Science Foundation.

6.7 References


Chapter 6  Identification of organic acids in SOA and gas phase


Chapter 6 Identification of organic acids in SOA and gas phase


Chapter 7

Identification of Polymers as Major Components of Atmospheric Organic Aerosols

adapted from
Science, 2004, 303, 1659-1662,
including supplementary material.
7.1 Abstract

Results from photo-oxidation of aromatic compounds in a reaction chamber show that a significant fraction of the organic aerosol mass is composed of polymers. This polymerization results from reactions of carbonyls and their hydrates. After aging for more than 20 hours, about 50% of the particle mass consists of polymers with a molecular size up to 1000Da. This results in a lower volatility of this secondary organic aerosol and a higher aerosol yield than a model using vapor pressures of individual organic species would predict.

7.2 Introduction

Ambient aerosol particles contribute to many important atmospheric processes including visibility reduction, cloud formation, direct radiative forcing and also a variety of adverse health effects. Although organic material is a major fraction of ambient aerosol mass (often 20-50% (Seinfeld and Pandis, 1998)), only a minor fraction was identified so far on a molecular level (Rogge et al., 1993). Up to 90% of the organic aerosol mass in urban areas is secondary organic aerosol (SOA) (Lim and Turpin, 2002), which is not directly emitted but formed in the atmosphere by the oxidation of gaseous precursors. Small aromatic compounds such as benzene, toluene, xylenes, or trimethylbenzenes are the major known compounds emitted by human activities (mainly from fossil fuels), which lead to the formation of SOA.

Efforts have been made to quantify the aerosol formation potential (aerosol yield) of these aromatic compounds (Cocker et al., 2001; Hurley et al., 2001). Odum et al. showed that the aerosol yield of whole gasoline vapor can be explained by the sum of the single SOA yields of its aromatic constituents (Odum et al., 1997). Models describing SOA formation assume a thermodynamic equilibrium of organic compounds between the gas and the aerosol phase (Cocker et al., 2001; Pankow, 1994). Although the physical mass formation of SOA can be parameterized with established models, (Cocker et al., 2001; Dechapanya et al., 2003; Griffin et al., 1999) the chemical composition of the SOA is still poorly understood. The current methods of identification are mostly gas chromatography-mass spectrometry (GC-
MS) along with infrared spectroscopy (Cocker et al., 2001; Forstner et al., 1997; Holes et al., 1997; Jang and Kamens, 2001). SOA compounds identified so far from aromatic photo-oxidation are small carbonyls as well as small amounts of alcohols and acids (Cocker et al., 2001; Forstner et al., 1997; Jang and Kamens, 2001). Jang et al. showed that some of the highly volatile carbonylic oxidation products (expected to be mostly in the gas phase) can lead to an increase of SOA mass if mixed with strongly acidic inorganic seed particles (Jang et al., 2002). They proposed condensation and polymerization reactions of carbonyls in the acidic particles as a possible explanation of the observed SOA mass increase. However, their analytical techniques did not allow the actual detection of the proposed polymers. Our reaction chamber measurements show that about 50% of SOA from aromatics oxidation is composed of polymers. This polymerization is a long-term process lasting over more than 20hrs.

### 7.3 Experimental

The aerosol was generated for measurements described here under controlled conditions in a 27m³ Teflon® bag by photo-oxidation of 1,3,5-trimethylbenzene (TMB) with initial mixing ratios of 20-650ppbv resulting in maximum particle mass concentrations between 2.7µg/m³ (40ppbv) and 170µg/m³ (650ppbv).

#### 7.3.1 Reaction Chamber Design

The PSI reaction chamber consists of a 27m³ transparent Teflon® bag suspended in a temperature controlled housing. Four xenon arc lamps (4kW each) are used to simulate the solar light spectrum as closely as possible and to mimic natural photochemistry. Primary gas components such as organics, oxides of nitrogen, purified air, and water vapor are flushed into the chamber where they diffuse and mix for 30-45 minutes before turning on the lights.
7.3.2 Instrumentation

Total particle number concentrations (diameter $D_p > 3$ nm) were monitored with TSI model 3022 and 3025A condensation particle counters (CPC). Particle size distributions from 7 to 316 nm were measured with a scanning mobility particle sizer (SMPS) along with a TSI model 3010 CPC (Wang and Flagan, 1990). A volatility tandem differential mobility analyzer (VTDMA) was used to measure the volatile fraction of size selected aerosols (Rader and McMurry, 1986). Chemical analysis of the particles was performed on-line with IC and off-line by GC-MS, IR, and LDI-MS, after sampling on filters and impactors. In the gas phase we measured $O_3$ (UV-photometer: Environics S300), NO and NO$_x$ (ML9841A), CO (AeroLaser AL 5002), the precursor hydrocarbon with a GC-FID (Varian, 3400) and a PTR-MS (Ionicon) and oxidation products with the PTR-MS, IC (sample collection in wet effluent denuder) and GC-MS (sample collection on polyurethane foam).

7.3.3 Measurements

7.3.3.4 Number and volume concentration

Figure 7-1 is a contour plot of the number (A) and volume (B) concentration size distributions as they evolve in the chamber during the first 10 hours of irradiation, after correcting for wall losses.
Figure 7-1: Evolution of a typical particle number (A) and volume (B) concentration size distributions after 10 hours of irradiating a mixture of 650 ppbv 1,3,5-trimethylbenzene, 320 ppbv NO\(_x\). Using primary component concentrations of ca. 20-650 ppbv TMB, 10-320 ppbv NO\(_x\), and 300 ppbv propene, at 40-50% relative humidity and 20°C, particle formation (D\(_p\) > 7 nm) is detected with the SMPS after approximately 25 minutes of irradiation. Propene was added to provide a sufficient level of OH radicals (Odum et al., 1996). The volume concentration plot shows that the particle volume growth slows considerably after 3 hours of irradiation. Measured aerosol yields of 6% for TMB-NO\(_x\) irradiation experiments in the chamber are comparable to other literature values under similar experimental conditions (Cocker et al., 2001).

7.3.3.5 VTDMA measurements

A Volatility Tandem Differential Mobility Analyzer (VTDMA) was employed to quantify the polymer fraction (Rader and McMurry, 1986). This technique characterizes the aerosols based on aerosol electrical mobility and thermodynamic behavior. The first of two DMAs in series allows selection of a specific narrow size channel from the chamber aerosol size distribution. The size selected aerosol is
subsequently heated to 100, 150, and 200°C. Any size reduction of the aerosol due to evaporation is detected downstream using a second DMA, which measures the conditioned aerosol size distribution.

7.3.3.6 Laser Desorption/Ionisation Mass Spectrometry (LDI-MS)

Smog chamber samples

Samples were collected on an ungreased steel plate of an impactor (Maenhaut et al., 1996). The steel plates were introduced into the MS without further treatment, minimizing contamination. A N\textsubscript{2}-laser was used to desorb organic material from the sample plate, and a linear time-of-flight mass spectrometer was used for mass analysis. For some test experiments KCl (aqueous solution) was added to the sample before analysis, forcing cationization with K\textsuperscript{+} to be the dominant ionization process. However, due to the always present potassium impurities of the plates this was not needed routinely.

Mass spectra at times as long as 20hrs were measured, however, due to the low particle concentration (due to wall losses) and bag depletion not enough material could be collected and resulted in low signal-to-noise ratio so that it was not possible to decide whether the polymer still grows in molecular size.

Synthetic polymers

Mixtures of the pure substances (methylglyoxal, formaldehyde, \textit{3,5-dimethylbenzaldehyde}, pyruvic acid) were dried in a desiccator to evaporate water. Due to the low laser light absorbance the polymers were mixed with graphite particles (1-2µm, Aldrich) and KCl (aqueous solution). Graphite enables to measure non-absorbing compounds with LDI-MS without interfering with the mass spectrometric measurement.

Due to the hydration of the carbonyl group the mass of an oligomer is equal to the mass of the single monomers plus one, two or three water molecules. In addition, in LDI-mass spectrometry analytes are often ionized by K\textsuperscript{+} or Na\textsuperscript{+}, which are present in the sample due to ubiquitous impurities. In the mass spectra for the surrogate co-polymers shown in Figure 7-5F and also for the pure methylglyoxal-polymer (Figure
7-5E) the polymers are clearly K\(^+\)-adducts. Therefore we assume that also the TMB-SOA polymers in Figure 7-4 and Figure 7-5A-D are mostly hydrated potassium adducts.

Precursor and small oxidation products (PTR-MS, GC-MS, IC)

A closer look at the chemistry of the gaseous and particle-bound oxidation products with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) and GC-MS reveals that a large number of carbonyls are formed during photo-oxidation of TMB. Formaldehyde, acetaldehyde, methylglyoxal, 2-methyl-4-oxo-2-pentenal, and isomers as well as about 20 more unidentified carbonyls were found in the gas phase (recognized by their specific fragmentation pattern in EI–MS after derivatization). Several of these small carbonyls (methylglyoxal, 2-methyl-4-oxo-2-pentenal, and about 10 unidentified carbonyls) were also found in the particle phase. In addition, several small acids (formic acid, acetic acid, pyruvic acid, and trace amounts of glyoxalic acid) were identified with GC-MS and ion chromatography (IC) in the gas and aerosol phase.

Figure 7-2 shows the temporal development of ozone, CO and four different m/z-signals measured with the PTR-MS over 20 hours.
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Figure 7-2: Mixing ratio vs. time for O$_3$, CO and the m/z 73, 89, 121, 135 corresponding to methylglyoxal, pyruvic acid, TMB and 3,5-dimethylbenzaldehyde, respectively, measured with the PTR-MS. Starting conditions: 490ppbv TMB. TMB was calibrated with a gas standard while the other mass signals were converted to mixing ratios using the reaction rate constants $k_{73}=2.05 \cdot 10^{-9}$, $k_{89}=3.5 \cdot 10^{-9}$, $k_{135}=4.09 \cdot 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The m/z-signals are assigned to protonated TMB (121), methylglyoxal (73), pyruvic acid (89) and 3,5-dimethylbenzaldehyde (135) as the most probable compounds. In principal other isobaric species or fragments could also contribute to the signal strength.

The PTR-MS data show that after an initial build-up during 3-6 hours most compounds are present in the smog chamber for many hours and decay only very slowly. Thus it is likely that also first generation reaction products such as methylglyoxal participate in the polymerization process till the end of the experiment. However, we do not exclude participation of second (or later) generation products in the polymerization.

The amount of gas phase material required for the polymerization is quite small: if we assume that 50% of the particle mass ($\approx 85\mu g/m^3$ for an initial TMB mixing ratio of 650ppbv) is a polymer composed of monomers with 50Da, then we need about 45ppbv of monomers. If we further assume that about 10 different monomer types participate in the polymerization then each of them is consumed by less than 5ppbv, which decrease will take place over a time period of about 15hrs. Thus, this small consumption will not be visible in any gas phase measurements. In the low
concentration case, 50% of the particle mass correspond to 1.4µg/m³, resulting in an expected decrease of less than 0.1ppbv for each of the assumed 10 monomers.

7.3.3.7 IR spectroscopy

SOA particles were collected on ZnSe impactor plates for IR spectroscopic analysis. Figure 7-3 shows IR spectra of samples collected 3hrs, 10hrs and 20hrs after start of the photo-oxidation experiment.

![IR spectra of SOA particles](image)

Figure 7-3: Infrared spectroscopy measurements obtained from SOA particles formed during photo-oxidation of TMB. Samples were collected on ZnSe impactor plates 3hrs, 10hrs and 20hrs after start of the photo-oxidation.

The OH-stretch band (3000-3600cm⁻¹) and the C=O band (1750cm⁻¹) are significantly broadening over time. The areas of these two peaks, normalized to the intensity of the CH band (2900-3000cm⁻¹), are broadening by a factor of 1.3 and 2.6 between the first and the third spectrum, respectively, indicating continuous chemical changes of the particles over a prolonged time.
7.4 Results and Discussion

Figure 7-4 shows a mass spectrum obtained with Laser Desorption/Ionisation Mass Spectrometry (LDI-MS) from an SOA sample collected 5-7.5hrs after start of the photo-oxidation.

![Mass Spectrum](image)

Figure 7-4: Laser desorption/ionisation time-of-flight mass spectrum (LDI-MS) of secondary organic aerosol resulting from photo-oxidation of 650ppbv 1,3,5-trimethylbenzene in the range of 50< m/z <1000. The particles were analyzed without further pretreatment after collection on steel plates using an impactor. Inset: a detail from 480< m/z <525 showing the repetitive groups with Δm/z of 14.

A large number of compounds up to a mass region of about m/z =1000 is seen. The group of peaks in the range 400<m/z<900 shows highly regular mass differences of m/z 14, 16, and 18 (see Figure 7-4, inset). Such a regular structure is typical for polymers, suggesting that polymerization reactions are taking place in the aerosol particles. TMB has a mass of 120Da, whereas masses up to m/z=900 become gradually visible with increasing intensity within 7.5 hrs after particle nucleation (Figure 7-5A to D).
Figure 7-5: Time evolution of polymers in SOA from 1,3,5-trimethylbenzene measured with LDI-MS after (A) 2.5hrs, (B) 3.5hrs, (C) 4.5hrs and (D) 6.5hrs. After 2.5hrs of irradiation, only a few peaks are detected at m/z> 400 (A). With increasing time the molecular size distribution shifts to higher masses. After 3.5hrs (B) the polymer structure for 400< m/z <600 becomes visible. Another hour later, the high mass end of the polymer distribution (600< m/z <900) becomes more visible (C) and the maximum of the polymer mass distribution shifts gradually to higher masses (up to about m/z=500 after 6.5hrs, (D)). LDI-MS of (E) methylglyoxal-oligomers and (F) of a synthetic mixture of methylglyoxal, pyruvic acid, formaldehyde, and 3,5-dimethylbenzaldehyde.
During the whole time peak intensities change, while the profile remains unchanged. Measurements of the gas and particle phase with GC-MS and ion chromatography (IC) showed that about 30 small carbonyls and acids are produced as reaction products of TMB. Most of these compounds were previously found by other authors (Smith et al., 1999; Yu and Jeffries, 1997). One of the most abundant gas phase oxidation products of TMB (with a molecular yield of about 0.9 (Smith et al., 1999)) is methylglyoxal, a C$_3$-dicarbonyl, which is also found in the ambient atmosphere up to ppbv mixing ratios (Grosjean et al., 1996).

