Biogenic Secondary Organic Aerosol

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1. Introduction

Within global climate change science, the role of Biogenic Secondary Organic Aerosol (BSOA) has been found as a major uncertainty. Up to date, it is well known that vegetation emits a vast number of Biogenic Volatile Organic Compounds (BVOC). Due to atmospheric conditions, these gases undergo oxidative processes, producing what we know as secondary organic aerosols. Aerosol science mainstream has focused on two main BVOC groups, monoterpenes and isoprene, due to their abundance and characteristics. Also, studies have tried to understand main processes by O_3, OH-radicals and NO_3-radicals. Nonetheless, aerosol studies have been approached in various perspectives in order to decrease the uncertainty with respect to formation pathways of Secondary Organic Aerosol (SOA). Better understanding of these has been achieved with field and laboratory studies which results are then applied in models. In overall, if the uncertainty on SOA is to be tackled it is required to build a link between what it is analysed through field studies and laboratory experiments and at the same produce accurate models that can project and simulate all the involved processes accordingly. Basically, modelling, field studies and laboratory studies of organic aerosols from biogenic sources improve knowledge but raise new questions. This document is an attempt to summarise the current status on the matter and the possible focus for tomorrow's organic aerosol science.

2. Modelling of BSOA

Effective modelling of biogenic organic aerosol is a challenging issue, beset by a lack of knowledge both in terms of the important VOC precursors as well as the chemical processes leading to SOA formation. This makes the use of modelling as a predictive tool fraught with difficulty. The uncertainties involved are currently huge, with current estimates of global secondary organic aerosol (SOA) production ranging from 2.5 to 70 Tg SOA yr^{-1} (Tsigaridis and Kanakidou, 2003; Kanakidou *et al.*, 2005). This dwarfs those from anthropogenic VOC of 0.05 to 2.62 Tg SOA yr^{-1} (Tsigaridis and Kanakidou, 2003), although SOA produced by oxidation of anthropogenic VOC's is also highly uncertain.

Generally there are two routes to representing SOA in chemistry transport models, either using gas-phase VOC oxidation schemes or use of empirical fits from laboratory chamber data. Currently not enough chamber studies have been carried out at sufficient parameter ranges to provide a wholly empirically based representation of SOA formation (Kanakidou *et al.*, 2005). Nonetheless, where the necessary data is available empirical parameterisations are often the method of choice (*e.g.* Pun and Seigneur, 2007). A method of fitting smog-chamber data for modelling has been outlined by Stanier *et al.*, (2008). However the mechanistic approach remains the only way to address species for which data is not available, and provides the avenue through which the processes may ultimately be explored most rigorously. Kanakidou *et al.* (2005) list four major areas that affect such mechanistic modelling; emissions of volatile organics, the subsequent gas-phase chemistry, nucleation and gas-particle partitioning, and aerosol/aqueous phase chemistry and cloud processing.

Correct estimation of volatile organic compound (VOC) emissions is vital as a first step to obtaining reasonable model output. The MEGAN model (Guenther *et al.*, 2006) currently represents the state of the art in terms of biogenic VOC emission estimation. However the sweeping simplifications that must be made for a model of this scale, combined with a lack of knowledge of emission factors for many tree species introduce estimations on the size of the uncertainty into the predictions. Much work has been done regarding the response of plant emissions to environmental factors such as temperature and light (*e.g.* Penuelas and Llusia, 2001; Kesselmeier and Staudt, 1999). Although many of the basic principles are understood, dramatic variability between species makes the large-scale response difficult to categorise.

Differing plant species emit different spectrums of BVOCs and the criteria for the emission of those compounds may vary widely. For instance, whilst isoprene is the most abundant BVOC, some plants do not emit isoprene at all, and this variability can be difficult to predict (Fuentes *et al.*, 2000). It is not practical to categorise emissions for every species, particularly on a global scale, even for isoprene alone. Furthermore some compounds are emitted as a response to quasi-random events, such as herbivore activity in the area (Penuelas and Llusia, 2001).

