



Formation and
chemical aging of
SOA

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Formation and chemical aging of secondary organic aerosol during the β -caryophyllene oxidation

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The secondary organic aerosol (SOA) production during the oxidation of β -caryophyllene by ozone (O_3) and hydroxyl radicals (OH) and the subsequent chemical aging of the products during reactions with OH were investigated. Experiments were conducted with ozone, hydroxyl radicals at low NO_x (zero added NO_x) and at high NO_x (100s of ppb). The SOA mass yield at $10\ \mu\text{g m}^{-3}$ of organic aerosol is 26% for the ozonolysis, 20% for the reaction with OH at low NO_x and 38% at high NO_x . Parameterizations of the fresh SOA yields have been developed. The average fresh SOA atomic O : C ratio varied from 0.24 to 0.33 depending on the oxidant and the NO_x level.

The chemical aging of the produced β -caryophyllene SOA was studied by exposing the fresh SOA to high concentrations (10^7 molecules cm^{-3}) of hydroxyl radicals for several hours. These additional reactions increased the SOA concentration by 15–40% and the O : C by approximately 25%. It was found that the exposure to UV-light has no effect on the β -caryophyllene SOA. Experiments suggested that there was a significant impact of the relative humidity in the chemical aging of the SOA.

We quantified the evaporation rates of β -caryophyllene SOA by using a thermodenuder. The corresponding volatility distributions and the effective vaporization enthalpies were estimated. An average density of $1.06 \pm 0.1\ \text{g cm}^{-3}$ of the β -caryophyllene SOA was estimated.

1 Introduction

Organic compounds represent approximately half of the total mass of sub-micrometer aerosol particles (Kanakidou et al., 2005). From a source perspective, organic aerosol is often classified as primary (POA) or secondary (SOA). POA refers to the organic mass that is emitted in the atmosphere in the particle phase. SOA is formed in the atmosphere when volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone (O_3), hydroxyl radical (OH) or nitrate radical (NO_3). These reactions form

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Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



low volatility products that can condense on preexisting particles in the atmosphere. Both POA and SOA have biogenic and anthropogenic sources.

The initial products of oxidation of volatile organic compounds in the atmosphere can undergo subsequent reactions in the gas and particulate phases leading to changes in their volatility and thus phase partitioning. This series of processes is called chemical aging and can be a significant source of SOA in the atmosphere (Donahue et al., 2012).

Biogenic VOCs, whose emissions exceed anthropogenic emissions on a global scale, play an important role in atmospheric chemistry at both regional and global scales (Kanakidou et al., 2005). Biogenic VOCs include monoterpenes (C₁₀H₁₆), sesquiterpenes (C₁₅H₂₄), and isoprene (C₅H₈). Although isoprene and monoterpenes have higher emission rates, the sesquiterpenes (C₁₅H₂₄) are of special importance due to their high reactivity towards atmospheric oxidants and their large aerosol formation potential (Griffin et al., 1999b).

Sesquiterpenes are mostly emitted by conifers, deciduous trees, and flowers (Knudsen et al., 1993). β -caryophyllene is the most abundant sesquiterpene (Helmig et al., 2007). It has two double bonds so its oxidation occurs in two steps. The reaction rate constants for the two reactions steps are $k_1 = 1.2 \pm 0.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Shu and Atkinson, 1995) and $k_2 = 1.1 \pm 0.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Winterhalter et al., 2009) respectively. Assuming an ozone mixing ratio of 40 ppb, the atmospheric lifetime of β -caryophyllene is $\tau_1 = 1.5 \text{ min}$ and the lifetime of the first generation products is approximately $\tau_2 = 2.5 \text{ h}$. The first and second generation oxidation products of β -caryophyllene that have been detected in the particle phase include β -caryophyllonic acid, β -caryophyllinic acid, β -caryophyllon aldehyde, β -nocaryophyllon aldehyde, etc. (Jaoui et al., 2003; Winterhalter et al., 2009; Li et al., 2011). The ambient concentrations of most of these have not been quantified due to the lack of suitable standards. The lifetime of β -caryophyllene due to the reaction with OH (assuming an OH concentration of $2 \times 10^6 \text{ molecule cm}^{-3}$) is approximately 40 min (Atkinson and Arey, 2003).