An aqueous solution of glyoxal is primarily composed of hydrated monomers but also contains a significant fraction of dimers and trimers forming acetals (Chastrette et al., 1983; Whipple, 1970). NMR measurements indicate that the equilibrium is shifted to higher acetal polymers with lower water content of the solution. LDI-MS measurements of methylglyoxal showed oligomers up to the 9-mer with m/z=723 (Figure 7-5E). Several hydrates for each oligomer were detected, with the dihydrate being mostly the prominent peak, confirming the above NMR studies.

An LDI mass spectrum of an equal-mass aqueous solution of methylglyoxal, formaldehyde, 3,5-dimethylbenzaldehyde, and pyruvic acid (all known oxidation products of TMB), a viscous liquid when dried, is shown in Figure 7-5F. An oligomer pattern similar to the TMB-SOA is observed in the range of 400< m/z <900 (Figure 7-5D). Based on the above-mentioned NMR studies and our LDI-MS measurements, Figure 7-6 shows the proposed non-radical induced acetal polymerization with methylglyoxal as the main monomer unit.
Figure 7-6: Chemical structure and formation reactions of the proposed SOA polymer from aromatics oxidation. Acetal polymers are formed from carbonyls and hydrated carbonyls or other alcohols. Route (A) shows a pure methylglyoxal polymer and route (B) and (C) the incorporation of 3,5-dimethylbenzaldehyde and pyruvic acid, respectively, into the polymer.

However, as shown for 3,5-dimethylbenzaldehyde and pyruvic acid, other carbonyls as well as carbonyl-containing acids may also be incorporated into the polymer (Chastrette et al., 1985). Although no evidence was found in these NMR analyses (Chastrette et al., 1983; Chastrette et al., 1985) other non-radical reactions such as aldol condensation reactions could occur in the complex organic mixture of the aerosol.

The repetitive groups of 4-5 compounds at 400< m/z <900 with mass differences of 14, 16, and 18 (Figure 7-4, inset) can be explained with the formation of hydrates (Δm/z=18), the addition of an acid instead of a carbonyl (that is, pyruvic acid instead of methylglyoxal, Δm/z=16), or the incorporation of compounds which have a mass equal to a multiple of 14, 16, or 18 (e.g., formaldehyde with mass 30 = 14+16). The polymer can be further oxidized within the particle by UV light or OH radicals, also resulting in mass increases.

All of the 4-5 highest peaks of the repetitive groups in this mass range can be explained by linear combinations of these four proposed monomers (methylglyoxal, formaldehyde, 3,5-dimethylbenzaldehyde, pyruvic acid), which are measured by PTR-MS during the full course of the experiment (Figure 7-2). However, other
carbonyls (among them likely also second and third generation products) may also be incorporated into these polymers. This explains the similar but not identical mass pattern for the SOA and the surrogate mixture spectra.

The polymer proposed in Figure 7-6 has a low carbon-to-oxygen atomic ratio of about 1:1; depending on the degree of oxidation. High-resolution mass spectrometry of the TMB-SOA samples with Fourier-Transform Ion Cyclotron Resonance (FT-ICR-MS) with a mass accuracy of about 10ppm supports this hypothesis. Assuming only C, H, and O atoms as constituents, the analyzed peaks (e.g., 463.17, 479.15, or 507.18) have a C:O ratio of 1:0.7 – 1:1.6. All SOA constituents identified so far in the literature were small, up to approximately 200Da (Cocker et al., 2001; Forstner et al., 1997; Jang and Kamens, 2001). The identification of acetal polymers as a major class of compounds will strengthen the qualitative and quantitative understanding of SOA formation.

A Volatility Tandem Differential Mobility Analyzer (VTDMA) was employed to quantify the polymer fraction (Rader and McMurry, 1986). Size reduction of the aerosol due to evaporation at 100, 150, and 200°C is detected. The VTDMA particle size selection ranged from 15 to 240 nm depending on the peak evolution of the size distribution.

The increase with time in the remaining volume fraction of particles after passing through the VTDMA at the three temperatures is shown in Figure 7-7.
Figure 7-7: VTDMA data from eight independent experiments. In contrast to the data at 100°C, the changes at 150°C and 200°C reflect a higher degree of polymerization and correspondingly lower volatility. The solid symbols are high concentration (650 ppbv TMB, 320 ppbv NOx) data; open symbols are low concentration (20 and 40 ppbv TMB, 10 and 20 ppbv NOx) data. This decrease in volatility is explained with continuing polymerization reaction within the aerosol particle. Polymerization at the lower concentration occurs more rapidly for the first 9 hour of irradiation; however, after this time the rate is slower than at high concentrations.

The high concentration (650 ppbv TMB, solid symbols) data show that after approximately one hour of irradiation, the particle volume fraction remaining at 100°C gradually increases from about 30% to more than 85% over the course of 27 hours. While the initial 30% non-volatile fraction at 100°C is interpreted to be due to low volatility monomers or small oligomers, the increase over time from 30% to more than 85% is mostly due to polymer formation. Similar trends were measured at 150°C and 200°C. These changes correspond to the temporal evolution of the mass spectra as discussed above.

Preliminary hygroscopicity TDMA measurements indicate no significant increase in hygroscopic growth of the particles after the first 8 hrs (with a growth factor of 1.10). This is an additional indication that polymers and not highly oxidized reaction
products (i.e., more hygroscopic compounds such as multifunctional acids) are mainly responsible for the increasing low-volatility fraction. After the initial build-up of the aerosol phase (0-5hrs), the aerosol volume (Figure 7-1) slowly increases. The mixing ratios of most of the ~40 gas phase products (Figure 7-2) remain constant or decrease slowly after this time (with the exception of the build-up of CO, methanol and small acids). These small changes in the gas phase are still much greater than the changes observed in the aerosol phase. Assuming 10 monomers to participate in the polymerization, only a few ppb are needed of each single monomer to build up the polymer. A change in chemical structure is also observed by IR spectroscopy, with a continuous broadening of the OH stretch and the C=O bands indicating that these groups get more pronounced over a prolonged time scale (Figure 7-3).

The results of experiments, performed with the use of atmospherically relevant initial mixing ratios (open symbols) of 40 and 20ppbv of TMB (20 and 10ppbv NOx, respectively), are also shown in Figure 7-7. At these lower concentrations, particles were observed to initially (1-9hrs) have higher volume fractions remaining for the same irradiation time. For example, after approximately 5 hours, the 100°C data have a volume fraction remaining value of 62%, in contrast to a value of 50% for the high concentration data at the same time and temperature. This higher initial polymerization rate could be explained by a higher surface to volume ratio of the particles in the low concentration case, resulting in a higher reaction rate for surface limited processes. However, there are also other possible reasons like higher acid concentrations in the aerosol (enhancing acid catalyzed reactions), or higher monomer concentrations in the aerosol (yielding a higher polymerization rate).

In contrast to the experiments of Jang et al. (2002), polymerization proceeds here without pre-existing strong acids on seed particles. SOA was formed here by homogeneous nucleation without any seed particles. Thus the only acids present in the system are formed in the photo-oxidation of TMB and NOx. Organic acids belong to the final oxidation products of organic compounds and thus increase over the whole time of the experiments in the gas and the aerosol phase. Organic acids collected after 2-6 hrs of irradiation and determined by IC (including formic, acetic acid and dicarboxylic acids) amounted to 1.0 equivalents per liter corresponding to about 7% of the total aerosol mass. In addition, nitric acid was found in appreciable amounts (0.1mol/l). This compares well with the total H+ concentration from weak acids of
about 1.4 mol/l obtained for an aliquot of the same sample by micro-titration \(^7\). Acids formed in the photo-oxidation are thus present in sufficiently high concentrations to catalyze acetal polymerization reactions. These measurements show that polymerization in atmospheric aerosols takes place also without acidic seed particles and in a wide range of atmospheric conditions.

So far, this polymerization has only been shown for TMB photo-oxidation products. However, methylglyoxal and glyoxal (which also readily polymerizes) are major oxidation products of all other important aromatic compounds in the atmosphere (Calvert et al., 2002). In other words, this type of polymer is expected to be formed in significant amounts from all aromatic precursors. Since aromatics are the main anthropogenic SOA precursors, these polymers are also likely to be found in urban polluted atmospheres. The polymerization observed here continued over more than 20 hours of irradiation. Considering an average lifetime of tropospheric aerosol of one week, one can expect that polymerization reactions occur in an organic aerosol during its entire lifetime; altogether, changing its chemical and thermodynamic properties continuously. It is to be expected that polymerizing reactants are diluted in the real atmosphere by preexisting organic material. This may to some extent reduce the polymerization rate, however further experiments with organic seed particles are required to verify this hypothesis.

In addition, aldehydes are also abundant oxidation products of biogenic terpenes (e.g., pinonealdehyde or norpinonealdehyde). Thus it is likely that acetal polymers are also formed in rural areas where emissions of aromatics are small. In recent years, many studies tried to correlate ambient measurements of gaseous organic compounds with observed particle nucleation events to identify possible SOA precursors concentrating mostly on low-volatility acids or diacids (Hoffmann et al., 1998). Accordingly, a closer look into compounds such as (di-)aldehydes (which readily polymerize) as potential nucleating agents is suggested.

\(^7\) Titration was performed from a 1:1 (water:acetone) extract with 0.01 M NaOH with a 809 Titrando (Methrom, Herisau, Switzerland).
7.5 Conclusions

These findings have a number of implications for SOA modeling. Current models estimating the SOA mass formation assume a thermodynamic equilibrium of gaseous oxidation products and the particle phase (Cocker et al., 2001; Odum et al., 1997; Pankow, 1994). However, the uncertainty in the specific partitioning parameters may result in huge discrepancies. A recent comparison of SOA models found predicted SOA concentrations to vary by a factor of 10 or more, where the partitioning parameters were a key difference (Pun et al., 2003). In other sensitivity studies, reducing the saturation concentrations for all precursors by a factor of 10 increased the predicted SOA mass more than twice, while with a fixed equilibrium gas mixing ratio of 2 ppt the total SOA concentration went up by a factor 3 to 4 (Koo et al., 2003). The latter had been used in early SOA modeling (Pandis et al., 1992) and was regarded as upper limit estimate for SOA formation. Model results with low vapor pressure will also yield diurnal variations that are more similar to measurements, with the maximum concentration in the afternoon (Turpin and Huntzicker, 1991), while high vapor pressure data tend to result in a minimum in the afternoon, when temperature is highest (Sheehan and Bowman, 2001).

Consequently, modeling studies addressing mechanistic aspects of SOA formation may need to readdress the current assumptions based on the polymerization reactions proposed here. While the concept of two different vapor pressures for lumped compounds (Cocker et al., 2001) might still be applicable, current interpretations of the model parameters might need to be revised. Revised models will result in higher SOA yields, especially at higher temperature, and with different temperature dependence. Further experiments are needed to explore the absorption behavior of the high volatility fraction in the polymerizing material. Moreover, it can be expected that these polymerization reactions affect a number of other aerosol properties such as optical parameters, hygroscopic growth, and cloud condensation nuclei potential, which are crucial for the role of aerosols in the global climate system.
7.6 Acknowledgements

We thank Rene Richter and Markus Furger for their help in the smog chamber construction and instrument development, and M. Reifler, Metrohm, Herisau for performing the acid titrations. This work was supported by the Swiss National Science Foundation.

7.7 References


Chapter 8

Time Resolved Infrared Spectroscopic Analysis of Aerosol formed by Photo-oxidation of 1,3,5-Trimethylbenzene and \(\alpha\)-Pinene

Adapted from Mirjam Sax, Renato Zenobi, Urs Baltensperger, Markus Kalberer Aerosol Science and Technology, 2005, 39 (9), 822.
8.1 Abstract

Secondary organic aerosol generated from the photo-oxidation of 1,3,5-trimethylbenzene and α-pinene in a smog chamber was investigated. Fourier Transform Infrared Spectroscopy was used to monitor the time dependent change of five different functional groups in the aerosol (carboxylic acids, alcohols, organonitrates, ketones/aldehydes = carbonyls, and aliphatic carbon) sampled with an impactor on zinc selenide discs. Based on model compounds for oxidation products of 1,3,5-trimethylbenzene and α-pinene, calibration factors for the different functional groups were calculated, and relative molar fractions of the functional groups were estimated from the analysis of the IR spectra of the smog chamber samples. We show chemical evolutions of secondary organic aerosol on a time scale of up to 20h. Time series with up to eight measurements per experiment show a strong increase in the relative amounts of carboxylic acid groups and a moderate increase of alcohol and carbonyl groups, whereas the relative amounts of organonitrates and the aliphatic carbon decrease. These findings support the assumption that the chemical composition of the aerosol continues to change for a long time after the particle formation has considerably slowed down. According to these observed changes with time average sum formula of the molecules in the secondary organic aerosol are suggested.
8.2 Introduction

Hydrocarbons, aromatic and non-aromatic, are abundant pollutants in the atmosphere. The atmosphere is a well known system for transport and deposition of organic compounds (Bidleman, 1988). Atmospheric aerosols contribute to many processes, such as cloud formation and visibility reduction, and have a significant impact on air quality, climate and human health. To understand the origin of aerosols and the importance of the different sources, it is necessary to understand the chemical composition of the aerosol. Organic compounds are a major fraction of the aerosols; although hundreds of individual organic compounds have been identified (Saxena and Hildemann, 1996), only a minor mass fraction of the total organic content has been identified so far on a molecular level (Puxbaum et al., 2000; Rogge et al., 1993). Up to 90% of the organic aerosol mass in urban areas is of secondary origin (Lim and Turpin, 2002), i.e., particles that are not directly emitted but formed during oxidation processes of gaseous precursors in the atmosphere. These gaseous precursors can be of anthropogenic or biogenic origin. The total biogenic organic emissions are estimated to range up to 1150Tg year\(^{-1}\) (Guenther et al., 1995) exceeding by far the anthropogenic emissions of estimated 103Tg year\(^{-1}\) (Singh and Zimmermann, 1992). An estimated average of 18.5Tg year\(^{-1}\) of secondary organic aerosol (SOA) is formed from biogenic precursors (Griffin et al., 1999).