Models such as MEGAN use satellite data such as that available from MODIS (*e.g.* Kinnee *et al.*, 1997; Zhang *et al.*, 2004) or AVHRR (*e.g.* Bonan *et al.*, 2002) to calculate the distribution of plant functional types and leaf area index. Along with estimations of emission factors of a selection of representative compounds for each plant functional type, and ambient meteorological data, what is largely an educated guess can be made at emissions. One problem with these models is that the emission factors are based upon data from a small selection of locations, typically centred around Europe and North America. As the majority of biogenic emissions occur in the tropics, these areas do not provide good proxy data. Recently a large amount of work has been done on categorising emissions in the Amazon basin (Karl *et al.*, 2007, Kuhn *et al.*, 2007), and some success in modelling has been achieved. However there is still a lack of knowledge about other tropical areas such as Equatorial Africa and South-East Asia, whose emissions may well be very different.

In a recent paper, Arneth *et al.* (2008) raised the concern, that given the lack of knowledge, global estimates of isoprene emission are perhaps a bit too similar, and the current approaches may not be adequately representing the uncertainty in this field. Furthermore, for every compound, for which we do have data, there are many more for which we do not; these are often lumped into a single "Other VOC" value. The chemistry and aerosol forming potential of these lumped species may vary, presenting a significant challenge for models (Kanakidou *et al.*, 2005). Of these compounds sesquiterpenes are especially important, with an aerosol forming potential as high as 100% in some estimates (Hoffman *et al.*, 1997; Vizuete *et al.*, 2004). As aerosol formation depends largely upon the structure of the precursor molecules, more emissions speciation would be an important step forward for aerosol modelling (Kanakidou *et al.*, 2005).

Accurate estimates of NO_x emissions are also very important, as the concentration of NO_x significantly affects the chemical oxidation pathways taken by VOCs (Seinfeld and Pandis, 2006). These emission estimates are subject to many of the same problems as those of BVOCs.

Isoprene is now known to produce some aerosol (Claeys *et al.*, 2004), and its high global emissions make this an important pathway. However chamber studies of terpene oxidation have produced SOA in much higher yields. Over 5000 terpenes have so far been identified (Geron *et al.*, 2000), with each of these degrading to produce a further multitude of reaction products, the complexities are clear, necessitating significant lumping of chemical mechanisms in order to reduce the demands on both computational resources and laboratory studies. Such lumping loses structural nuances that are often important for aerosol formation. As semi-volatile compounds that may partition to the particle phase are typically several steps down the oxidation chain, there may be several lumped stages before they are reached. For example, in the alpha-pinene oxidation scheme of Jenkin (1996), the condensible product, pinonic acid, is the fourth lumped species in the chain from alpha-pinene oxidation by OH. Of course lumping may not be a disadvantage if detailed kinetic data for each reaction is absent, as is the case for oxidation of most reaction products.

At present, detailed mechanistic studies of chemical degradation have only been performed on isoprene, a-pinene and b-pinene, and complications in measuring the intermediates leave significant uncertainties in the product yields under different chemical environments (see *e.g.* Saunders *et al.*, 2003). Further work is needed to better understand the other classes of terpene compounds that these two cannot effectively represent (*e.g.* monocyclic terpenes such as limonene or acyclic monoterpenes such as ocimene). Elucidation of possible mechanisms is the role of chamber studies, but it is important that these are backed up by field measurements to ensure that the chemical environments are representative of atmospheric conditions.

Traditionally gas-particle partitioning is utilised to represent aerosol formation (*e.g.* Seinfeld and Pandis, 2006). Partitioning of a species is primarily affected by temperature, relative humidity and existence of other organics. So accurate modelling of meteorological parameters is also very important. Saturation vapour pressures must be obtained empirically and the wide variety of compounds involved makes this a challenging task. To further complicate matters, recent work (*e.g.* Kroll and Seinfeld, 2005) suggests oligimerisation processes may cause relatively high volatility compounds to contribute to SOA formation; something which is currently not represented in models.