A number of earlier studies have measured the SOA yield of β -caryophyllene ozonolysis. The SOA yield does increase with increasing OA levels as predicted by

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Odum et al. (1996). Winterhalter et al. (2009) reported SOA yields from 6 to 41 % for 50–440 $\mu\text{g m}^{-3}$ of SOA, while Chen et al. (2012) measured an SOA yield of 24.3 % for 10 $\mu\text{g m}^{-3}$ SOA. Lee et al. (2006a) found a yield of 45 % for 336 $\mu\text{g m}^{-3}$ SOA while Jaoui et al. (2013) measured an SOA yield of 53 % for 55.4 $\mu\text{g m}^{-3}$ SOA. Ng et al. (2006) measured an SOA yield of 45 % for 336 $\mu\text{g m}^{-3}$ SOA. These results are quite inconsistent with relatively low values suggested by Winterhalter et al. (2009) and Lee et al. (2006a, b) and higher for the other studies.

Oxidation of β -caryophyllene by hydroxyl radicals in the presence of light has also been studied. In such studies hydroxyl radicals were produced by the photolysis of HONO. Lee et al. (2006b) measured an SOA yield of 68 % for 212 $\mu\text{g m}^{-3}$ while Ng et al. (2006) reported an SOA yield of 53 % for 212 $\mu\text{g m}^{-3}$ SOA. Other studies investigated the photo-oxidation β -caryophyllene/ NO_x mixtures. Griffin et al. (1999a) found an SOA yield of 37–79 % for 18–82 $\mu\text{g m}^{-3}$ SOA while Hoffmann et al. (1997) found an SOA yield of 103–125 % for 845–998 $\mu\text{g m}^{-3}$, Alfarrá et al. (2012) reported an SOA yield of 9.5–26.7 % for 35.6–128.8 $\mu\text{g m}^{-3}$ and Jaoui et al. (2013) measured an SOA yield of 30 % for 54 $\mu\text{g m}^{-3}$ SOA. Jaoui et al. (2013) also reported an effective enthalpy of vaporization of 43.9 kJ mol^{-1} for aerosol generated from β -caryophyllene ozonolysis and 41.1 kJ mol^{-1} for aerosol generated from β -caryophyllene photo-oxidation.

There are significant discrepancies among the results of previous studies regarding the SOA yield in this system. Potential reasons for the differences include the absence, in some of the studies, of correction of the mass of the particles that is lost on the walls of the smog chamber reactor. Other reasons include challenges with the injection and measurement of β -caryophyllene (Jaoui et al., 2013; Lee et al., 2006a; Helmig et al., 2004). The objective of this work is to measure the amount of aerosol produced by the reaction of the β -caryophyllene with ozone or hydroxyl radicals and suggest aerosol yield parameterizations for atmospheric chemical transport models. We also examine the effect that UV light and temperature has on the β -caryophyllene SOA. The volatility and the effective vaporization enthalpy of β -caryophyllene SOA are estimated.

Finally, the chemical aging of the SOA as it continues reacting with hydroxyl radicals is investigated.

2 Experimental methods

Experiments were carried out in the smog chamber of Carnegie Mellon University Center for Atmospheric Particle Studies (CAPS). The smog chamber is a 12 m³ Teflon reactor (Welch Fluorocarbons). A major complication in smog chamber experiments is that particles and potentially vapors are continuously lost to the walls of the reactor. As a result the number and the mass concentration of the particles decrease. The particle wall loss rate in general depends on particle size, the geometry of the smog chamber, the turbulence and electric field within the chamber, and the charge distribution of the particles (Crump and Seinfeld, 1981). A semi-empirical approach for calculating the particle wall losses (Pathak et al., 2007) involves measuring an average mass wall-loss rate constant in the chamber after the reactions are completed and then applying this constant to the entire experiment. This method assumes that the wall loss rate is first order and independent of particle size. Most previous studies have neglected the losses of organic vapors on the walls deposited particles. Hildebrandt et al. (2011) developed a method that calculates SOA yields in two extreme cases: when there are no vapor losses on the particles deposited on the walls ($w = 0$), similar to Pathak et al. (2007), and also the case in which organic vapors condense on the particles on the walls in a way similar to the suspended particles in the reactor ($w = 1$). Matsunaga and Ziemann (2010) and Zhang et al. (2014) reported loss of the organic vapors onto the Teflon walls. Measurements of these losses are challenging. We assume that these losses are negligible for this fast reacting system.