FT-IR spectroscopy has been used by a number of authors to investigate the chemical composition of organic aerosols. FT-IR is used to determine functional groups in the organic mass rather than individual compounds. It provides information on the overall functional group composition helping to characterize the degree of oxidation of SOA. Very little sample mass is needed due to the high sensitivity of FT-IR. Measurements can be directly made from deposited particles without extraction or other sample processing. FT-IR has been used for ambient aerosol measurements (Blando et al., 1998; Maria et al., 2002) to detect and/or quantify carbonyl-, aliphatic CH- and organonitrate functional groups (Garnes and Allen, 2002; Mylonas et. al., 1991), as well as the inorganic fraction (Allen et al., 1994; Maria et al., 2002). Russell (2003) used FT-IR spectra from ambient aerosol to calculate organic mass to organic carbon ratios.
FT-IR has been employed previously for the analysis of functional groups of SOA components in smog chamber experiments (Jang and Kamens, 2001a; Jang and Kamens, 2001b), where FT-IR was used in addition to gas chromatography-mass spectrometry to confirm the presence of organonitrates in SOA. Heterogeneous reactions involved in SOA formation were also investigated with FT-IR (Czoschke et al., 2003; Jang et al., 2002; Kalberer et al., 2004) by comparing carbonyl absorbances under different conditions. It was shown that the addition of acidic seed aerosol increases the SOA yield (Jang et al., 2002) and that chemical changes in the particle occur over prolonged time scales (Kalberer et al., 2004).

Various publications (Allen et al., 1994; Dekermenjian et al., 1999a; Dekermenjian et al., 1999b; Garnes and Allen, 2002; Holes et al., 1997; Laurent and Allen, 2004; Palen et al., 1992) used FT-IR spectroscopy to calculate molar fractions of various functional groups of organic aerosols – generated in a reaction chamber or from ambient samples. Smog chamber samples focused mainly on carbonyls showing that the molar loadings of carbonyl groups were significant. The spectra were interpreted using model compounds and were referenced to the aliphatic C-H absorption. This allows to estimate the molar loading of functional groups in SOA and to calculate the functional group distribution of average product molecules.

In this study we generated SOA particles in smog chamber experiments from an anthropogenic gaseous precursor, 1,3,5-trimethylbenzene (TMB), and a biogenic gaseous precursor, α-pinene (APIN). The gas phase oxidation of APIN (Jang and Kamens, 1999; Kamens et al., 1981; Yu et al., 1999; Zhang et al., 1992) and TMB (Cocker et al., 2001; Hamilton et al., 2003; Kleindienst et al., 1999; Smith et al., 1999; Yu et al., 1997) has been well studied in the literature. The methods mostly included filter sampling of the particle phase, extraction and gas chromatography mass spectrometry analysis of single compounds.

Using FT-IR spectroscopy, the focus of our study was to determine the temporal changes of a variety of functional groups in the SOA as indicators of an ongoing oxidation in the SOA particles. We present for the first time a temporal evolution of five different functional groups in SOA generated in a smog chamber over an extended time period. During the SOA formation in TMB and APIN systems, aerosol mass growth slows considerably after 4-5 hours in the smog chamber. However, a slow oxidation of the particle bulk continues over a time period of more than 20h. We
observed a strong increase in carboxylic acids, a moderate increase in alcohols and carbonyls and a decrease in organonitrates.

8.3 Experimental Method and Data Analysis

8.3.1 Sample preparation and measurement

SOA was produced in photo-oxidation experiments performed in the new indoor smog chamber of the Paul Scherrer Institute (PSI), Villigen, Switzerland. The smog chamber facility has been described in detail by Paulsen et al. (2005). Briefly, the chamber consists of a 27m³ Tedlar bag in a wooden housing, equipped with air conditioning. Four xenon arc lamps (4kW each) are used to simulate the solar light spectrum as closely as possible and to mimic natural photochemistry. The primary gas components such as organics, oxides of nitrogen, purified air, and water vapor are flushed into the chamber where they diffuse and mix for 30-45 minutes before the experiment is started by turning on the lights. In our experiments 1,3,5-trimethylbenzene (TMB) and α-pinene (APIN) are injected into a heated glass tube (85°C) to completely evaporate the liquid while purified air carries the vapor into the chamber. The initial hydrocarbon mixing ratios were 656 and 1312ppb for TMB (three experiments) and 300ppb for APIN (two experiments). The NO and NO₂ mixing ratios were 160ppb each (for 656ppb TMB) and 320ppb (for 1312ppb TMB) each for TMB experiments, and 120ppb for APIN (300ppb). Propene was used as radical initiator at mixing ratios of 300ppb. Relative humidity in the chamber was between 57 and 64%.

Particle formation started about 30min (for TMB) and 90min (for APIN) after turning on the lights. The size distribution was measured using a scanning mobility particle sizer (SMPS) system. The decrease of the gas phase concentration of the hydrocarbons was monitored with gas chromatography – flame ionization detection and proton transfer reaction mass spectrometry, NO and NO₂ were measured via chemiluminescence detection, and ozone was monitored by UV-absorption.

The main focus of this work is to monitor the temporal change of the functional groups present in the SOA. Seven to eight samples were collected from the beginning of particle formation up to 22h after the start of the experiment. SOA was sampled
with a 12-stage impactor (Maenhaut et al., 1996) at a flow rate of 11 lmin\(^{-1}\) for 50-120min. Zinc selenide plates (25mm * 2mm, Fluka, Switzerland) were used as impaction plates in stages 2, 3 and 4, corresponding to particle sizes of 86-153nm, 154-231nm and 232-343nm, respectively. Depending on the size of the SOA we used the corresponding impactor stage. At about 12h after switching on the light, the sampling interval was extended to 4h, because the particle number concentration decreased due to wall losses. The size distribution of the aerosol generated in a smog chamber is very narrow and no size dependence of the SOA composition could be observed. Results are thus not reported as a function of size.

Prior to the experiments ZnSe plates were cleaned in a sonication bath with acetonitrile and methanol. They are transparent to IR radiation and allow for direct analysis after sampling, without further treatment. Spectra were taken with a Perkin Elmer Spektrum BX II FT-IR instrument (Software Spektrum, version 5.0.1.). Prior to analysis the sample holder was flushed with N\(_2\) to decrease the absorption due to CO\(_2\), then 10 scans were taken at a resolution of 2cm\(^{-1}\) from 4000-600cm\(^{-1}\), using a clean ZnSe disc as background. The flushing of the spectrometer with N\(_2\) could potentially lead to off-gassing of high volatility particle components. However, the fast IR measurement (<1min) minimizes such artifacts, and repetitive measurements of the same sample did not result in measurable changes in the spectra. Thus, such artifacts are thought to be not significant. The instrument software and a scientific data processing package (Igor Pro, Version 4.09A, WaveMetrics) were used for integration of the peaks.

Spectra of the calibration compounds were taken with the same instrument. All spectra of liquid calibration compounds were obtained by directly applying a small amount of liquid between two ZnSe discs, whereas the solid calibration compounds were dissolved in a suitable volatile solvent, dropped onto a single disc and the solvent was allowed to evaporate.

### 8.3.2 Spectral Analysis

In the following, a thorough description of the spectral analysis is given explaining the method to obtain the integrated peak areas for interpreting the results in terms of possible uncertainties and intercomparison of various experiments.
The following absorbances of the smog chamber spectra were analyzed: aliphatic carbon CH (2800-3000 cm\(^{-1}\)), alcohols OH (3200-3600 cm\(^{-1}\)), carboxylic acids COOH (3200-2400 cm\(^{-1}\), 1670-1870 cm\(^{-1}\)), ketones and aldehyde (1670-1870 cm\(^{-1}\)) and organonitrates RONO\(_2\) (1230-1320 cm\(^{-1}\)). Aromatic CH absorbance is often weak around 3000-3100 cm\(^{-1}\) and covered by the broad COOH peak. No such peaks were observed in the TMB sample and thus we assumed a negligible amount of aromatic components for the TMB-SOA. Compounds with organonitrate groups show three bands at 1630 (asymmetric stretch vibration), 1280 and 850 cm\(^{-1}\) (both symmetric), and we chose the absorbance at 1280 cm\(^{-1}\) for integration due to its strong intensity and fairly good isolation. Organonitrate and carbonyl peaks were integrated using the FT-IR instrument software. Figure 8-1a (TMB) and b (APIN) show the spectra of SOA from TMB and APIN with the integration baselines for the single peaks at 1280 cm\(^{-1}\) for organonitrates and 1720 cm\(^{-1}\) for C=O.
Figure 8-1: Original FT-IR spectra from 4000-6000 cm\(^{-1}\) for SOA generated in the PSI smog chamber from TMB (a) and APIN (b). Lower traces are sections of the spectra from 4000-2000 cm\(^{-1}\) without the aliphatic CH bands. The bold dotted line is the sum of the three (TMB) and four (APIN) Gaussian functions, respectively.
To differentiate between the C=O absorbance from ketones/aldehydes and from carboxylic acids, additional spectral features have to be used, because all three functional groups contribute to the strong peak at 1720 cm\(^{-1}\). Furthermore, C=O in acids has a much higher molar absorptivity than C=O in ketones/aldehydes. In the region from 2400 cm\(^{-1}\) to 3600 cm\(^{-1}\) overlapping peaks from carboxylic acids and alcohols were separated using Gaussian curve fits. Lorentzian curve fits resulted in much less agreement with the spectra so that Gaussian curve fits were used as fit function. The O-H stretching vibration at 2400-3200 cm\(^{-1}\) (associated/H-bonded OH) due to carboxylic acids was then used for separation of ketones/aldehydes and carboxylic acids. A distinction between aldehydes and ketones was not possible, because the weak C-H absorbance of aldehydes (2720-2820 cm\(^{-1}\)) could not be observed in any of the smog chamber spectra. Figure 8-1 shows the fitted Gaussian peaks underneath the overall fit, resulting in a very good agreement with the measured absorbances. The CH absorbance between 2800 and 3000 cm\(^{-1}\) was replaced with a linear fit assuming that the CH band is superimposed on the broad O-H peak and does not contribute to the dominant O-H valence vibration from carboxylic acids in this region. The resulting broad peak originates from alcohols and acids with different hydrogen bonding features. The OH group in alcohols, usually absorbing between 3600-3200 cm\(^{-1}\), was assigned to the Gaussian fits 1 and 2 (Figure 8-1a and 1b), and OH in carboxylic acids absorbing mostly below 3200 cm\(^{-1}\) was assigned to fit 3 (Figure 8-1a) and fit 3 and 4 (Figure 8-1b). For the area from carboxylic acids in APIN, two Gaussian curves were necessary to fit the measured O-H absorption band (3034 cm\(^{-1}\) and 2611 cm\(^{-1}\)). The small peak at 2611 cm\(^{-1}\), interpreted as absorption band from associated O-H groups of carboxylic acids, is hardly visible in the TMB spectra and therefore the COOH area in TMB spectra could be fitted with one Gaussian curve (3000 cm\(^{-1}\)).

Water present in the particles would also contribute to the OH band leading to an overestimation of acids and alcohols. However, due to the following reasons the water content of the particles during the IR measurements is negligible. Liquid water has an absorption band reaching >3600 cm\(^{-1}\), which is clearly not observed in the SOA spectra (Figure 8-1, 8-2). In addition, particles experience an atmosphere in the spectrometer with a relative humidity close to 0%, due to the flushing with N\(_2\). Hygroscopic growth measurements for TMB-SOA were performed down to 15% relative humidity, where a hygroscopic growth of only 1.01 was measured.
(Baltensperger et al., 2005). Extrapolating this value to even lower relative humidities (as expected during the measurement) shows that the water content of the SOA particles during the measurement was well below 1%.

The integrated areas were used to determine the relative mole fractions of five functional groups in the SOA: alcohol group, carboxylic acid group, aliphatic carbon group, organonitrate group and carbonyl group from ketones and aldehydes. The equations presented below are adapted from Palen et al., (1992) and Holes et al. (1997). Note that the term “mole fraction” refers here to functional groups in a molecule and not entire molecules. The equations relate the integrated areas for each functional group, normalized to the CH absorbance area, to the relative molar absorptivities for each functional group derived from calibration compounds.

The relative mole fraction of the organonitrate group is calculated according to Equation 8-1 (n=number of moles, A=absorbance area of the integrated peak of the SOA spectrum, n_c=moles of calibration compound, A_c= absorbance area from calibration compound).

\[
\frac{n (RONO_2)}{n (CH)} = \frac{A (RONO_2 1280 cm^{-1})}{A (CH 2800 - 3000 cm^{-1})} \times \frac{A_c (CH) / n_c (CH)}{A_c (RONO_2) / n_c (RONO_2)}
\]

Equation 8-1

The first term on the right side of Equation 8-1, the ratio of the integrated absorbances, is calculated using the spectra from the smog chamber samples. This relative absorbance area is multiplied with the relative molar absorptivity, which accounts for the different oscillator strengths of each of the functional groups derived from the calibration compounds given in Table 8-1a and b (“calibration factors”).

- 180 -
## Table 8-1a: Relative molar absorptivities of calibration compounds used for TMB – individual values and average.