Heterogeneous chemistry and cloud processing are complex areas which require simulation of a variety of effects, such as the specific reaction characteristics and cloud droplet composition. However they can have a profound impact on the residence time of compounds in the aerosol phase as well as altering the physical characteristics of the aerosol. Heterogeneous reactions of condensed SOA and semi-volatile organics could cause SOA yield to exceed those calculated solely on gas-particle partitioning (Kanakidou *et al.*, 2005). As relatively little is known about these reactions it is difficult to represent them explicitly, although a framework has been put forward by Pöschl *et al.*, (2007). These areas are emerging as important fields for research.

To summarise, modelling biogenic secondary organic aerosol is handicapped both by a lack detailed knowledge of the processes involved and by the uncertainties in the preceding chemistry and emissions parameterisations. A great deal of work in the laboratory and field is required to reduce the uncertainties involved and perhaps in the long term a focus on accurate chemistry and emissions representation will provide a stronger base upon which to model aerosol.

3. Field Studies of BSOA

3.1 Physical Analysis - Formation and Growth Rates

It is important to describe the formation and growth of BSOA in order to estimate the impact the particles have on climate and health. As a result of modelling and laboratory studies, these processes can be described in qualitative terms, but quantitative information of particle production rates in the atmosphere is scarce. Generation of particles has been observed in a variety of environments, such as the Arctic atmosphere, above forests and around coastal areas (Holmes, 2006). However, the lack of measurement methods capable of detecting and characterising the nucleation particles restricts our understanding in the field.

Formation and growth rates of BSOA can be inferred from measurements of nanoparticle size distributions. However, the lower limit of detection for state of the art particle counters is around 3-5 nm, which means that they have already grown for some time starting from the size of nucleated clusters that are around 1 nm (McMurry *et al.*, 2000). Kulmala *et al.* (2004) suggests that a full understanding of atmospheric new particle formation processes depend on instrumental improvements. A solution would be an instrument with the following properties:

- Ability to detect ~1nm particles and clusters (current limit is about 3 nm)
- Size resolution involving multiple channels, in order to detect particle growth after nucleation
- High time resolution

- Ability to measure low particle concentrations as well as high, in order to study both clean and polluted air

Another limitation of most observations is that measurements are made either at a fixed point, or on a platform which does not always move along with the same air parcel. Observations of BSOA formation may therefore be biased by spatial variations or variations in different air parcels (Kulmala *et al.*, 2000).

Measurements that provide information on the concentrations of the nucleating gases (or their precursors) and the composition of freshly nucleated particles provide further insight.

3.2 Chemical Analysis – Composition and Tracer Identification

Along with the study of physical properties and characteristics of organic aerosols, it is important to characterise constituents, which improve our knowledge about aerosol sources and possible formation mechanism of SOA. It is so, as this in turn will determine its latter impacts in the atmospheric processes. As it has been previously mentioned secondary organic aerosols are the oxidation products of biogenic volatile organic compounds in the atmosphere. Monoterpenes and isoprene have been recognized as major precursors for these. Therefore, most of SOA show similar molecular structure and composition to their precursor. The analysis of chemical composition of organic aerosols has been developed and adapted by various research groups, yet Figure 1 shows a flow chart of the general process. It is important to consider the following points prior sampling and analysis.

- Type of filter
- Type of environment to be sampled
- Volume flow for sampling
- Time of sampling
- Preparation of standards
- Selection of extraction method (solvent, micro-extraction, etc)
- Selection of analytical instrument for separation (LC, GC, etc)
- Selection of analytical instrument for detection (FID, MS, etc)
- Calibration of instrument

Currently, there are special concerns regarding artefacts from filter preparation and during sampling. These may include activation of the filter, reactivity, and volatility (Discussed in the EAC 2008 Sampling working group):