The chamber was suspended inside of a temperature-controlled room. The walls of the smog chamber room were lined with UV lights (General Electric model 10526 black). Prior to an experiment, the chamber was flushed with purified air for 12–48 h.

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air was purified by passing through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity to < 10 %.

Ozone was added to the chamber using an electrical discharge generator (AZCO, model HTU-500ACPS). 0.5 mL of 2-butanol (Sigma-Aldrich, ReagentPlus, $\geq 99\%$) was also introduced into the chamber before selected experiments as an OH-scavenger to avoid the oxidation of the precursor by the OH produced during the ozonolysis experiments. For the photooxidation experiments we used HONO and H_2O_2 (Sigma-Aldrich, 50–50 % solution) photolysis as the source of OH radicals. HONO was produced by mixing a 4.9 g L^{-1} sulfuric acid solution with a 6.9 g L^{-1} sodium nitrite with a volumetric ratio of 2 : 1. HONO or H_2O_2 were injected in the chamber using a bubbler. We tested the injection method by measuring the concentration of the hydroxyl radicals using 2-butanol as a tracer and a GC/FID (Chromatotec airmoBTX) with 15 min time resolution. The estimated concentration of hydroxyl radicals was approximately $10^7\text{ molecules cm}^{-3}$ for HONO photolysis and $10^6\text{ molecules cm}^{-3}$ for H_2O_2 photolysis. We did not add any NO_x in the chamber for the ozonolysis experiments and the low NO_x experiments. The measured NO_x level was of the order of a few ppb for these experiments. For the high NO_x experiments the corresponding NO_x concentrations due to the dissociation of HONO were more than 1 ppm.

β -caryophyllene (Sigma-Aldrich, $\geq 98.5\%$) was injected through a heated septum injector in which clean air was passed over the injected liquid to vaporize and transfer it to the chamber via Teflon tubing. Previous studies have reported tubing losses during the injection of “sticky” compounds like the sesquiterpenes (Jaoui et al., 2013; Lee et al., 2006a; Helmig et al., 2004). To overcome this problem, we gently purged the Teflon tubing with clean air (5 L min^{-1}) for 1 h after the injection. The concentration of the β -caryophyllene that reacted in the chamber was calculated using the organic volume that was injected in the chamber. This method was tested by measuring the signal of m/z 81 using a Proton-Transfer Reactor Mass spectrometer (PTR-MS, Ionicon Analytic GmbH) which has been found to be a strong signal for β -caryophyllene (Lee et al., 2006a, b). During the tests the initial signal of m/z 81 was zero and after

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

the injection and the gentle purge of the line for one hour the signal increased and reached a plateau.

In some of the previous studies ammonium sulfate particles were used as seeds. β -caryophyllene reacts with ozone and OH radicals sufficiently fast so that nucleation occurs immediately even in the presence of seed aerosols, resulting in two aerosol modes (nucleation and condensation mode), making data analysis (particularly the wall loss correction) difficult (Lee et al., 2006b; Ng et al., 2006). Thus, in our experiments no seed particles are used. Formation of particles took place less than a minute after the reactant injection.

A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3772 or 3010) was used for the measurement of the number and the volume distributions of aerosols. The mass concentration and the chemical composition of the particles were monitored using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). The reported SOA mass concentration is calculated by using the volume distribution and the density of the β -caryophyllene SOA. In each experiment we used the algorithm of Kostenidou et al. (2007) to estimate the effective density of the SOA and the collection efficiency (CE) of the HR-ToF-AMS. This algorithm combines the volume and mass distributions of the aerosol measured, respectively, by the SMPS and HR-ToF-AMS. The concentration of O_3 was measured using a continuous O_3 analyzer (Dasibi 1008-PC) and the concentration of nitrogen oxides was measured using a Teledyne chemiluminescent NO/NO₂/NO_x analyzer Model 200A.

The oxidation of β -caryophyllene took place at a constant temperature of $20 \pm 2^\circ\text{C}$ and at RH < 10% in most experiments. Two experiments were conducted at higher relative humidity equal to 50 and 90% respectively.