<table>
<thead>
<tr>
<th>functional group</th>
<th>absorption band in cm$^{-1}$</th>
<th>calibration compound</th>
<th>relative molar absorptivity</th>
<th>Average of relative molar absorptivities</th>
</tr>
</thead>
<tbody>
<tr>
<td>aliphatic CH</td>
<td>2800-3000</td>
<td>-</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>C=O in ketones</td>
<td>peak max between 1694 and 1720</td>
<td>4-ethylcyclohexanone</td>
<td>8.24</td>
<td>10.11$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,5-hexanediione</td>
<td>11.98</td>
<td></td>
</tr>
<tr>
<td>C=O in aldehydes</td>
<td>peak max between 1694 and 1720</td>
<td>2,5-dimethylbenzaldehyde</td>
<td>6.02</td>
<td>6.02$^a$</td>
</tr>
<tr>
<td>C=O in organic acids</td>
<td>peak max between 1694 and 1720</td>
<td>acetic acid</td>
<td>76.84</td>
<td>54.01</td>
</tr>
<tr>
<td>H-bonding of hydroxyls</td>
<td>3380 broad</td>
<td>3-methylbenzylalcohol</td>
<td>43.44</td>
<td>43.44</td>
</tr>
<tr>
<td>H-bonding of organic acids</td>
<td>3100 broad</td>
<td>acetic acid</td>
<td>301.89</td>
<td>185.69</td>
</tr>
<tr>
<td>organonitrates</td>
<td>1200-1298</td>
<td>isopropylisobutyl nitrate</td>
<td>9.76</td>
<td>7.93</td>
</tr>
</tbody>
</table>

$^a$ average of 8.07 as used in Equation 8-3a.
### Table 8-1b: Relative molar absorptivities of calibration compounds used for APIN – individual values and standard deviation (SD) for more than two compounds.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Absorption band in cm⁻¹</th>
<th>Calibration compound</th>
<th>Relative molar absorptivity</th>
<th>Average of relative molar absorptivities and SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic CH</td>
<td>2800-3000 peak max</td>
<td>2-butanone</td>
<td>10.79</td>
<td>10.77ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>methylvinylketone</td>
<td>17.43</td>
<td>(SD 3.97)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-ethylcyclohexanone</td>
<td>8.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-hydroxy-2-butanol</td>
<td>10.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-hydroxy-3-pinane</td>
<td>7.33</td>
<td></td>
</tr>
<tr>
<td>C=O in ketones</td>
<td>1694 and 1728 peak max</td>
<td>n-butanal</td>
<td>6.88</td>
<td>5.1ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>octylaldehyde</td>
<td>3.31</td>
<td></td>
</tr>
<tr>
<td>C=O in aldehydes</td>
<td>1694 and 1728 peak max</td>
<td>octanoic acid</td>
<td>13.84</td>
<td>13.84</td>
</tr>
<tr>
<td>C=O in organic acids</td>
<td>1694 and 1728 peak max</td>
<td>octanoic acid</td>
<td>13.84</td>
<td>13.84</td>
</tr>
<tr>
<td>H-bonding of hydroxyls</td>
<td>3380 broad 1-octanol</td>
<td>1-octanol</td>
<td>22.59</td>
<td>25.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-butanol</td>
<td>14.99</td>
<td>(SD 14.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-hydroxy-2-butanol</td>
<td>45.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-hydroxy-3-pinane</td>
<td>17.35</td>
<td></td>
</tr>
<tr>
<td>H-bonding of organic acids</td>
<td>3100 broad octanoic acid</td>
<td>octanoic acid</td>
<td>43.32</td>
<td>74.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cis-pinonic acid</td>
<td>105.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>isopropyl-</td>
<td>9.76</td>
<td>7.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>isobutylnitrate</td>
<td>6.09</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ average of 7.94 as used in Equation 8-3 b.

For example, isobutylnitrate has nine aliphatic CH groups and one ONO₂ group. The calibration factor is determined by dividing one ninth of the CH absorbance area by the ONO₂ area. For the CH absorption the average molar absorptivity is used, i.e., there is no distinction between acetylen, methylene and methyl absorbances. The equations for alcohol (Gaussian fits 1 + 2 in Figure 8-1a and b) and carboxylic acid (Gaussian fits 3 in Figure 8-1a and 3 + 4 in Figure 8-1b) mole fraction calculations are
analogue to Equation 8-1. The determination of the mole fraction of the C=O functional group from aldehydes and ketones in Equation 8-2 is slightly different ($X_{C=O}$ = mole fraction of the carbonyl functional group from ketones and aldehydes):

$$\frac{n(C=O)}{n(CH)} = \frac{A(C=O_{1726cm^{-1}})}{A(CH_{2800-3000cm^{-1}})} \times \frac{A_c(CH)/n_c(CH)}{\left[A(C=O)/n(C=O)\right]_{\text{average}}} \times X_{C=O \text{from carbonyls}}$$

Equation 8-2

The first term on the right side is from smog chamber spectra. The numerator of the second term is derived from the calibration sample as in Equation 8-1, whereas the denominator (see Equation 8a and b) includes the mole fraction of the carboxylic acid group from the smog chamber spectrum ($X_{COOH}$ in Equation 8a and b), which was obtained from the peak between 2400-3200cm$^{-1}$, to account for the contribution of the COOH group to the peak at 1726cm$^{-1}$. The third term is derived from the calibration compounds.

$$\left[\frac{A(C=O)}{n(C=O)}\right]_{\text{average for TMB}} = \frac{8.07 \times X_{C=O} + 54.01 \times X_{COOH}}{X_{C=O} + X_{COOH}}$$

Equation 8-3 a

$$\left[\frac{A(C=O)}{n(C=O)}\right]_{\text{average for APIN}} = \frac{7.94 \times X_{C=O} + 13.84 \times X_{COOH}}{X_{C=O} + X_{COOH}}$$

Equation 8-3 b

The relative molar absorptivities in Equation 8-3a and 3b (8.07, 54.01, 7.94 and 13.84) are obtained empirically from the calibration compounds, with an average of aldehydes and ketones, because a separation of the two groups was not possible.

Table 8-1a and b present the calibration compounds and the calculated relative molar absorptivities. They compare well with literature values from Palen et al. (1992) and (Holes et al., 1997). The calibration compounds were chosen to represent known oxidation products of TMB and APIN, e.g., acetic and formic acid were found to be abundant compounds in TMB-SOA (Fisseha et al., 2004). Some known SOA compounds could not be obtained commercially, or did not result in satisfying liquid-phase or solid-phase IR-spectra, therefore surrogates with similar ratios of CH and the
functional group of interest were used. Table 8-1a and b list the individual values for each compound measured. For each functional group with more than two calibration compounds the average values with standard deviations are given. The calibration factors in Table 8-1a and b were used to calculate the relative mole fractions (Table 8-2) of the respective functional groups in the SOA with Equation 8-1 to 8-3, assuming that only these five groups are present in the molecule and the mole fractions add up to one. Note that the term “mole fraction” denotes the ratio of moles of functional groups, not molecules.
### Table 8-2: Mole fractions of five functional groups in SOA from TMB and APIN.

<table>
<thead>
<tr>
<th>TMB sample number</th>
<th>functional groups</th>
<th>sampling time after turning on the light /h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O-H</td>
</tr>
<tr>
<td>V1</td>
<td>start 1.5</td>
<td>end 3.3</td>
</tr>
<tr>
<td>V2</td>
<td>start 4.4</td>
<td>end 5.4</td>
</tr>
<tr>
<td>V3</td>
<td>start 7.4</td>
<td>end 8.8</td>
</tr>
<tr>
<td>V4</td>
<td>start 8.9</td>
<td>end 9.9</td>
</tr>
<tr>
<td>V5</td>
<td>start 11.4</td>
<td>end 12.9</td>
</tr>
<tr>
<td>V6</td>
<td>start 13.4</td>
<td>end 16.2</td>
</tr>
<tr>
<td>V7</td>
<td>start 16.3</td>
<td>end 20.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>APIN sample number</th>
<th>functional groups</th>
<th>sampling time after turning on the light /h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O-H</td>
</tr>
<tr>
<td>V1</td>
<td>start 1.3</td>
<td>end 2.4</td>
</tr>
<tr>
<td>V2</td>
<td>start 3.1</td>
<td>end 4.2</td>
</tr>
<tr>
<td>V3</td>
<td>start 4.6</td>
<td>end 5.7</td>
</tr>
<tr>
<td>V4</td>
<td>start 6.7</td>
<td>end 8.1</td>
</tr>
<tr>
<td>V5</td>
<td>start 8.5</td>
<td>end 9.9</td>
</tr>
<tr>
<td>V6</td>
<td>start 10.3</td>
<td>end 11.6</td>
</tr>
<tr>
<td>V7</td>
<td>start 11.7</td>
<td>end 15.2</td>
</tr>
<tr>
<td>V8</td>
<td>start 17.6</td>
<td>end 21.6</td>
</tr>
</tbody>
</table>

The relative temporal changes as shown in Figure 8-3a and b are not dependent on the calibration factors, because they cancel out (see Equation 8-1), except for the CO group. The mole fraction for the carbonyl group depends on the calibration factors of both acids and carbonyls (Equation 8-2 and Equation 8a and b). The calibration factors are only relevant for the results shown in Table 8-2 and 3. Thus, these results have to be taken with care due to the partially large variations of the calibration factors in Table 8-1a and b.
8.4 Results and Discussion

Figure 8-2 gives a qualitative overview over the chemical changes of the SOA with time.

![Diagram showing IR spectra over time]

Figure 8-2: Comparison of TMB (upper two traces) and APIN IR spectra at the beginning of the experiment (2h and 1.5h, respectively, after turning on the lights) and after 13.5h and 17.5h, respectively (the vertical lines at 1726, 1652 and 1282 cm\(^{-1}\) indicate the peaks in all four spectra).

The \(\text{ONO}_2\) band at 1282 cm\(^{-1}\) and 1648 cm\(^{-1}\) clearly decreases whereas the C=O band at 1726 cm\(^{-1}\) increases and broadens. Also the O-H vibration at 2400-3600 cm\(^{-1}\) is clearly broadening. With increasing time a peak evolves at 2670 cm\(^{-1}\) for APIN (Gaussian fit 4 in Figure 8-1b), which is not the case for TMB. The APIN spectra also show an increase of the peak around 3260 cm\(^{-1}\) with time. For TMB-SOA the peak around 3400 cm\(^{-1}\) features a gradual separation into two peaks. The already broad peak around 2900 cm\(^{-1}\) becomes broader with time but no second peak around 2600 cm\(^{-1}\) evolves.

Figure 8-3 shows the temporal changes of the relative mole fraction of the functional groups C=O (from aldehydes and ketones), OH, COOH, \(\text{ONO}_2\) and CH, calculated according to Equation 8-1 to -3. Table 8-2 gives the relative mole fractions for 7 and 8.
samples as a function of time for the TMB and APIN experiment, respectively, as shown in Figure 8-3. Note that the mole fractions relate to the relative abundance of bonds of the respective functional group replacing C-H bonds in a molecule and that the five mole fractions add up to one.
Figure 8-3: Time-resolved changes of mole fractions of 5 functional groups present in SOA from TMB (a) and APIN (b).

For TMB (Figure 8-3a, Table 8-2) an increase of the abundance of COOH, C=O and OH is measured, which is in agreement with the photo-oxidation products found by
GC-MS for TMB in the aerosol phase (Yu et al., 1997; Cocker et al., 2001). According to Table 8-2, the mole fractions of the carboxylic acid group show a clear increase, starting with less than 1% (see Table 2) at the beginning to about 4% in the last sample. The alcohol and carbonyl functional groups also increase with time, however to a smaller extent. Because the carboxylic acid, alcohol and carbonyl functional groups increase with time the CH group decreases accordingly. The main oxidation pathway of TMB is via the addition of a hydroxyl radical to the aromatic ring to form an alkylated hydroxycyclohexadienyl radical (OH-aromatic adduct). The OH-aromatic adducts react predominantly with \( \text{O}_2 \) leading mainly to ring-opened products (Atkinson, 1998). Only about 3% of the initial oxidation starts with an \( \text{H} \) abstraction from one of the methyl groups maintaining the aromaticity (Atkinson, 1994). However, it is likely that part of these first generation aromatic oxidation products also undergo ring cleavage at a later stage. Therefore it can be expected that the aromatic content in aged SOA (i.e. after 2-3h) is likely very small, which is supported by the lack of aromatic CH bonds in the IR spectra of TMB-SOA. The trends described here are in agreement with other TMB experiments performed under the same conditions (not shown here).

In APIN-SOA (Figure 8-3b, Table 8-2) the carboxylic acid mole fraction more than doubles over the 22h of the experiment (from 3% to 8%, Table 8-2), which is a smaller increase than for TMB. The significance of carboxylic acids in APIN-SOA was also reported by others (Jang and Kamens, 1999; Yu et al., 1999). The ketone/aldehyde and the alcohol fraction increase by a factor of about 1.5, similar to the TMB-SOA. Other authors found that gas phase carbonyls are the major reaction products in APIN oxidation (Glasius et al., 2000; Tolocka et al., 2004) with all ring opening products due to ozonolysis of the double bond leading to carbonyls, however, in SOA only low concentrations were found so far. The \( \text{ONO}_2 \) and aliphatic CH groups decrease in APIN at about the same rate as in TMB-SOA. For both SOA types the increase in COOH is the highest, but major changes are also observed for the carbonyl and OH functional groups.

In Table 8-3 the relative mole fractions from Table 8-2 are converted into an average amount of each functional group in a hypothetical molecule, and respective sum formula are given.
Table 8-3: Functional group distribution in an hypothetical average SOA molecule from TMB and APIN.

<table>
<thead>
<tr>
<th>TMB – C6 sample number</th>
<th>sum formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>C_{6}H_{16}(=O)<em>{1.3}(OH)</em>{1.4}(OOH)<em>{0.3}(ONO</em>{2})_{0.8}</td>
</tr>
<tr>
<td>V4</td>
<td>C_{6}H_{16}(=O)<em>{1.6}(OH)</em>{2}(OOH)<em>{0.4}(ONO</em>{2})_{0.4}</td>
</tr>
<tr>
<td>V7</td>
<td>C_{6}H_{16}(=O)<em>{2.2}(OH)</em>{2}(OOH)<em>{0.6}(ONO</em>{2})_{0.2}</td>
</tr>
<tr>
<td>APIN – C10 $^a$ sample number</td>
<td></td>
</tr>
<tr>
<td>V1</td>
<td>C_{10}H_{16}(=O)<em>{1.7}(OH)</em>{0.4}(OOH)<em>{0.4}(ONO</em>{2})_{0.4}</td>
</tr>
<tr>
<td>V5</td>
<td>C_{10}H_{16}(=O)<em>{2.0}(OH)</em>{2}(OOH)<em>{0.3}(ONO</em>{2})_{0.3}</td>
</tr>
<tr>
<td>V8</td>
<td>C_{10}H_{16}(=O)<em>{2.3}(OH)</em>{1.6}(OOH)<em>{0.6}(ONO</em>{2})_{0.2}</td>
</tr>
</tbody>
</table>

$^a$average of typical APIN oxidation products (Glasius et al., 2000; Tolocka et al., 2004).

For TMB, an average molecular structure was assumed with 6 aliphatic carbons and a maximum of 14 C-H groups, assuming ring cleavage reaction products. C6 molecules are abundant oxidation products of TMB (Kleindienst et al., 1999). For APIN, hypothetical oxidation molecules with a four-membered ring after ozonolysis of the double bond were assumed, resulting in a molecule with 10 carbon atoms and at most 15 C-H bonds.