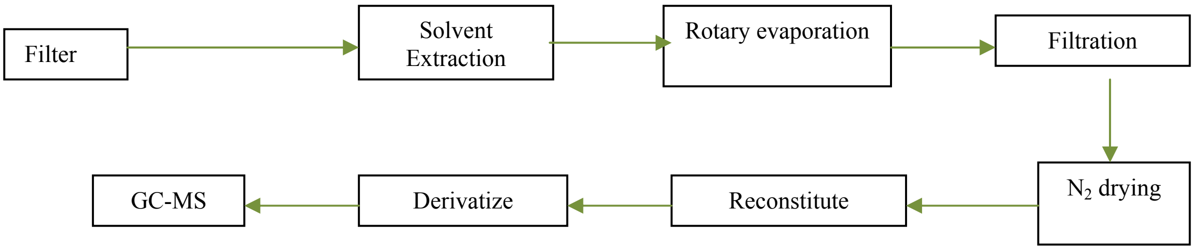

Figure 1 General known process for the chemical analysis of aerosol samples, based on quartz filter loading. Method detailed by Kubatova *et al.* (2000).

Once the samples have been prepared for analysis the most important thing is to know what to look for. It is common that analytical instruments separate and detect various unknown compounds. Therefore it is difficult to know at sight what compound is observed in the spectrogram. To date, many of the SOAs mass/charge ratio or ions have been reported which allow an easier way to identify the compounds in the analysed sample. Nonetheless, it is relevant to note that many of the known compounds have been changed with more recent studies. In other words, reported SOA components are not well established as definite. Yet, currently believed SOA tracers are 2-methylthreitol and 2-methylerythritol from isoprene (Claeys *et al*., 2004), and pinic acid, pinonic acid, etc from monoterpenes (Yu *et al*., 1999).

4. Laboratory Studies of BSOA

4.1 Chamber Experiments

The step between field measurements and modelling is the use of chamber experiments. The use of chambers allows the study of atmospheric processes under controlled conditions *e.g.* temperature, pressure, light and composition of gases. One well defined system can be studied over time (minutes, hours or days) in a chamber or frozen in time by the use of a flow reactor. Results of chamber experiments constitute the majority of the data used to currently understand SOA formation mechanisms. There are several approaches and designs of chambers build and used in Universities and Institutes in Europe, most of them are members of the EUROCHAMP (Integration of European Simulation Chambers for Investigating Atmospheric Processes) or the ACCENT (Atmospheric Composition Change the European Network of Excellence) infrastructures. The chambers differ a lot in material, size, shape and applications (Table 1) and have to be well characterised.

Table 1 Overview of a few of the European chambers used in the research of organic aerosols.

Short Name	Location	Long Name	Type	Shape	Volume (m^3)	Material
SAPHIR	Forschungszentrum Jülich, Germany	**S**imulation **A**tmosphärischer **PH**otochemie In einer großen **R**eaktionskammer	Outdoor Photoreactor	Cylinder	270	FEP (fluorine-ethene-propene)
EUPHORE 1&2	Fundación Centro de Estudios Ambientales del Mediterráneo, Valencia, Spain	**EU**ropean **PH**oto**RE**actor 1&2	Outdoor Photoreactor	Half Sphere	200	FEP
AIDA	Forschungszentrum Karlsruhe, Germany	**A**erosol **I**nteractions and **D**ynamics in the **A**tmosphere	Dark Chamber	Cylinder	84.5	Aluminum Chamber
PSI	Paul Scherrer Institute, Villigen, Switzerland	PSI Smog Chamber	Indoor Photoreactor	Cube	27	FEP
LISA One	Creteil, Université Paris, France	**L**aboratoire **I**nter-Universitaire des **S**ystèmes **A**tmosphériques	Indoor Photoreactor	Cylinder	0.977	Pyrex Glass
LEAK	Leibniz Institute for Tropospheric Research, Germany	**LE**ipziger **A**erosol **K**ammer	Indoor Aerosolchamber	Cylinder	19	FEP
HIRAC	School of Chemistry, University of Leeds, UK	**H**ighly **I**nstrumented **R**eactor for **A**tmospheric **C**hemistry	Indoor photoreactor	Cylinder	2.3	Grade 304 Stainless Steel
G-FROST*	Atmospheric Chemistry, University of Gothenburg, Sweden	**G**öteborg- **F**low **R**eactor for **O**xidation **S**tudies at low **T**emperatures	Indoor Dark Flowreactor	Cylinder	0.015	Pyrex Glass

All except * collected from http://saphir.fz-juelich.de/eurochamp/public/table4eurochamp/Table4Eurochamp.Version3.html

4.1.1 Challenges in Chamber Experiments

What do we learn from chamber studies?