After the reactions were completed the chamber was heated to 40°C to investigate the evaporation of the particles produced. For investigation of the behavior of the SOA at higher temperatures we used the thermodenuder of An et al. (2007). The temperatures in the thermodenuder were in the range of 25–120°C with a centerline residence

Formation and
chemical aging of
SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

⏴

⏵

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



time of 26 s. Table 1 lists the initial conditions and the calculated SOA yields for all experiments.

3 Results and discussion

3.1 Ozonolysis

5 The results of a typical ozonolysis experiment (Exp. 1) are shown in Fig. 1. Initially, we injected 2-butanol and ozone in the chamber and at time zero we injected the β -caryophyllene. The mass of the aerosol started increasing right away and 30 min later the SOA concentration reached $32 \mu\text{g m}^{-3}$. 2.5 h after the beginning of the experiment, the temperature was increased to 40°C . Approximately $6 \mu\text{g m}^{-3}$ of suspended SOA
10 evaporated in 20 min (Fig. 1). The wall loss corrected SOA mass decreased 15 % due to evaporation. After 20 min the system appeared to reach equilibrium and the suspended mass decreased again slowly due to wall losses.

The average density of the SOA formed in the ozonolysis experiments was $0.97 \pm 0.03 \mu\text{g m}^{-3}$ (Table 1). The corresponding average collection efficiency of the HR-ToF-AMS was $\text{CE} = 0.58 \pm 0.12$. The wall losses corrected aerosol mass concentration is
15 presented in Table 1 for two extreme cases: when there are no vapor losses on the particles deposited on the walls ($w = 0$), and also the case in which organic vapors condense on the particles on the walls in a way similar to the suspended particles in the reactor ($w = 1$) (Hildebrandt et al., 2011). Because reactions are fast in this system
20 the $w = 1$ case results are at most 20 % higher than that the $w = 0$ ones. The average O : C ratio of the fresh SOA produced was 0.32 ± 0.03 .

The SOA yields for the ozonolysis experiments were similar to the yields reported by Chen et al. (2012) (Fig. 2). The dashed line in Fig. 2 represents the fitting of the
25 data from the two studies using the volatility basis set framework (Donahue et al., 2006). The resulting parameters (mass yields of the products of the various volatilities) are shown in Table 2. This fitting suggests that 16 % of the SOA had rela-

Formation and
chemical aging of
SOAA. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tively low volatility ($C^* = 1 \mu\text{g m}^{-3}$). Traditionally, the mass yields for the ozonolysis products of sesquiterpenes that have been used in CTMs (Lane et al., 2008) for $C^* = \{1, 10, 100, 1000\} \mu\text{g m}^{-3}$ are $\alpha_1 = 0.05$, $\alpha_2 = 0.1$, $\alpha_3 = 0.5$, $\alpha_4 = 0.6$ respectively. This parameterization is a fit of the experimental studies of Griffin et al. (1999a), Hoffmann et al. (1997), and Ng et al. (2006). Chen et al. (2012) reported mass-based stoichiometric yields $\alpha_1 = 0.17$, $\alpha_2 = 0.11$ and $\alpha_3 = 1.03$ for corresponding saturation concentrations of 1, 10, and $100 \mu\text{g m}^{-3}$. These results suggest that practically all the products of the β -caryophyllene ozonolysis have effective saturation concentrations less or equal than $1000 \mu\text{g m}^{-3}$.

3.2 Oxidation via OH

In another series of experiments β -caryophyllene was oxidized by hydroxyl radicals produced by HONO photolysis. NO and NO_2 are formed when HONO is injected in the chamber. Thus, in these experiments the oxidation happened under high NO_x conditions ($\text{NO}_x/\text{VOC} = 0.17 \text{ ppb ppbC}^{-1}$). The initial reactant concentrations and the results of these experiments are listed in Table 1. The average density of the SOA formed in these series of experiments was $1.19 \pm 0.1 \mu\text{g m}^{-3}$. The average collection efficiency of the HR-ToF-AMS was 0.38 ± 0.11 . Figure 3 depicts the measured SOA yields as a function of SOA mass concentration. The SOA yields in these experiments were higher than the yields of ozonolysis experiments. The average O : C ratio was 0.33 ± 0.06 . The ozone produced during the oxidation was always less than 10 ppb.