For TMB, a major increase with time is observed for carbonyls, alcohols and carboxylic acids, with carbonyls and alcohols as dominating groups (about 2 carbonyl and alcohol groups per molecule in a TMB-C6 molecule). In a recent publication by Fisseha et al. (2004) analyzing TMB-SOA with ion chromatography combined with mass spectrometry, an acid contribution up to 45% of the total aerosol mass was observed. Their experiments show a relative increase of the total acid fraction of about a factor of 1.5 in the first 7.5h of the experiment. Our data compare reasonably well, as we observe an increase of the acid mole fraction by a factor of three in the first 7.5h. This translates for TMB-C6 molecules into an increase in carboxylic acids from one in ten molecules (V1, Table 8-3) to 4 in 10 molecules (V7, Table 8-3) corresponding to an acid concentration of about 40%, which compares well with the results from Fisseha et al. (2004).
The SOA from APIN is also dominated by carbonyl and OH groups, although slightly less alcohols are present than in TMB. The number of COOH functional groups more than doubles during the experiment. Alfarra et al. (2005) showed in a recent study with an aerosol mass spectrometer that the relative intensity of a mass fragment, assigned to carboxylic acids, increases significantly during the eight hours of the experiment. They also observed a substantially larger increase of acids in TMB-SOA compared to APIN experiments. Spectra from both compounds were dominated by mass fragments assigned to carbonyls and carboxylic acids. Generally, the studies of Fisseha et al. (2004) and Alfarra et al. (2005) are in good agreement with the main results reported here.

In Table 8-3 and Figure 8-3 no error bars for the mole fractions are indicated. Equation 8-1 to -3 show that the calculated mole fractions depend directly on the model calibration compounds. Palen et al. (1992) report for a model compound of the same carbon number a 25% difference in molar absorptivity. This generates an uncertainty of 10-20% in SOA composition based on FT-IR measurements. Not using the actual aerosol product but model compounds creates additional uncertainties. Figure 8-3a and b show the changes of the relative mole fractions of all functional groups with time, according to Equation 8-1 to -3 and using the calibration factors in Table 8-1a and b. However, since the first value is set to one the calibration factors of Table 8-1 do not influence the slope of the curves except for the mole fraction of the C=O group. For the C=O group the molar absorptivity of the COOH group has to be considered, because the peak at 1726cm\(^{-1}\) is due to C=O from aldehydes, ketones and carboxylic acids. The accuracy of the calibration factors influences only the absolute numbers of the relative mole fractions (Table 8-2) and the average sum formula deduced (Table 8-3) but not the relative changes of the mole fractions shown in Figure 8-3a and b, except for the C=O group.

For TMB, three experiments were conducted. By comparing the trends of the functional groups over 16.3h (=running time of the shortest experiment) a very good agreement with Figure 8-3a can be observed for all experiments. At the end of the experiment i.e., after 16.3h the relative standard deviation in percent ranges between 4-39% for the different functional groups (19% for OH, 30% for CO, 4% for CH, 23% for ONO\(_2\), and 39% for COOH). For APIN only two experiments were performed, with very good trend agreement with Figure 8-3b during 15.3h (=running time of the shortest experiment). The values at 15.3h after the lights were switched on
differ only by about 3% for OH, 16% for CO, 4% for CH, 13% for ONO$_2$, and 15% for COOH. In both cases, the COOH and CO values show the largest variation. Despite these uncertainties FT-IR spectroscopy can be used to determine the distribution of functional groups in the aerosol and especially their relative changes with time during the course of an experiment. By intercomparison of different experiments the above-mentioned uncertainties have to be taken into account, but the observed trends are consistent throughout the experiments.

8.5 Conclusions

This work demonstrates the use of FT-IR spectroscopy to monitor the continuous changes of functional groups of SOA from the photo-oxidation of TMB and APIN in a smog chamber. A time resolution of 2-4 hours during 22h was obtained for five different functional groups (alcohol, organonitrate, carboxylic acid, carbonyl and aliphatic CH) by integrating their absorbances in the spectra. TMB and APIN both show a strong increase in COOH, carbonyls and OH groups; while carbonyls and alcohols are the dominant functional groups in the SOA. ONO$_2$ plays a minor role for both SOA types as the low content per average molecule is decreasing with time to even lower values. The data show an ongoing oxidation in the SOA over the course of an experiment (up to 22h). This is in contrast to the aerosol mass evolution, which slows down considerably after about 4-5h. This long-term continuous change of the chemical composition of the particle is not inconsistent with recent studies showing oligomerization processes (Kalberer et al., 2004), which also proceed over tens of hours. Heterogeneous oxidation reactions of aerosol components or continuous uptake of highly oxidized compounds from the gas phase could contribute to the observed increase in oxidized functional groups. Incorporation of carbonyl and carboxylic acid functionalities into the oligomers could be a possible reason for their strong and continuous increase. The organonitrate functional group, however, might not take part in the oligomerization process, so that possible losses such as further reactions, or desorption into the gas phase could occur.
8.6 Acknowledgement

This work was supported by the ETH grant TH-10./01-2, the Swiss National Science Foundation and the EC project EUROCHAMP. We thank the smog chamber crew at the Paul Scherrer Institute for their help during the experiments.

8.7 References


Chapter 9
Derivatization of carbonyl functional groups in SOA – Method development
9.1 Introduction

Carbonyl compounds, C=O (aldehydes and ketones), play an important role in many environmental oxidation processes. They are byproducts of incomplete combustion and intermediates in the atmospheric oxidation of organic compounds (see Chapter 1). Some carbonyls undergo photolysis and are therefore important radical producers, necessary to produce tropospheric ozone.

Photo-oxidation of aromatic compounds leads to ring-opening products, and the radical induced oxidation leads to the formation of carbonyl containing compounds, mono- and multifunctional (Calvert et al., 2002). The oxidation of monoterpenes also yields multifunctional products, the functional groups being aldehydes, ketones, carboxylic acids and alcohols (Yu et al., 1999). So far, only a minority of all products of atmospheric oxidation processes has been identified. Carbonyls, especially multifunctional carbonyls, such as hydroxy carbonyls and dicarbonyls are often among the missing carbon due to a lack of suitable analytical techniques (Yu, 1996).

Detecting and measuring the various carbonyl compounds are essential steps to understand and explain the importance of the various fates and reactions related to the parent hydrocarbon. Oxidation to C=O groups changes the polarity and therefore water solubility, which is important regarding the possible health impacts of SOA e.g. due to uptake into the lung. The approach followed in this thesis is the analysis of the overall carbonyl concentration within the duration of a smog chamber experiment.

Thus, not the sum of all single derivatized carbonyls is determined, but the overall carbonyl content, which is so far an unknown parameter in SOA analysis, is calculated from the consumption of the derivatization agent. The focus of this study was to determine the temporal changes of the carbonyl functional groups in the SOA as indicators of an ongoing oxidation in the SOA particles. These changes would support the assumption that the chemical composition of the aerosol continues to change for a long time after the particle formation has slowed down.
9.1.1 Methods for the measurement of carbonyls

To measure carbonyl compounds in gaseous and/or particulate samples, a variety of techniques has been employed, mostly GC and high performance liquid chromatography (HPLC). The problem with direct GC measurement is the high polarity of the compounds, their volatility and also the thermal stability in the system. Chromatographic techniques coupled with a derivatization method have been proven very useful in identifying C=O compounds. There is a large number of derivatization agents for carbonyls (and other functional groups, see Chapter 11), e.g. 2,4-dinitrophenylhydrazine (DNPH). DNPH, usually used with an HPLC-UV-system, has some disadvantages, such as the failure in distinguishing α–hydroxy carbonyls from the corresponding dicarbonyls, or the lack of direct information about unidentified carbonyls (Yu et al., 1995). Another derivatization agent has been found and used with great success: O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine, PFBHA. The review of Cancilla and Que Hee (1992) describes the initial use of PFBHA for identification of steroids by oxim formation. The oxims were found to be easily separated and stable under a variety of analytical conditions. PFBHA was used for the derivatization of a wide variety of metabolic products and drugs, for determination of acetaldehyde in blood or to monitor enzymatic reactions in aqueous solutions. Environmental applications of PFBHA are, e.g., the analysis of contaminants in drinking water (Cancilla et al., 1992; Glaze et al., 1989). The chromatographic method used was usually GC, coupled with flame ionization detector (FID), electron capture dissociation (ECD) or MS. Lelacheur et al. (1993) developed a method for PFBHA derivatization with GC-MS for model compounds relevant to aquatic and atmospheric systems. Yu et al. (1995, 1997, 1998) modified the technique to analyze gaseous and particulate carbonyls from smog chamber studies.

So far, the methods used focused on the identification of single oxidation products. The limit in analyzing single carbonyls is the amount available, especially in atmospheric samples. In smog chamber experiments the amount of parent hydrocarbon can be increased to increase the mass of the products, but only within reasonable limits, that is to still mimic atmospheric reaction conditions.
9.1.2 Derivatization with PFBHA

PFBHA has proved to be a valuable derivatizing agent for the analysis of C=O compounds. PFBHA readily forms oxims (Figure 9-1) in both aqueous and organic solutions over a wide pH range.

PFBHA forms two geometric isomers. The dashed line indicates the prominent MS ion m/z 181 used for identification of carbonyl compounds and PFBHA itself.

Figure 9-1: Derivatization reaction of PFBHA with a carbonyl compound. PFBHA forms two geometric isomers. The dashed line indicates the prominent MS ion m/z 181 used for identification of carbonyl compounds and PFBHA itself.

PFBHA has to be added in at least 10fold excess to assure full derivatization even of sterically hindered and/or multifunctional carbonyls. The procedure used for model compounds in atmospheric samples (Yu et al., 1995) was adapted from the one described by Cancilla et al. (1992). Basically, the PFBHA solution in water and AcN (a minimum amount of water is necessary to dissolve PFBHA) is added at room temperature (RT) to the solution containing the C=O compounds. The mixture was allowed to stand at RT for 16-24h. This time span is necessary to assure full derivatization of e.g. dicarbonyls like glyoxal or methylglyoxal, which require a longer derivatization time (Yu, 1996). The method used in the mentioned publications was to acidify the mix with HCl after standing to keep the excess PFBHA in the aqueous phase; the oxim derivatives were extracted with hexane and measured with GC-MS.

For many smog chamber samples (Yu et al., 1998; Yu et al., 1999) a two-step derivatization technique was employed, to first derivatize C=O groups and then hydroxyl groups by applying a silylation agent. The PFBHA derivatives often show multiple peaks for non-symmetric parent carbonyls (Figure 9-1) and these isomers can often be resolved by the GC-column. A rather apolar GC column usually resolves the
derivatives very well. The mass spectra of the derivatization products show a common ion fragment at m/z 181, the pentafluorotropylium ion \([\text{C}_6\text{F}_5\text{CH}_2]^+\) (indicated with a dashed line in Figure 9-1). This ion can be used to identify compounds bearing carbonyl groups, especially in a mix of tens of oxidation products from atmospheric samples. Further common fragments are the molecular ion M or M-197, that is \([\text{M-C}_6\text{F}_5\text{CH}_2\text{O}]^+\). The 181 ion, besides serving as indicator for C=O compounds, is suitable for quantification due to its strong intensity.

As mentioned before, we are interested in the overall carbonyl content and therefore the single compound analysis is not suitable. Firstly, there are still many unknown peaks in a smog chamber chromatogram from either TMB or APIN. Due to fragmentation with EI, the molecular ion is sometimes very weak or not present at all (Lelacheur et al., 1993), hampering the identification of unknowns, thus rendering the quantification impossible. Secondly, there might be carbonyls with too low a concentration to be detected. Besides, PFBHA derivatizes only carbonyls, but many oxidation products contain more than one functional group. Identification of these products is impossible if there is no indication what and how many other functionalities are present. In addition, multifunctional compounds might still be too polar to be transported through the GC column, e.g., C=O groups and acid groups. Therefore we decided to monitor the decrease of the derivatization agent PFBHA itself to account for the amount of carbonyls present in a sample, which has not been done so far. For the experimental procedure it involves only adding PFBHA solution, allowing the mix to react and directly measure with GC-MS.

### 9.2 Gran Plot

By determining the amount of PFBHA, the amount of reacted carbonyls can be calculated, as the ratio PFBHA to C=O is 1:1. For quantification of PFBHA the ratio of m/z 181 to an internal standard is applied.

The problems arising with monitoring PFBHA are the following: the amount of C=O in the sample is not known and PFBHA has to be added in an at least 10fold excess; thus, a small decrease of a big signal in a calibration curve increases the uncertainties. Therefore we decided to use a titration curve (Figure 9-2) to determine the equivalence point (EP) where the ratio PFBHA to C=O is 1:1.
Figure 9-2: Alkalimetric titration of rainwater (a) and the Gran Plot (b) derived from the titration shown in (a) as dotted line. The dashed line indicates the association between the pH jump in (a) and $e_1$ (adapted from Stumm and Morgan (1996)).

Figure 9-2a shows a titration curve for a strong acid titrated with a strong base (solid line); the pH jump indicates the EP. The dotted line shows the titration of rainwater, which consists of a mix of strong and weak acids with a strong base. The pH jump for the weak acids is not sharp, but rather blurred. The Gran plot (Figure 9-2b) allows to determine the EP of the strong acid ($e_1$) and the EP of the total acidity ($e_2$). The
Chapter 9  Derivatization of carbonyl functional groups

difference \((e_2 - e_1)\) is the sum of the weak acids; the total acidity is the sum of mineral acidity (strong acids) and acidity of the weak acids. With the titration curve shown in (a), determination of \(e_2\) is not possible. Note that the EP for strong acids is the same, with and without weak acids present (solid and dotted line in Figure 9-2a are the same until the pH is ca. 8). For the Gran plot, the added volume of base (or here: PFBHA) has to be known as well as the volume at beginning of the titration.

The “titration” of carbonyls with PFBHA corresponds to the titration curve “strong acid – strong base”, where the PFBHA peak areas replace the pH value and the added amount of PFBHA replaces the added amount of base. Practically, a titration with as many points as required to exactly define the EP is not possible. After each addition of PFBHA a reaction time of 16-20h is required to ensure complete derivatization of all carbonyls. A titration curve that takes 15-20 days to complete is not reasonable. To exactly determine the EP, pH measurements (or peak areas in case of PFBHA) before and after the pH jump are necessary. However, there is no signal if all PFBHA is used up by the derivatization reaction.