Chamber studies are essential for the development and evaluation of chemical mechanisms or models which deal with the formation of secondary pollutants and secondary organic aerosol

(SOA). They are particularly suitable to obtain a better understanding of selected atmospheric processes in a certain time scale.

Atmospheric oxidation processes can be partially simulated in such environmental chambers as the initial conditions which influence the processes, such as relative humidity (RH), temperature (T) and hydrocarbon concentration (HC) and a type of oxidant and concentrations can be controlled. This enables us to study atmospherically relevant reactions under defined conditions and will provide a better understanding of VOC oxidation in the atmosphere.

What are their limitations?

Although chamber studies are widely performed to simulate atmospheric oxidation processes and the formation of SOA, their experimental designs inherit certain problems for the atmospheric simulation. They are generally used in a batch reactor mode, with no continuous VOC or oxidant flux unlike the real atmosphere. Additionally, the concentration of the hydrocarbon used for chamber experiments is often by a factor of 10 higher compared to the atmosphere. This affects the phase-partitioning as well the chemistry, so that great care has to be taken for the interpretation and relevance of the results (*e.g.* product distributions and SOA yields) to the atmosphere. The SOA formation in chamber studies is highly dependent on a wide range of experimental conditions, including pre-existing aerosol mass, NOx and RO_2 level (*i.e.* by using OH scavengers in ozonolysis experiments), particle acidity and concentrations of oxidant and hydrocarbon. The simulation of complete atmospheric conditions cannot be achieved in chamber studies; *e.g.* the chemistry in VOC oxidation as well the SOA formation in the atmosphere can occur under different schemes from those employed in chambers.

Important parameters for the SOA formation and the product distribution are the NOx concentration as well as the NO/NO_2 ratio. SOA yields are generally found to decrease as NOx level increases, which can be largely explained by the major branching reaction in VOC oxidation (initiating oxidant, fate of RO_2 and RO radical); for more details see the review by Kroll and Seinfeld 2008.

Another important parameter is the type and the acidity of the used seed particles in chamber studies, which influence also the chemistry and the resulting products.

Other differences between the chamber studies and field observations concerning product distribution may be derived from the time scale of chamber experiments. Compared to the possible oxidation processes in the atmosphere and the lifetime of aerosols (≈ 10 days), the duration of chamber experiments is mostly very short (max. 1 day). This is another challenge for chamber studies because a multi-step oxidation process plays an important role in the atmosphere.

What improvements have been made?

A number of improvements have been made regarding chamber engineering to minimize reactor effects in VOC oxidation studies. These includes characterisation of NOx and formaldehyde offgasing, which can act as additional sources for radicals, and the determination of particle loss rates and background PM formation by using appropriate instruments with lower detection limit. Additionally, large volume chambers which minimise wall losses of aerosol are now commonly used in VOC oxidation and SOA formation studies.

The combined utilisation of aerosol size distributions and newly developed instruments which enable *e.g.* high time resolution measurements of gas-phase species concentration and additional measurements of aerosol microphysical properties, such as hygroscopicity, allow a more comprehensive characterisation of laboratory SOA.

In addition, the off-line analysis itself is improved by applying new analytical techniques such as HPLC/ESI-TOFMS that allow us to identify a range of important constituents in SOA which are also present in ambient samples.

Compared to earlier studies, recent experiments are carried out using lower concentrations of precursor compounds that resemble realistic ambient conditions. However, the higher conversion rate can result in different product distribution compared to the atmosphere and show the still existing challenge for chamber studies.

What needs to be done?