Similar experiments were performed using hydroxyl radicals produced by H_2O_2 photolysis. The SOA yields when H_2O_2 photolysis was used as source of hydroxyl radicals were similar to the yields of ozonolysis of β -caryophyllene (Table 1). The average density of the SOA formed in these series of experiments was $1.05 \pm 0.04 \mu\text{g m}^{-3}$ and the average O : C ratio was 0.24 ± 0.02 . The average collection efficiency of the HR-ToF-AMS was 0.67 ± 0.1 . The SOA yields at low NO_x conditions are lower than the ones at high NO_x conditions. These results agree with Ng et al. (2007) who found that SOA

**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



yield increases with increasing NO_x levels during the formation of SOA from sesquiterpenes (longifolene and aromadendrene) oxidation by OH. These authors suggested that the formation of low volatility organonitrates might be one reason for the higher SOA yields. Before the reaction started the nitrate signal at the HR-ToF-AMS was zero.

5 After the SOA formation the ratio of the nitrate over the organic signal ($\text{NO}_3 : \text{Org}$) was 0.15 ± 0.04 at the high NO_x experiments, while at the low NO_x experiments the ratio was 0.01 ± 0.00 . The formation of organonitrates at the high NO_x experiments can explain this difference. Another potential reason for the difference in the SOA yield is the concentration of the oxidant. HONO photolysis produced one order of magnitude
10 higher concentration of OH than H_2O_2 photolysis. We estimate that the exposure of the organics to OH was 10 times higher in the HONO experiments compared to the H_2O_2 ones for the period until the maximum yield was achieved.

Our results suggest that there are substantial differences in β -caryophyllene SOA produced under different NO_x conditions. The density of the SOA produced under high
15 NO_x conditions is approximately 20% higher than the one produced under low NO_x conditions. Furthermore, during the oxidation of β -caryophyllene under high NO_x conditions less volatile compounds are produced (Table 2). In Fig. 4 we compare the mass spectra of the β -caryophyllene SOA produced by ozonolysis (Exp. 8), reaction with OH at high NO_x (Exp. 15), and low NO_x (Exp. 24). The ozonolysis SOA spectra had significant
20 differences from those produced by the OH reaction (lower m/z 43, higher m/z 44, etc.) and θ angles of 19.5° with the high NO_x SOA and 20.1° for the low NO_x case. The high and low NO_x spectra (without accounting for the nitrate) were quite similar to each other ($\theta = 8.1^\circ$).

3.3 Chemical aging of fresh β -caryophyllene SOA

25 In another series of experiments we studied the chemical aging of the β -caryophyllene SOA produced in this first set of reactions. The formed SOA in these experiments was produced by the oxidation of the β -caryophyllene with ozone in the presence of hydroxyl radicals (without the addition of OH scavenger). The SOA yield of this reaction

is higher than the yields of the reactions of β -caryophyllene with the individual oxidants. The reason is probably the synergism between the two oxidants reacting with the first generation products of the oxidation of β -caryophyllene.

Initially, we studied the effect of UV light on the SOA. In Exp. 2 the β -caryophyllene SOA produced in the dark during ozonolysis was exposed to UV-light. The SOA formed had a wall loss corrected mass of $57 \mu\text{g m}^{-3}$ and $\text{O} : \text{C} = 0.38$. Approximately 1.5 h after the mass of the SOA started decreasing in the smog chamber we turned on the UV light. The SOA was exposed to UV light for one hour. During this period no change in the mass or the chemical mass spectrum of the SOA was observed. This suggests that the presence of UV light does not have a major effect on the chemical composition of these particles.

In experiments 27–33 (Table 3) we investigated the effect that subsequent exposure to OH radicals has on β -caryophyllene SOA. In experiments 27–31 the OH radicals were produced by HONO photolysis while in experiments 32–33 they were produced by H_2O_2 photolysis.

The SOA mass concentration time series of Exp. 27 is presented in Fig. 5. SOA was formed by the reaction of 300 ppb of ozone and 3 ppb of β -caryophyllene. Approximately 1.5 h after the mass of the SOA started decreasing in the smog chamber, HONO was injected in the chamber and the UV lights were turned on resulting in the production of significant levels of OH radicals (around $10^7 \text{ molecules cm}^{-3}$). This resulted in an immediate increase of the aerosol corrected mass concentration by approximately $3 \mu\text{g m}^{-3}$ (17%).