As can be seen in the Gran plot, \(e_1\) and \(e_2\) are determined by linear extrapolation of the Gran functions (solid lines in Figure 9-2b). That means for the rainwater titration, \(e_2\) is determined from the part of the titration curve where the pH does no longer change substantially. For the PFBHA titration a large excess of PFBHA over C=O is necessary, meaning when no PFBHA is consumed anymore after addition of PFBHA, then the requirements for the Gran plot are fulfilled. Also, the Gran plot takes into account the gradual dilution of the solution by adding PFBHA solution.

9.3  Experimental

All chemicals were purchased from Fluka. The titrations were carried out at RT. Until analysis the filters were stored in the fridge to prevent volatilization; the filters were transported with cooling units in a cooling box.

9.3.1  Sampling setup

For sampling, Fluoropore\textsuperscript{TM} Membrane Filters (Millipore Switzerland, Volketswil), pore size 3\(\mu\)m were used. The filters were cut out for a diameter of 15mm, cleaned in
toluene (15min sonication) and air dried in the hood. With GC-MS no peaks were observed with and without derivatization with PFBHA with blank, cleaned filters. Figure 9-3 shows the sampling setup for the filter samples.

Figure 9-3: Schematic of the sample setup for the filters (F). The setup is inside the wooden housing of the smog chamber to ensure constant controlled temperature. Samples are taken from the center of the smog chamber.

The setup consists of two Teflon filters in a row. Quartz filters are more susceptible to adsorption of gaseous organics than Teflon filters due to the larger surface; and the surface is not chemically inert, unlike Teflon (Turpin et al., 1994). However, also for Teflon filters positive (adsorption) artifacts lead to an overestimation of the organic aerosol mass concentration. The dual filter strategy is to correct for possible positive sampling artifacts. It relies on the assumption that the front filter collects all particles and becomes saturated with adsorbed gaseous organic species, whereas the back filter collects only gas-phase species up to saturation. It has been shown that Teflon filters reach saturation and therefore equilibrium between gas and particle phase faster than quartz filters (Mader and Pankow, 2001). The difference between front and back filter gives then the corrected aerosol mass.

Negative (volatilization) artifacts are in general less significant than positive artifacts (Gelencser, 2004); they are affected most by temperature. To minimize losses, a change in temperature during sampling should be avoided. This is ensured by sampling inside the temperature-controlled wooden chamber.
9.3.2 Sampling and Titrations with PFBHA

Smog chamber experiments

The experiments were performed at the smog chamber at PSI (see Chapter 4). In these experiments TMB and APIN are injected into a heated glass tube (85°C) to completely evaporate the liquid while purified air carries the vapor into the chamber. The initial hydrocarbon mixing ratios were 1312 ppb (200 µl) for TMB and 300 ppb (54 µl) for APIN. The NO and NO$_2$ mixing ratios were 320 ppb each for TMB and 120 ppb each for APIN. Propene was used as radical initiator at mixing ratios of 300 ppb. Relative humidity in the chamber was between 50 and 67%. Particle formation started about 15 min (for TMB) and 30 min (for APIN) after turning on the lights. Particle formation from APIN occurs later, but is then followed by a higher growth rate, resulting in significantly larger particles.

Figure 9-4 shows the course for the particle volume concentration of an experiment for TMB for about 10 h. Filter samples (front and back) were taken during the indicated times. The decrease in particle mass concentration after reaching the maximum concentration is due to wall losses.
Figure 9-4: Integrated volume concentration for a typical TMB experiment (nominal initial conditions: 1300ppb TMB, 320ppb NO and NO₂ each). The vertical lines show the time slots when filter samples were taken (F1-F5).

PFBHA was dissolved in AcN with a minimum amount of water with a concentration of 16mg/ml. The internal standard (IS) used was nonadecane - C₁₉H₄₀ - in hexane with a concentration of 5mg/ml. The sampling duration of the SOA was between 50min and 90min with flowrates between 19-27l/min. Per experiment five samples in time were taken, that is 10 filters (front and back).

After sampling, the filters were transferred to a glass vial; 2ml AcN and IS were added and the samples were extracted 15min in a sonication bath; the filter was removed and discarded. Because after each addition the reaction time was 16-20h, only one point in the titration curve per day can be obtained. To speed up the process, each sample (e.g. F1) was split in two equal parts, 1ml each (=F-1a and F-1b). 1ml was transferred to another vial, the reminder stayed in the extraction vial and PFBHA was added according to the schedule (see Table 9-1). This was done right after sampling at PSI. Later additions were done at the lab at ETH. Per filter 5 data points were obtained in 3 days. Until analysis the solutions are stored in the fridge.
Table 9-1: Protocol for addition of PFBHA to the filter samples from TMB and APIN. (DOS= day of sampling, )

<table>
<thead>
<tr>
<th>2ml divided in</th>
<th>PFBHA added at DOS in the ratio PFBHA:CO</th>
<th>PFBHA added at day 1 after reaction time</th>
<th>PFBHA added at day 2 after reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x1ml</td>
<td></td>
<td>16-20h reaction time</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-1a</td>
<td>10:1</td>
<td>15:1</td>
<td>30:1</td>
</tr>
<tr>
<td>F-1b</td>
<td>20:1</td>
<td>25:1</td>
<td></td>
</tr>
</tbody>
</table>

Each filter sample was injected in the GC-MS (for model and column details see Chapter 3) after a reaction time of about 20h at RT. The temperature program was isothermal at 60° for 0.1min, then ramped at 27°/min ramp to 320° and isothermal at 320° for 0.5min. The injector and detector temperatures were constant at 250° and 300°, respectively, and the injection volume was 1µl. The MSD was run in scan mode for the analysis. The ions for quantification were m/z 181 for PFBHA and m/z 85 and 71 for the internal standard.

Blanks and test titrations

Prior to smog chamber experiments serveral tests were performed. Cleaned filters were treated the same way as SOA filters and the resulting solution was titrated with PFBHA. Also, known amounts of C=O containing compounds were dissolved in AcN and PFBHA was added stepwise. GC-MS method and analysis were done as described above. Results will be discussed in Chapter 9.4.3.
9.4 Results and Discussion

9.4.1 Results from the PFBHA titration

A typical titration curve for a filter titration from one of the TMB experiments is shown in Figure 9-5. There is a significant difference in the amount of PFBHA added on the front and the back filter.

Figure 9-5: Gran-Plot titration curves for a front (F-Front) and a back filter (F-Back) for a TMB experiment, 5.88-6.86h after switching on the lights (corresponding to F3 from Figure 9-4). The y-axis denotes the measured signal for m/z 181 per IS signal multiplied with the sum of the volume at the beginning (V0) and the added volume (V).
At the EP of each titration curve the amount of PFHBA used up is determined which is proportional to the amount of C=O in the sample. The difference between front and back filter gives the amount C=O in SOA per filter. With the flow rate, the sampling duration and the SMPS data for the sampled mass we obtain the data for Figure 9-6.

Figure 9-6: Time-resolved amount of 2 experiments each for µgC=O per µg SOA from the titrations of TMB-SOA (upper graph) and APIN-SOA (lower graph); shown is the point at the beginning of sampling; sampling durations vary between 50 and 90min. The dashed line indicates the maximum amount of functional groups per SOA possible.
This time-resolved experiments (two for TMB, two for APIN) show the course of µg carbonyls per µg SOA with an assumed particle density of 1.37g/cm$^3$ for TMB and 1.30g/cm$^3$ for APIN (Baltensperger et al., 2005). Each trace represents one smog chamber experiment; each point in time is the result from one filter sample (difference between front and back filter). For each experiment five points (filter samples) in time were taken over a duration of up to 9h.

From each front filter the respective back filter value was subtracted. The back filter is expected to consume less PFBHA, because only gas phase adsorption is assumed to account for the signal observed.

The upper graphs in Figure 9-6 are the results for the TMB-SOA. In the graph indicated with ● an increase from 0.35 to 0.45 in the end, that is after almost 9h after start of the experiment, is observed. The graph marked with ◆ shows a decrease from 0.37 to 0.28 during the 8h of the experiment.

In the APIN plots (lower graph in Figure 9-6) the first point seems to be an outlier in both cases, then a decrease in the ratio follows in the range between 0.50-0.20 and 0.34-0.12. For one experiment (○) the SMPS data were not available due to instrumental problems. As shown previously the chamber performs consistently well when repeating experiments (see Chapter 4.5.2), so we assumed for both the same course for the volume concentration and obtained the mass data from the successful SMPS plot.

9.4.2 Discussion

In Chapter 8 we could show with FT-IR a strong increase in the carbonyl functional group.

The data in this chapter were not reproducible within acceptable error limits. Five data points were obtained for each titration curve. The correlation coefficients of the linear fits in the Gran plots (see Figure 9-5) were acceptable: 70% were above 0.90, 45% of which were above 0.95. More datapoints per filter could be a solution, but that would also extend the duration of the analysis.

All four graphs have the range of ratios in common, that is 12-50% (weight) of the SOA are carbonyl groups. But TMB shows time trends less consistent than APIN.

- 210 -
In SOA formed by APIN and TMB many products contain C=O groups (Forstner et al., 1997; Hatakeyama et al., 1989; Hatakeyama et al., 1991; Hoffmann et al., 1998; Jaoui and Kamens, 2003b; Odum et al., 1996; Yu et al., 1997; Yu et al., 1999). Although for many C=O products the yield is known (Jaoui and Kamens, 2003a; Larsen et al., 2001; Yu et al., 1999) the overall carbonyl content is not known, because that would mean, all single products have to be identified and quantified. For APIN, Yu et al. (1999) estimated compounds consisting of OH, COOH and C=O functional groups to account for about 29-67% of the reacted carbon mass. For C₂ molecules like glyoxal or methylglyoxal the functional groups account for almost 100%. For Cₙ molecules with n≥6, our obtained data are not unlikely considering the already known oxidation products of APIN such as pinonaldehyde, pinonic acid or norpinonic acid or TMB with 3,5-dimethylbenzaldehyde or 2-methyl-4-oxo-2-pentenal. E.g. 4-oxo-2-pentenal has a molecular weight of 112, the two C=O groups (MW=56) would account for 50% of the mass. However, the observed trends are not consistent and values >1 are due to overestimation of the C=O mass for possible reasons explained in the next section.

9.4.3 Problems and possible solutions

This method has not been employed in the quantification of the carbonyl content of SOA so far. Also, time resolved monitoring of functional groups in smog chamber experiments is still a wide field to explore as not many references are available. But we encountered several problems, which will be discussed here. At its current state, this method cannot be used for the quantification of the carbonyl concentration.

Blanks and test titrations

Blank experiments consisted of an AcN extract of a clean filter and stepwise addition of PFBHA. The resulting Gran plots of 10 blank experiments showed blank values between 1.3µmol (equal to 20.48µl addition of PFBHA solution) and 0.018mmol (equal to 293µl addition) in acetonitrile – two titrations could not be evaluated, because the slope did not intersect with the x-axis. 11 test titrations in AcN with known amounts of carbonyl functional groups were performed: 3,5-
dimethylbenzaldehyde, glyoxylic acid, methylglyoxal were tested, individually and mixtures of them. The ratio of experimental vs. calculated value varied between 2.2 and 8.5, that is without any blank subtraction due to the large variation of the blank values. These variations and also the variations in the blank titrations are not within acceptable limits; the reasons for the big deviation are speculative and probably connected to contaminations (see below).

For comparison: the values resulting from back filters are in the range of 0.65µmol to 2.1µmol.

Different internal standards in water (used later as solvent, see next section) and AcN were tested: Nonadecane, decafluorobiphenyl, morpholine, acetic acid and triethylamine and many many more, but the 5 mentioned ones were then actually used in titrations with AcN or water as solvent. The seemingly random selection is due to the difficulties of finding an IS especially for water, that is water-soluble, does not contain a C=O group, is not too volatile (no evaporation over night), and which is sufficiently resolved on the GC column (therefore not too polar, that contradicts somewhat the prerequisite of being water soluble).

Contaminations

The high and additionally highly varying blank values in AcN led to the assumption that there are contaminations either in PFBHA itself, the solvent, or the surrounding laboratory air. The contaminants must be molecules with a carbonyl group that can be derivatized and therefore results in an overestimation of PFBHA used up by the aerosol sample. The $^1$H- and $^{13}$C-NMR of PFBHA in both D$_2$O and DMSO-d$_6$ showed no contamination peaks. MS spectra of PFBHA in ethanol (EtOH), water and AcN differed by a few peaks, which also showed the characteristic ion 181 of carbonyl derivates: in EtOH peaks with m/z 239, 250 and 253 were found, in AcN m/z 239 and 250 and in water only m/z 239 with by far the smallest peak area of this ion among the three solvents. Lelacheur et al. (1993) found carbonyls with the above-mentioned ions as dominant peaks: m/z 239 was found in all linear saturated aldehydes larger than propanal, m/z 253 is present for all 2-ketones and m/z 250 for the linear unsaturated aldehydes larger than propenal.
Water that contained only the 239 ion, was never the desired solvent, because it would mean that only the water soluble SOA could be analyzed and this was not the intention of the project. Nevertheless, 7 blanks and 3 test titrations were performed in water: It led to blank values of 7-25µmol (113-392µl addition) of PFBHA used up, which is not better than the blanks in AcN; titrations in water of known amounts of C=O resulted in ratios between 1.12-1.6, without any blank subtraction, again due to large variations in the blanks. The blank values in water were even higher than in AcN, and the test titrations also not satisfactory. The conclusions drawn from this were as follows:

The contaminations are to some degree in the solvent. Considering the variations of the blanks and the test titrations the contaminations in the laboratory air seem higher than in any solvent and not controllable.

A possible solution would be the analysis under inert gas, e.g. Argon or Nitrogen. This approach was employed with the method described in the next chapter.