Discrepancies between chamber and ambient field studies need to be addressed in future studies. There is a need for laboratory studies to be carried out under the full range of atmospherically relevant conditions so that volatility distributions (SOA yield) correspond to the atmosphere and multi-generation oxidation can be performed.

The SOA yields obtained from chamber studies lead to underestimation of SOA formation in global models. In addition there are differences in the SOA yields between flow tube experiments (higher SOA yields) (*e.g.* Jonsson *et al.* 2006, 2008a and 2008b; Berndt *et al.* 2003) and chamber studies (lower SOA yields) (*e.g.* Shilling *et al*. 2008 and references therein). This needs to be addressed in future chamber studies.

Newer experimental designs can improve our knowledge on SOA formation and their composition. The new designs include simulation of atmospheric emission inventories and their reactions in plant chambers. Additionally, multi-generation oxidation products and the identification of important intermediates in SOA formation are important issues.

The formation of hetero-molecular compounds (*e.g.* nitrooxy-organosulphates) which are present in ambient samples and the explanation for their formation pathway needs to be addressed.

Further improvements include higher time resolution of analytical techniques for chemical information. In this regard, the AMS and the particle into liquid sampler system (PILS) are often used for chamber studies.

Other improvements are the applications of LC-MS or CE-MS systems for highly time resolved chemical speciation. This may give us a possibility to detect intermediates for important SOA formation compounds.

4.2 Volatility Properties of SOA from BVOCs

A significant fraction of air particulate matter is formed from the products of atmospheric reactions with volatile organic compounds (VOCs). Some of these products will be less volatile and will therefore be possible to nucleate to form new particles or more likely partition into, or condense on already existing ones. Vast amounts of these VOCs are of biogenic origin including isoprene and different monoterpenes, which are responsible for hundreds of Tg/year. To increase the understanding of these processes that effect both climate and health further work is of great importance.

Different biogenic precursor gases effect on volatility

Experiments with different SOA-precursor compounds of biogenic origin *e.g.* α-pinene and limonene in both flow tube reactors and smog-chambers (Jonsson *et al.* 2007) show precursor gas dependency in volatility. Possible explanations to these diversities lie in the reaction and nucleation rates. If a compound with high reaction rates that readily forms low volatile products, a lot of accessible particle surface will form and more semi-volatile products will be able to condense or partition into the particle phase. This will result in a more volatile aerosol. So it is clear that changes in mixing ratios of the precursor gases will result in a changed aerosol product. Things that can influence the ambient concentrations of these gases are change in climate and land use which both are topics of current interest.

Different oxidation agents (OH-radical, NO_3-radical, O_3)

SOA-precursor gases of biogenic origin *e.g.* monoterpenes are reactive unsaturated hydrocarbons with relative short lifetimes in ambient atmosphere. Typical oxidative atmospheric species studied are O_3, OH-radical and NO_3-radical, see Table 2.

Table 2 Calculated tropospheric lifetimes for selected BVOCs with respect to gas-phase reactions with O_3, OH-radical and NO_3-radical (Fuentes *et al.* 2000).

Compound	O_3	NO_3	OH
Limonene	2 h	3 min	50 min
Alfapinene	4.6 h	5 min	2.6 h
Δ3-carene	11 h	4 min	1.6 h

Products formed from reactions with these different reactants will divide in chemical composition due to reaction rates and the addition of functional groups such as nitrate, carbonyl, carboxyl, hydroxyl, peroxy groups.

How is the chemical composition reflected in the volatility of an aerosol?

The chemical and physical properties of an aerosol particle origin from the different compounds it consists of and their interactions both with the surrounding gases and the particle phase. That is also the case with the volatility, highly oxidised compounds or compounds with additional polar functional groups will have decreasing effect. Chemical processes in the condensed phase *e.g.* liquid phase reactions and further oxidation “aging processes” will also have effect on the volatility. There is also evidence that possible interactions like oligomerisation and formation of macromolecules will have the same effect (Vesterinen *et al.* 2007). Fragmentation reactions of the SOA constituents can also cause an increased evaporation rate.