The time series of the HR-ToF-AMS signals m/z 43 and m/z 44 for the same experiment (Exp. 27) are shown in Fig. 6a and b. Chemical aging resulted in an increase of f_{43} from 0.08 to 0.09 and f_{44} from 0.065 to 0.08. Also, the ratio f_{44}/f_{43} increased approximately 10% when OH was introduced into the chamber. The $\text{O} : \text{C}$ ratio increased from 0.26 to 0.32, after the production of the hydroxyl radicals in the chamber indicating chemical aging of β -caryophyllene SOA (Fig. 6c). The results of all aging experiments

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

are summarized in Table 3. The SOA yields increased 10–30 % because of the aging reactions.

Matsunaga and Ziemann (2010) and Zhang et al. (2014) have stressed the possibility of losses of vapors, to the Teflon chamber walls. During chemical aging these compounds could be transformed to SOA and therefore these vapor losses may be introducing significant negative artifacts in chemical aging experiments. In order to test this hypothesis, we conducted experiments in which chemical aging of the SOA was initiated immediately after the SOA was formed. In Exp. 29 we initiated chemical aging of the β -caryophyllene SOA approximately 10 min after the maximum SOA mass concentration was reached instead of around 1.5 h in other experiments. The chemical aging of the SOA resulted in a SOA corrected mass increase from 31 to 41 $\mu\text{g m}^{-3}$, approximately 32 %. The O : C ratio increased from 0.26 to 0.29.

To test the role of RH two experiments were performed under higher RH conditions, 50 and 90 % respectively (Exp. 30, 31). The high relative humidity did not affect the SOA production; the SOA yield and the O : C for this set of experiments were similar to the low relative humidity experiments of these series. Figure 7 depicts the SOA mass concentration time series of Exp. 31. Ten minutes after the maximum SOA mass concentration was reached, we increased the OH concentration in the chamber by injecting HONO. In both experiments the chemical aging resulted in a 40 % increase of the corrected mass concentration. The chemical aging of the β -caryophyllene SOA under high relative humidity gives the largest additional mass production. In Exp. 30 (RH = 50 %) the O : C increased from 0.28 to 0.35. Similarly in Exp. 31 (RH = 90 %) the O : C increased from 0.21 to 0.28.

In experiments 32 and 33 we investigated the chemical aging of the β -caryophyllene SOA in the presence of OH radicals when photolysis of H_2O_2 was used as a source of OH. In Exp. 32 the wall losses corrected mass concentration of the fresh SOA was 30 $\mu\text{g m}^{-3}$, and the O : C was approximately 0.28. Approximately 1.5 h after the mass of the SOA had started decreasing in the smog chamber the photolysis of H_2O_2 was initiated. The exposure of the SOA to hydroxyl radicals was one order of magnitude

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



lower than in the previous aging experiments (Exp. 27–31). After the production of hydroxyl radicals the mass concentration of the SOA remained stable and the O : C was 0.29. The results of Exp. 33 were similar.

3.4 The vaporization enthalpy of β -caryophyllene SOA

Using a thermodenuder we examined the behavior of the SOA at high temperatures. The mass fraction remaining (MFR) of SOA for the thermodenuder experiments is presented in Fig. 8. We used the volatility distributions of the reaction products estimated from the measured yields (Table 2) as inputs to the thermodenuder model described by Ripiinen et al. (2010) and estimated the vaporization enthalpy and the accommodation coefficient (α) of the β -caryophyllene SOA. For the particles that are produced from the ozonolysis of β -caryophyllene (Exp. 3) the calculated effective enthalpy of vaporization was 70 kJ mol^{-1} and $\alpha = 0.04$. The mass fraction remaining during the ramp of the temperature in the chamber (Exp. 1) was also used as input in the model. Finally, a combination of the two experiments was used. In all cases, the estimated enthalpy of vaporization and accommodation coefficient did not change. For β -caryophyllene reacted with OH in the presence of high concentrations of NO_x (Exp. 21), the SOA formed had an effective enthalpy of vaporization of 44 kJ mol^{-1} and $\alpha = 0.08$. The SOA produced by the reaction with OH at low NO_x concentration had an effective enthalpy of 56 kJ mol^{-1} and $\alpha = 0.05$.