### 9.5 References


Chapter 9

Derivatization of carbonyl functional groups


Chapter 10
Derivatization of hydroxyl functional groups in SOA – Method development
10.1 Introduction

Oxygenated organic compounds are ubiquitous organic aerosol constituents throughout the troposphere and many studies show that a significant portion of these compounds result from photo-oxidation of biogenic and anthropogenic hydrocarbons (see also Chapter 9). Alkanes, alkenes and aromatic compounds form hydroxyl compounds upon oxidation (Atkinson, 1997; Calvert et al., 2002; Yu et al., 1998). A number of products identified are polar oxygenated products, containing functional groups, such as hydroxyl, carbonyl and carboxylic acid groups (Edney et al., 2003). Carboxylic acids can make up 20-45% of the total aerosol mass as shown in smog chamber studies (Chapter 6). With our FT-IR study (Chapter 8) we could show an increase of the OH functional group with time in a smog chamber study. Information on these oxidation products is important to understand the atmospheric oxidation mechanism and the formation of SOA. Because hydroxyl groups (from carboxylic acids) are mainly responsible for the hygroscopicity of an organic particle the concentration of these compounds is also important to estimate their cloud formation potential. The motivation for this study is to quantify the absolute amount of OH groups (or carbonyl groups in Chapter 9) in carboxylic acids and alcohols in SOA, which is an unknown parameter in SOA analysis so far. Furthermore, the functional group analysis allows estimations about the level of oxidation and further insight into chemical aging of SOA, even if the particle formation has considerably slowed down.

This chapter focuses on the analysis of hydroxyl groups from alcohols and carboxylic acids by using a specific derivatization method for this functional group.

10.1.1 Methods for measurements of hydroxyl groups

High polarity and low concentrations of some acids and alcohols exclude direct GC-MS measurements. On-line and off-line methods, such as atmospheric pressure chemical ionization coupled with ion trap MS (Warscheid and Hoffmann, 2002), PTR-MS (Gascho et al., 2005), HPLC-MS (Glasius et al., 2000), IC-MS (Chapter 6) or capillary electrophoresis ESI-MS (Iinuma et al., 2004) can be employed to identify
and/or quantify organic products from oxidation processes. All these methods suffer from the same difficulties in identifying unknowns and therefore, no quantification is possible. Also, for single compound analysis of unknowns the mass spectra are complicated by fragmentation and sometimes due to lack of separation prior to detection.

Current procedures described in the literature for analyzing oxidized compounds are based on single step or multistep derivatization; one advantage of derivatization is the easier identification of unknowns due to characteristic ions in the mass spectra (e.g. \( \text{m/z} 181 \) for PFBHA, see Chapter 9). Carboxylic acid groups can be methylated with diazomethane in ether, but this method involves toxic and explosive chemicals. Less explosive is methanol or 1-butanol in the presence of a strong acid, e.g. \( \text{BF}_3 \) or \( \text{BCl}_3 \), which rapidly converts the \( \text{OH} \) group into an ester and has been used since a long time, e.g. for fatty acids (Metcalfe and Schmitz, 1961). It can also be used for atmospheric aerosol samples with molecules containing multi functional groups (Christoffersen et al., 1998; Jaoui et al., 2005). But we are interested in a derivatization technique that derivatizes both, alcohols and carboxylic acids in one step.

Silylation has long been employed in organic chemistry as protective method for alcohols (Mawhinney and Madson, 1982), but also for derivatization of acids, e.g. fatty acids (Bandi and Ansari, 1986; Kim et al., 1987; Kim et al., 1989) or for alcohols and acids together (Lelacheur et al., 1993).

The term “silylation” is defined as the substitution of a hydrogen atom bound to a hetero atom (-OH, =NH, -SH) by a silyl group, forming a silicon hetero atom bond, without any further alteration of the molecule. In synthetic organic chemistry it has been in use for a long time as protective group mainly for the hydroxyl group. This very common reaction is employed in practically every total synthesis in intermediate steps. In analytical chemistry, silylation has been used since the late 1950ies in GC-MS. Silylation of polar compounds results in reduced polarity, enhanced volatility and increased thermal stability and therefore enables the GC-MS analysis of many compounds otherwise involatile or too unstable for this technique (van Look et al., 1995). There are many different silylation agents available; the most popular is the trimethylsilyl (TMS) group. Depending on the properties expected, such as volatility, silylation by-products, reactivity, selectivity, a variety of TMS agents is available. \( \text{N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA)} \) is the most commonly used
trimethylsilylating agent. The advantage of BSTFA over other TMS agents is the higher volatility of its by-products and therefore they cause less interference in chromatograms. It has been used successfully with aerosol samples to derivatize carboxylic acids and alcohols (Kalberer et al., 2000; Yu et al., 1998). However, TMS containing compounds are extremely sensitive to hydrolysis; the tert-butyldimethylsilyl (TBDMS) group is much more stable to hydrolysis than the TMS analoges (Corey and Venkateswarlu, 1972). Also, for synthesis the TBDMS silylation products are much more favourable (easier and selective cleaving of the protective group, direct conversion into other functional groups), and for analysis the enhanced hydrolytic stability is important, as well as the faster reaction. Also, the products provide more diagnostic mass spectra with an abundant [M-57] fragment. There exists a wide selection of TBDMS derivatization agents, and the most commonly used is N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA).

The approach followed with this project is (as with PFBHA for carbonyls in Chapter 9) the quantification of the overall hydroxyl content within the duration of a smog chamber experiment.

10.1.2 Derivatization with MTBSTFA

The advantages of MTBSTFA vs. other TBDMS compounds are the enhanced reactivity (for carboxyls, hydroxyls, thiols), easier work-up and neutral reaction conditions; the derivatization reaction proceeds rapidly at RT (van Look et al., 1995) and the reaction mixture can be directly injected in the GC-MS. Commercial MTBSTFA contains ca. 1% v/v TBDM chlorosilane to enhance the silylation power of MTBSTFA. Figure 10-1 shows the derivatization scheme of MTBSTFA with OH groups.
Figure 10-1: Derivatization of OH groups with MTBSTFA. The $m/z [M^+ - 57]$ ion is a typical fragment of derivatization products and for MTBSTFA ($M-57 = 184$) itself.

MTBSTFA is added in a 5-10 fold excess to the mix in an aprotic solvent (such as AcN, pyridine or THF) and allowed to stand for 5-20 min until direct analysis by GC-MS.

It is more stable to hydrolysis than other reagents. This is an advantage in handling, because MTBSTFA comes under argon, capped with a septum in bottles, that can be easily stored in the fridge, whereas e.g. BSTFA is delivered in glass flasks which need to be cut open, leaving no option other than exposure to (humid) air, which is not desired. For the monitoring of the decrease of the derivatization agent, any moisture must be excluded, because water hydrolyzes MTBSTFA and the consumption will be overestimated. The derivatization reactions were performed under an inert atmosphere (see Chapter 10.3), but also sampling needed special precautions.

To exclude moisture, smog chamber experiments were conducted with RH=0%; the RH increased only up to 2% during experiments (personal communication Jonathan Duplissy).

### 10.1.3 Possible Influence of Humidity

Cocker et al. (2001) performed smog chamber experiments with APIN or TMB under dry (RH <2%) and humid (RH up to 57%) conditions with and without seed aerosols (ammonium sulfate, ammonium hydrogen sulfate, calcium chloride) in dark ozonolysis experiments (Cocker et al., 2001a) or with light (Cocker et al., 2001b; Cocker et al., 2001c). Without seed aerosols the SOA yield in experiments was not affected by the presence of gas phase water; only in dark experiments the yield was reduced in the presence of aqueous salt aerosols. With increased RH the size of the SOA increases.
due to water uptake. Contrary to the experiments performed by Cocker, we never used seed aerosols and the only difference between the two chamber systems is the light source: Blacklights used by Cocker do not emit > 400nm, whereas the lamps at the PSI smog chamber produce a spectrum from 300-800nm.

Recently, at the PSI smog chamber, experiments were performed with TMB and isoprene as SOA precursors under dry (0-2%) and humid (RH up to 80%) conditions. Surprisingly, the yield under dry conditions was much higher. This is contrary to Cocker’s findings and interpretations are speculative at this point and are analyzed thoroughly in other projects.

Docherty et al. (2005) showed that for APIN no statistically significant differences were observable for SOA yields and organic peroxide yields as an example for a SOA product at RH<0.5% and 50% during reactions without light. Dry and humid conditions might change the amount of individual products on the chemical composition of SOA. Water, alcohols, carboxylic acids and aldehydes compete with each other in stabilized biradical reactions. Water reacts much more slowly than the mentioned competing organic compounds, but the concentrations of water vapour compared to this species is higher even only at 2% RH. Therefore, the reaction products are not expected to change but in relative concentrations to each other. Tobias et al. (2000) examined the SOA products of 1-tetradecene with ozone at 0.1% and 30% RH. With GC-FID they found the same products but in slightly different concentrations.

10.2 Gran-Plot

The silylation reaction is a 1:1 reaction of a hydroxyl group with the derivatization agent molecule therefore at the equivalence point (EP) the amount of functional group on the filter sample can be obtained in the same way as described in Chapter 9. Due to a much faster reaction time more data points per titration can be measured.

10.3 Experimental

All chemicals were purchased from Fluka; only dibenzothiophene was from Aldrich. MTBSTFA is kept under argon in the fridge. Dry (water-free) AcN was obtained from
C. Ruflin, group Prof. Grüzmacher, the Schlenk line from Prof. Togni. AcN was refluxed over calcium hydride for several days and then distilled shortly before use. It was stored under N$_2$ in the hood.

### 10.3.1 Sampling and Analysis setup

The sampling setup was analog to the PFHBA method described in Chapter 9. For sampling, also Fluoropore$^\text{TM}$ Membrane Filters (Millipore Switzerland, Volketswil), pore size 3µm were used. The filters with a diameter of 15mm were cut out, cleaned in toluene (15min sonication) and air dried in the hood. With GC-MS no product peaks were observed with and without derivatization with MTBSTFA with blank, cleaned filters. The analysis was done under inert gas with a “Schlenk” line. It is another common term for vacuum line. This setup provides a convenient means of handling air and water sensitive materials without using an inert atmosphere glove box. All glassware and connecting tubes prior to use were evacuated and then flushed with N$_2$ several times; from then on the flasks were constantly under a N$_2$ atmosphere or stream, respectively.

The titrations were carried out at RT. Until analysis the filters were stored in a desiccator over P$_2$O$_5$ to keep the samples as humidity-free as possible.

### 10.3.2 Sampling and Titrations with MTBSTFA

Smog chamber experiments

Four TMB and three APIN experiments were performed: the initial mixing ratios for TMB were 1312ppb (200µl) with NO and NO$_2$ 320ppb each, for APIN 300ppb (54µl) with NO and NO$_2$ 120ppb each. Propene was added at mixing ratios of 300ppb. The relative humidity was kept at 0%, it rose during the experiments to about 1-2%. Four to five filter samples in time were taken - both front and back filters. The sampling duration varied from 1h16min to 2h15min and flow rates between 24 and 12 l*min$^{-1}$. The flow rate decreased during the sampling duration as the filters were loaded with SOA.
All of the following steps were done under inert gas (nitrogen). Dibenzothiophene C_{12}H_8S in dry AcN (10mg/ml) and decafluorobiphenyl C_{12}F_{10} in dry AcN (13.2mg/ml) were used as internal standards.

After sampling, the filters were transferred to a glass flask and extracted for 15min in a sonication bath in 3ml AcN; then the ISs were added. The filters were removed and discarded. MTBSTFA was added in 1-6µl steps to the SOA solution and allowed to react for 10-15min. After the derivatization, 1µl was directly injected into the GC-MS. Samples were not diluted due to the possibility of adding moisture in an additional step to the flask. After several titration points (i.e. successive MTBSTFA addition) the MTBSTFA peak intensity caused a saturation of the electromultiplier (EM) of the MS. Thus the repeller voltage (RV) and the EM voltage (EMV) were changed to prevent shutdown of the system due to excessive signal. The EMV was decreased by 518V (from 1976V as set with autotune) and the RV was set to 8.08V (from 14.99V). Decrease of the RV results in less ions being pushed into the mass analyzer. The temperature program was isothermal at 60° for 0.1min, followed by a 30°/min ramp to 310° and isothermal at 310° for 0.5min. The injector and detector temperatures were kept constant at 250° and 300°, respectively, and the injection volume was 1µl. The MSD was run in scan mode for the analysis.

MTBSTFA was identified by m/z 184 ([M^{+} - tert-Bu], see Figure 10-1), 134 and 77 (possibly [SiMe_{2}F]^{+} from: Little (1999)); for quantification m/z 184 and 77 were used. The IS dibenzothiophene and decafluorobiphenyl were identified by their molecular ions M^{+}, that is m/z 184 and m/z 334.

Contrary to the titrations with PFBHA between addition of derivatization agent and GC-MS measurement there were only 10-15min. Therefore up to 17 data points per titration curve were obtained. This allowed the analysis of max. 3 filters per day.

Blanks and test titrations

Prior to smog chamber experiments serveral tests were performed. Cleaned filters were extracted the same way as SOA filters and the resulting solution was titrated with MTBSTFA. Also, known amounts of OH containing compounds were dissolved in AcN and MTBSTFA was added stepwise. GC-MS method and analysis were done as described above.
10.4 Results and Discussion

10.4.1 Results from the MTBSTFA titration

A typical Gran plot titration curve for a filter titration from one of the TMB experiments is shown in Figure 10-2.

Figure 10-2: Titration example with MTBSTFA for front (F-Front) and back (F-Back) TMB filters (12.63-14.6h after starting the experiment). The y-axis denotes the measured signal for m/z 77 per IS signal multiplied with the sum of the volume at the beginning (V0) and the added volume (V).
For the front filter it is nicely visible how the derivatization agent is used up until at a certain addition the signal is detectable. Then the extrapolation of the linear increase yields the amount of MTBSTFA used up at the EP. The back filter does not show the transition as the front filter does, but instead there is an increase in signal from the first addition of MTBSTFA on. Again, the linear extrapolation yields the amount of MTBSTFA at the EP. There is a significant difference in the amount of MTBSTFA added on the front and the back filter. The back filter is expected to consume less MTBSTFA, because only gas phase adsorption is assumed to account for the signal observed.

Figure 10-3 shows the results for 4 TMB and 3 APIN experiments.
Figure 10-3: Time-resolved amount of μg OH per μg SOA from the titrations of TMB-SOA (upper graph) and APIN-SOA (lower graph); shown are the points at the beginning of sampling; sampling durations vary between 76 and 135 min. The dashed line indicates the maximum amount of functional groups per SOA possible. Each trace represents one smog chamber experiment.