Methods to quantify aerosol volatility properties

The volatility properties of an aerosol sample can be measured by studying the decrease in diameter when a poly or mono disperse sample is heated in a thermodenuder *e.g.* with a Volatility Tandem DMA system to trace rather small changes in chemical composition in aerosol samples (Rader *et al.* 1987). For an example of a VTDMA setup see Figure 2.

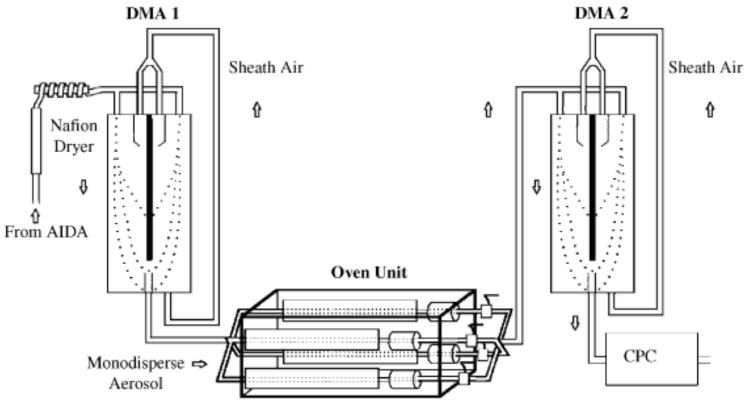

Figure 2 Schematic of a VTDMA (Jonsson *et al.* 2007).

To avoid re-condensation and re-partitioning the evaporated gaseous species need to be removed with some kind of scrubber *e.g.* activated charcoal. A thermodenuder can also be used at high temperatures to sample and analyse the non-volatile fraction of an aerosol sample by means of size/mass distribution (Philippin *et al.* 2004) or its chemical composition by using filter sampling techniques and their off-line analysis (Clarke and Papapanayotou 1987). Other on-line instruments like an aerosol mass spectrometer (AMS) can also be used with the thermodenuder.

4.3 Aqueous Phase Oxidation of BVOCs

Aqueous-phase oxidation is a potentially important source of organic aerosol and cloud. The possibility of BVOC oxidation in cloud and fog droplets was first raised 25 years ago (Graedel and Goldberg, 1983). Aqueous-phase OH reaction in cloud and fog droplets were proposed as pathways for the oxidation of aldehydes to their corresponding carboxylic acids (Chameides, 1984; Graedel *et al.,* 1986; Seinfeld and Pandis, 1998).

Aqueous-phase oxidation (in clouds and aerosols) explains the atmospheric presence of oxalic acid. Methylglyoxal, a water-soluble product of isoprene, oxidizes further in the aqueous phase to pyruvic acid. Aqueous-phase photochemical reactions of puryvic acid and hydrogen peroxide at pH values typical of clouds were conducted and demonstrated that photochemical oxidation of pyruvic acid yields glyoxylic, oxalic, acetic and formic acids (Carlton *et al.,* 2006).

There is growing evidence that just as sulphate is formed through aqueous phase reactions, SOA is also formed through aqueous phase reactions in clouds, fogs and aerosols.

Claeys *et al.* (2004a, 2004b) discovered two isomers of 2-methyl-butane-1,2,3,4-tetrols in aerosol samples collected over the Amazon rain forest. Originally, the authors suggested that tetrols were formed in a series of gas-phase reactions starting from the oxidation of isoprene by OH and photooxidation of isoprene, and just condensed to aerosols (Claeys *et al.,* 2004b). Such a mechanism required low NO_x conditions, but in subsequent field campaigns, more tetrols were found at high NO_x conditions (Claeys *et al.,* 2004a).Thus, the authors hypothesized that tetrols were formed in acid-catalysed reaction of isoprene with hydrogen peroxide, presumably heterogeneously or in the aqueous-phase.