4 Conclusions

In this study we examined the formation of secondary organic aerosol from the reaction of β -caryophyllene with ozone and hydroxyl radicals. The SOA yield for the ozonolysis of β -caryophyllene was 26 % at $10 \mu\text{g m}^{-3}$ SOA. These results agree with the results reported by Chen et al. (2012). The average density of the SOA formed in the ozonol-

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ysis experiments was $0.97 \pm 0.03 \mu\text{g m}^{-3}$. The average O : C ratio of the SOA produced was 0.32 ± 0.03 .

The reaction of β -caryophyllene with OH at low NO_x gave an SOA yield equal to 20 % at $10 \mu\text{g m}^{-3}$ SOA, similar to the SOA yield measured for the ozonolysis experiments. The average density of the SOA formed in these series of experiments was $1.05 \pm 0.04 \mu\text{g m}^{-3}$ and the average O : C ratio was 0.24 ± 0.02 .

The SOA yield at the reaction of β -caryophyllene with OH at high NO_x , is 38 % at $10 \mu\text{g m}^{-3}$ SOA. The average density of the SOA formed in these series of experiments was $1.18 \pm 0.1 \mu\text{g m}^{-3}$, 20 % higher than the low NO_x experiments. The average O : C ratio was 0.33 ± 0.06 . While the reactions under low NO_x conditions had similar SOA yields, the presence of high NO_x concentration during the reaction seems to benefit the production of β -caryophyllene SOA leading to the production of less volatile compounds.

A series of chemical aging experiments were performed. During these experiments the SOA was produced from the reaction of β -caryophyllene and ozone in the presence of hydroxyl radicals. The addition of hydroxyl radicals into the system of β -caryophyllene SOA, under high NO_x levels, led to 13–17 % increase of SOA mass concentration at dry conditions, and the O : C increased by 0.04 to 0.06 units. An experiment in which the chemical aging was initiated faster was conducted. The chemical aging of the SOA resulted in a SOA mass increase of approximately 32 %, indicating that in this system the vapor losses to the Teflon chamber walls were not negligible. The exposure of the β -caryophyllene SOA in UV light and in hydroxyl radicals under low NO_x conditions had no effect in the SOA.

Experiments at 50 and 90 % relative humidity were conducted in which β -caryophyllene reacted with ozone in the presence of hydroxyl radicals. The high relative humidity did not affect the fresh SOA production and its AMS spectrum. On the contrary, the high relative humidity conditions enhanced the chemical aging of the β -caryophyllene SOA. The exposure of the SOA to hydroxyl radicals under high NO_x and

Formation and
chemical aging of
SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



high relative humidity conditions led to an increase of the SOA concentration by 40 % and the O : C increased by 0.07 units.

For the particles that are produced by the ozonolysis of β -caryophyllene the calculated effective enthalpy of vaporization was 70 kJ mol^{-1} , while for the experiments that β -caryophyllene reacted with OH at low NO_x conditions was 56 kJ mol^{-1} , and at high NO_x conditions 44 kJ mol^{-1} . In all cases there was evidence of moderate resistances to mass transfer (mass accommodation coefficient 0.04–0.08).

Acknowledgements. We would like to thank Eleni Karnezi for her help with the thermodenuder simulations and Evangelia Kostenidou for experimental advice. This study was supported by EPA STAR program (grant RD-835405).

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Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Table 1. Initial conditions and results of the β -caryophyllene oxidation experiments.

Experiment	β -caryophyllene (ppb) ^a	Ozone (ppb)	SOA density (g cm ⁻³)	SOA concentration ($\mu\text{g m}^{-3}$) ^b		SOA yield (%) ^c
				$w = 0$	$w = 1$	
Ozonolysis						
1	13	300	1.01	41.2	45	41.7
2	14	300	0.97	47.6	50.7	43.3
3	5	600	0.93	10.9	11	24.2
4	32	300	0.97	89.2	95.1	34.8
5	2	600	0.97	0.3	0.3	1.9
6	4	300	0.95	8.9	9.4	29.4
7	21	300	0.98	108	119	65.2
8	11	300	0.96	44.8	52	57.1
9	27	300	0.95	88.6	97.7	42.8
10	19	300	1.03	84.6	96.2	58.6
11	30	300	0.96	140	163	63.7
12	13	300	0.96	56	65.4	59.7
13	24	300	0.99	162	194	96.1
14	3	300	0.99	12.4	13.2	48.2
OH radicals at high NO _x						
15	11	–	1.12	78.1	81.2	89
16	24	–	1.25	223	229	113.9
17	32	–	1.21	303	311	113.5
18	5	–	1.12	43.2	44.4	97.4
19	3	–	1.06	7.8	8.4	30.7
20	4	–	1.34	20.1	20.1	55.2
21	19	–	1.22	222.1	226.3	137.8
OH radicals at low NO _x						
22	32	–	1.02	156	193	70.3
23	16	–	1.08	55.7	56.9	41.6
24	11	–	1.07	47.2	49.0	53.7
25	5	–	0.99	8	8.8	19.3
26	21	–	1.09	97.8	97.7	53.5