The assumed particle density is again 1.37 g/cm$^3$ for TMB and 1.30 g/cm$^3$ for APIN (see Chapter 9). Each point in time is the result from one filter sample (difference
between front and back filter). For each experiment 3-5 points (=filter samples) were taken over a duration of up to 13h. Contrary to PFBHA, the values exceed the maximum of 1 more than once; these are no accidental outliers anymore. For TMB (upper graph) the time and duration for sampling for two experiments (● and ■) was very similar, so are the SMPS data, but the results in µg OH per µg SOA are different. The trend is similar for the last three points, but both curves show values higher than the theoretical possible. For APIN there is no trend in the three plotted curves observable, besides the majority of the values is also too high.

In the case of PFBHA the total amount of the functional group was determined by subtracting the respective back filter from the front filter. This seemed reasonable for the PFBHA filters, because the amounts used for the back filters did not vary as much as here with MTBSTFA and were within a sound percentage; the average of 20 back filters to the respective front filter was 28% with a standard deviation of 11%.

Subtracting the back filter values from the front filter values for MTBSTFA was more problematic, because the back filter values varied much more; for some front/back filter pairs, the consumption of derivatization agent on the back filter was higher than on the front filter, which resulted in negative values. To prevent that, the subtraction of an average value of 37.6% for back filter absorption was subtracted from every front filter. This value was obtained from 6 selected front-back filter pairs, where the titration curve was linear within acceptable limits and the back filter value was smaller than the front filter value. For the 29 filters analyzed (7 experiments with 3-5 filters) the average back filter value was 64% of the front filter with a standard deviation of 59%, which is not acceptable.

### 10.4.2 Discussion

The results from the FT-IR experiments (Chapter 8) show an continuous increase over 14h of the OH concentration in SOA, i.e., the time scale shown here. The data presented here are not consistent with the FT-IR results within acceptable limits. No consistent time trend for the TMB- and APIN-repetitive experiments was measured (Figure 10-3). Obtaining Gran plots with a linear increase as shown in Figure 10-2 was in some cases not possible and in some cases the correlation coefficient was below 0.7, even with as much as 10 or more data points per titration. The problem
was not the number of data points, but to obtain a clear linear increase within these points. With TMB, most of the values are above 1; that leads to the interpretation that an unknown systematic error is part of the unsatisfying results. The SMPS data for the SOA mass are reproducible and constant for the experiments performed; they do not seem to cause the high values of the ratio OH to SOA mass.

### 10.4.3 Problems and possible solutions

At its current state, this method cannot be used for the quantification of the overall OH group content of SOA; therefore possible errors are discussed in the following sections. Several problems will be discussed, but also the data of tests and blank titrations, which looked promising for the MTBSTFA titration and particularly better than in the case of PFBHA.

**Blanks und test titrations**

As described with PFBHA (Chapter 9), the blank experiments consisted of an AcN extract of a clean filter and the stepwise addition of MTBSTFA. 4 out of the 7 blank titrations were performed under argon in laboratory H136, 3 under nitrogen in our lab E334. One of the filters was stored over P$_2$O$_5$ in a desiccator over night, and one of the filters was kept for 2h in a continous air stream (compressed air provided in the hood in the lab), but the air was not sucked through the filter. The filter over P$_2$O$_5$ and the “air” filter did not show a significant deviation from the other filter values. The titration curves (6 out of 7, one could not be analyzed due to GC-MS problems) resulted in an average blank value of 4.7µmol consumption of MTBSTFA with a standard deviation of 2.1µmmol. For comparison: 3 out of 29 back filters had a similar value (1, 5, 5µmol), 26 out of 29 were clearly higher (all above 10µmol). The titrations of the front filters resulted in 26 out of 29 filters in consumption of MTBSTFA about 14µmol with a maximum value of 242µmol. This indicates that these blank titrations do not seem to cause major source of systematic or statistical error of the experiments shown in Figure 10-3.
Chapter 10  Derivatization of hydroxyl functional groups

Five test titrations were performed with known amounts of carboxylic acid groups in the sample: 3 test series with 2,5-dimethylbenzoic acid, and 2 series with a mix of 2,5-dimethylbenzoic acid and oxalic acid. After blank subtraction one of the single acid series resulted in a value smaller than zero. The ratios experimental vs. calculated value of the two others with 2,5-dimethylbenzoic acid were 2.15 and 1.39, the mix series resulted in ratios of 0.02 and 1.09. The value of 0.02 seems to be an outlier, the reference value was 1\(\mu\)mol, which is smaller than the blank value; the uncertainty rises the smaller the values are. Despite this relatively high scatter, these test titrations agreed within a factor of 2 with the theoretical values and thus produced more satisfying results than with PFBHA, therefore the decision was made to continue with this method.

Contaminations

The titrations were all carried out under nitrogen or argon. Due to fairly low blanks and satisfying test titration results, no contaminations seem to be in the inert gases. This would also be valid for AcN as the extraction solvent. Water as contaminant would lead to overestimation of the MTBSTFA consumption, because MTBSTFA is sensitive to hydrolysis. The filters for the test experiments were not treated exactly like the smog chamber filters were, the test compounds were not on the filter as aerosols, but as solution in AcN. A possible experiment would be to pump dry clean air from the smog chamber for up to 2h through a filter and titrate the AcN extract with MTBSTFA. This would show, if there is water adsorption on the filter, which causes the high values of MTBSTFA consumption for the titrations of smog chamber filters. The RH sensor of the smog chamber shows a rising RH value from 0% to 2% throughout the experiment (personal communication Jonathan Duplissy) but this could be enough to hydrolyze significant amounts of MTBSTFA if it is adsorbed on the filter. Recent test experiments with cleaned, empty filters showed that water seems indeed to play a role by adsorbing onto the filter fibres: Three filters were cleaned as described before and air from the clean air generator at the smog chamber was blown through the filters for ca. 90min to simulate as close as possible the conditions during “real” sampling. The air from the pure air generator is dry and measured RH is 0%.
(accuracy of the sensor ±1.5%). The filters were then extracted in AcN and titrated under inert gas as described before. The results show for two out of three filters a 10 times higher blank value than from the blank filters described above. Also the titration curves were not as linear as expected, which could be another sign for unwanted slow reaction with water: when the reaction with water is much slower than the expected derivatization time of 10-15 min and the amount of water adsorbed onto the fibres is not the same for every filter, then the titration will exhibit a varying slope. This was the case for these tests. Another option, not tested yet, is the use of a denuder before sampling with filters to completely dry the smog chamber air to minimize the water content with a suitable denuder coating.

Artefacts due to silylation reactions

The review by Little (1999) shows multiple derivatization reactions that can lead to unwanted products. Some compounds form additional unexpected derivatives or by-products, both referred to as artefacts. Ketones and aldehydes with α-hydrogen can form enolic species leading to consumption of the derivatization agent. But the equilibrium constant for aldehydes and ketones are usually very small, resulting the equilibrium to shift largely to the keto form. But there are carbonyls which prefer the enol form for stability reasons, e.g. 2,4-pentanedione, which is stabilized by intramolecular H-bonds in the enol form. Also, aldehydes can form adducts with silylation agents as observed with MSTFA (Ende and Luftmann, 1984). After nucleophilic attack of the silylation agent at the carbonyl group the trimethylsilyl group (would be the tert-butylsilyl group in case of MTBSTFA) moves to the carbonyl oxygen atom. For aromatic aldehydes the speed of adduct formation depends on the substituents of the aromatic ring, it can be as fast as several minutes, e.g. with benzaldehyde.

In SOA many carbonyls are not known, which leaves the possibility of preferred enol forms of certain compounds open, which then could react with MTBSTFA. Jaoui et al. (2004) reported silylation artefacts form model compounds used for developing a new method for identification of aerosol compounds. They derivatized – among many others - 3-hydroxy-2-butanone, 3-acetylpentanedioic acid and 2-
ketoglutaric acid with BSTFA and reported products from the derivatization of the enolic form with GC-MS.
In this study a different derivatization agent was used, but Little (1999) showed these artefacts also for silylation agents very similar to MTBSTFA. Therefore we carried tests with MTBSTFA out to derivatize 2-ketoglutaric acid (=2-oxopentanedioic acid), 4-hydroxy-2-butanone, α-hydroxymalonic acid (all with α-H atom), 3,5-dimethylbenzaldehyde (possible adduct formation). MTBSTFA was added to the mix of the four compounds in a 10fold excess and allowed to react at RT for 20min. No unexpected product due to artefacts could be observed with these four compounds.

There are several ways to avoid or minimize these artefacts. By characterizing all products of the silylation reaction with GC-MS it can be seen if there are products from unwanted reactions. This is not possible for the SOA mix, because too many products itself are not known, and also, many might not be detected due to low concentrations or insufficient elution from the GC column.
Selecting a different silylation agent could minimize artefact production. But for the appropriate choice, again the products should be known.
The best way to avoid unwanted derivatization of carbonyls would be to derivatize the aldehydes and ketones first and then derivatize the OH groups with MTBSTFA. The artefacts from enolic forms and also adducts at aldehyde groups would be eliminated. Depending on the type of carbonyl derivatization agent, the first step might take up to 20h (e.g. with PFBHA). The carbonyl derivatization products and agent could stay in solution when the silylation agent is added, which is favourable, because the silylation would still need inert atmosphere, and every additional step creates the possibility of adding air. In the literature (Jaoui et al., 2004) protocols are described to distinguish even hydroxyl and carboxylic acid groups after carbonyl groups with the use of appropriate derivatization agents.

All additional derivatizations of carbonyls cannot explain values > 1 in Figure 10-3. Although water contamination was carefully avoided, it seems likely that traces of water caused mainly the scatter of the data and the values mostly too high.
10.5 References


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Chapter 11
Summary and Outlook
11.1 Summary

Organic aerosols have been in the focus of researchers for a long time. Many organic aerosol precursors (e.g. aromatic compounds or alkenes) are known, but still the chemical composition of the overall mass cannot yet be accounted for. Single compound analysis is still widely employed, but there is another focus on the overall concentration of functional groups.

To simulate particle formation and growth under controlled conditions, a reaction chamber was constructed and characterized in detail. It took over 1.5 years to set it up before the first experiment was running. The characterization of the chamber is described in Chapter 4 and the gas phase chemistry and analysis is presented in more detail in Chapter 5.

Once the smog chamber was set up and running, experiments were performed, at the beginning exclusively with 1,3,5-trimethylbenzene, an anthropogenic precursor of secondary organic aerosol, SOA. The focus of the chemical analysis was on the change of functional groups with time to monitor significant changes in the chemical composition of the SOA phase even if the aerosol mass evolution slowed down considerably. With various methods it could be shown that there is an increase of oxidation products with time which might be due to heterogeneous oxidation reactions of aerosol components or continuous uptake of highly oxidized compounds from the gas phase.

The amount of carboxylic acids in the gas and aerosol phase was quantified with IC-MS and GC-MS. So far, IC-MS was not available for online analysis, but will be soon. Individual carboxylic acids were monitored over the course of an experiment as well as the sum of organic acids. A clear increase during the first hours of a photolysis experiment could be shown, absolut as well as relative to the aerosol mass.

Similar results were found for FT-IR analysis of SOA (Chapter 8). Here, even more functional groups could be monitored and relative changes over time could be determined, but no quantification was possible. The increase of carbonyls, carboxylic acids and hydroxyl functional groups was observed for 22h. This is a further indication of ongoing oxidation after slowing down of particle growth.
The absolute quantification of carbonyl and hydroxyl functional groups with GC-MS would have provided new evidence for the oxidation hypothesis, but this work was not fully completed yet due to unexpected difficulties.

Another topic that was only treated superficially in this thesis is the detection of polymers in SOA generated in the smog chamber (Chapter 7). We could show that about 50% of SOA from oxidation of TMB is composed of oligomers. The oligomers evolve over 7.5h forming products with masses of up to 1000Da. This has important implications for aerosol modeling; however, this field of aerosol research is only at the beginning and needs further investigation.

11.2 Outlook

With the new smog chamber at PSI a new tool for studying aging of SOA under controlled conditions has been built. It presents many opportunities for experiments on the chemical analysis side and on the physical evolution of SOA from different precursors. So far, APIN and TMB have been studied, with TMB more extensively.

The derivatization methods described in Chapter 9 and 10 are promising methods for the quantification of functional groups once the mentioned problems are understood and solved. The silylation reaction has to be investigated more thoroughly; with respect to the possible influence of water and for the artefacts mentioned. These could be avoided by employing a two-step derivatization reaction with carbonyl functional groups derivatized first. The carbonyl derivatization reagent seems to be more sensitive to ambient air than expected, therefore, working under inert gas could be a promising way to quantify the amount of carbonyl functional groups in SOA.

More and more online methods are now employed at the smog chamber. Online IC-MS will give insight into the carboxylic acid development in SOA over time and will help to identify new acids that were so far below the detection limit of GC-MS. A new Aerosol Mass Spectrometer (AMS) is now operated at the smog chamber to measure online and with high time resolution the chemical signatures of the SOA as a function of irradiation time (Alfarra et al., 2005). The AMS monitors m/z values as indicators of certain functional groups. The data obtained can be compared with ambient aerosol data also measured with the AMS.
The new PTR-MS setup will provide new information on the aerosol phase and at the same time about the gas phase, so that conclusions might be drawn on which gas phase compound partitions to which extent into the particle phase (Gascho et al., 2005).

Offline analysis will still give valuable analytical information on single compounds and their quantification. Therefore the GC-MS method mentioned in Chapter 3 can be used to monitor, e.g., glyoxal or methylglyoxal formed from aromatic precursors in the gas and particle phase. For single compound analysis the ESI-MS at the ETH with its potential for MS/MS and accurate mass measurements will yield interesting results by comparing them with ambient samples.

More LDI data with a higher time resolution and for experiments starting from different precursors should be taken, in parallel with the investigation of other aerosol properties such as optical parameters and hygroscopic growth. This will provide more information for SOA modeling where so far an equilibrium between gas and particle phase has been assumed. In addition, HNO$_3$ and H$_2$SO$_4$ are abundant compounds in the atmosphere, and their effect on oligomerization needs to be investigated.

In smog chamber experiments the focus is on single precursors and the concentrations are higher, which is beneficial due to the limited sensitivity of most instruments and inherent wall losses, but in general, to study SOA under atmospheric conditions would be ideal.

11.3 References


Curriculum Vitae

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