There are also general reasons that justify further research on the heterogeneous and the aqueous-phase transformation of isoprene. Several reviews on atmospheric processes reflect a common awareness of a general importance of heterogeneous and multiphase reactions (Fuzzi and Ebel, 2000; Herrmann, 2003; Ravishankara, 2003). Von Kuhlmann *et al.,* (2003) showed by modelling that the global balance of isoprene did not close, and called for research on heterogeneous sinks for isoprene. Few current chemical models describe the formation pathways of di- and ketocarboxilyc acid by aqueous phase process. Moreover, the heterogeneous and the aqueous-phase chemistry of isoprene may play a role in local air quality and health problems, that occur close to the sources of isoprene-in the cities, forests, offices and habitats, transport facilities and vehicles, and in the industry. For example, isoprene or products of isoprene reaction with ozone cause eye and airways irritation (Wilkins *et al.,* 2001; Wolkoff and Nielsen, 2001; Rohr *et al.,* 2002).

Chamber experiments with isoprene made contribution to our understanding of the chemistry of isoprene. Chambers were used in the research on gas-phase, heterogeneous reactions of isoprene and other atmospheric trace compounds. The field is open for attempts to introduce clouds, fogs, rains and haze into chambers and investigate the multiphase and heterogeneous processes therein. Many technical ideas and solutions can be borrowed for this purpose from chemical engineering.

4.4 Peroxy Radicals and SOA

Alkyl peroxy radicals (RO_2) are intermediate, reactive products of O_3, OH and NO_3 initiated oxidation of all BVOC's (Atkinson 2007, Monks 2005). Alkyl radicals are produced by the reaction of OH and NO_3 with alkenes and alkanes, as well as by the decomposition of Criegee intermediates which are generated in the ozonolysis of alkenes. These alkyl radicals react almost immediately in the presence of O_2 to produce alkyl peroxy radicals.

Because alkyl peroxy radicals are reactive intermediates which are common to most BVOC / oxidant oxidation pathways, the fate of these radicals has a large impact on the distribution of stable products produced by atmospheric oxidation of BVOC's. Peroxy radicals have relatively fast rate constants with most other radical species, such as other RO_2's, NO, NO_2, NO_3, HO_2 as well as halogen radicals. In the troposphere however, the fate of RO_2's is dominated by reaction with $RO_{2,}$ NO, HO_2 and NO_3. Reactions of RO_2 with other RO_2's and with NO_3 produce carbonyls and alcohols and peroxides. NO reactions can produce organic nitrates and carbonyls. Reactions with HO_2 produce hydroperoxides. The vapor pressures of the final product will vary depending on which of these functionalities is produced (Pankow 2008).

Observations of secondary organic aerosol formation by oxidation of BVOC's are consistent with equilibrium partitioning of semi-volatile oxidation products between condensed and vapor phases (Donahue 2006, Shrivasta 2006). Because the equilibrium partitioning coefficients are directly related to the vapor pressures of the oxidation products (Odum 1996), the intermediate chemistry of the peroxy radicals will have a strong influence on the yield of SOA observed by any given BVOC / oxidant reaction through the production of stable products of varying functionality and therefore vapor pressures.

The applicability of any given chamber experiment to the prediction of SOA yields in the atmosphere is therefore dependent on a realistic mix of radicals in the chamber for reaction with the peroxy radicals. A classic example of peroxy radical chemistry artificially reducing the observed yield is the photooxidation of isoprene, originally through to produce no SOA because of the excessive levels of NO_x used in these experiments (Kroll 2006). Furthermore, because different conditions in the atmosphere can produce very different relative concentrations of peroxy radical reaction partners (i.e. polluted vs clean environments, day vs night), a single chamber experiment of a BVOC / oxidant system may not be capable of evaluating the SOA potential of such a system. For example, cleaner parts of the troposphere which are more removed from urban environments generally have lower concentrations of NOx (and frequently higher concentrations of BVOC's). Conversely, cities produce high levels of NOx where BVOC emissions are lower. In all environments, throughout the night, the NO/NO2 ratio decreases, and NO_3 concentrations can build up to significant levels, while a photochemical source of HO_x is absent. Therefore, in order to apply chamber experiments to modeling of ambient SOA, an understanding of the RO_2 fate is required for both the chamber experiment, and under various atmospheric conditions and locations.

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