^a This concentration is calculated based on the amount of β -caryophyllene injected into the chamber.

^b Wall losses corrected mass concentration measured by the SMPS using the corresponding density.

^c The SOA yields are calculated using the wall losses corrected SOA mass concentration for $w = 1$.

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Formation and
chemical aging of
SOA**A. Tasoglou and
S. N. Pandis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 2.** Product mass yields for the three different reactions using a four product volatility basis set.

Reaction	Saturation concentration ($\mu\text{g m}^{-3}$)			
	1	10	100	1000
Ozonolysis	0.16	0.14	0.36	0.74
OH radicals at high NO_x	0.01	0.59	0.79	0.01
OH radicals at low NO_x	0.1	0.11	0.57	0.62

Formation and chemical aging of SOA

A. Tasoglou and S. N. Pandis

Table 3. Initial conditions and results of the aging experiments.

Experiment	β -caryophyllene (ppb) ^a	Ozone (ppb)	RH (%)	SOA density (g cm^{-3})	Fresh SOA			Aged SOA				
					SOA concentration ($\mu\text{g m}^{-3}$) ^b		O : C	SOA yield (%) ^c	SOA concentration ($\mu\text{g m}^{-3}$) ^b		O : C	SOA yield (%) ^c
					$w = 0$	$w = 1$			$w = 0$	$w = 1$		
27	3	300	< 10	1.12	17	17.6	0.26	64.4	18.6	20.6	0.32	75.4
28	5	300	< 10	1.09	60.4	64.4	0.31	141.2	65.2	72.5	0.35	159
29	3	300	< 10	1.12	30.7	31.1	0.26	113.5	39.8	41	0.29	149.7
30	3	300	~ 50	1.15	32.8	33.7	0.28	123.3	44	47.2	0.35	140
31	3	300	~ 90	1.21	22.7	23	0.21	84.2	29.4	32.1	0.28	117.5
32	5	500	< 10	1.00	28.6	30.5	0.28	66.9	28.8	30.8	0.29	67.6
33	3	400	< 10	1.13	16	16.3	0.31	59.6	16.2	16.7	0.31	61.1

^a This concentration was calculated based on the amount of β -caryophyllene injected into the chamber.

^b This is the wall losses corrected mass concentration measured by the SMPS.

^c The SOA yields are calculated using the wall losses corrected SOA mass concentration for $w = 1$.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

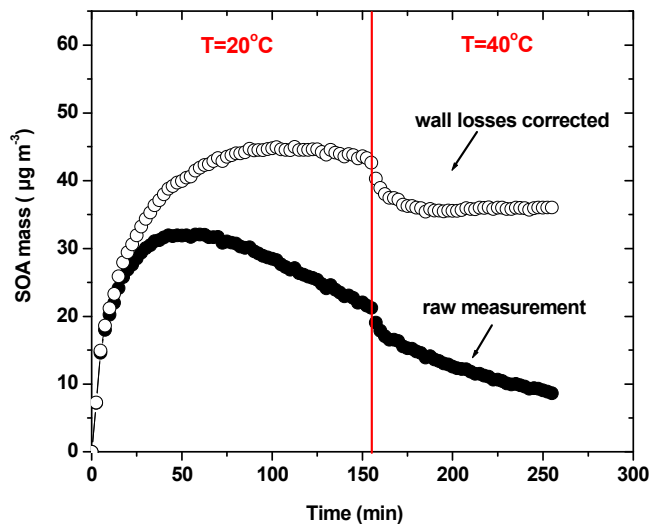


Figure 1. The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for $w = 1$) for Exp. 1. Also shown, the time when the temperature inside the chamber room was increased.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

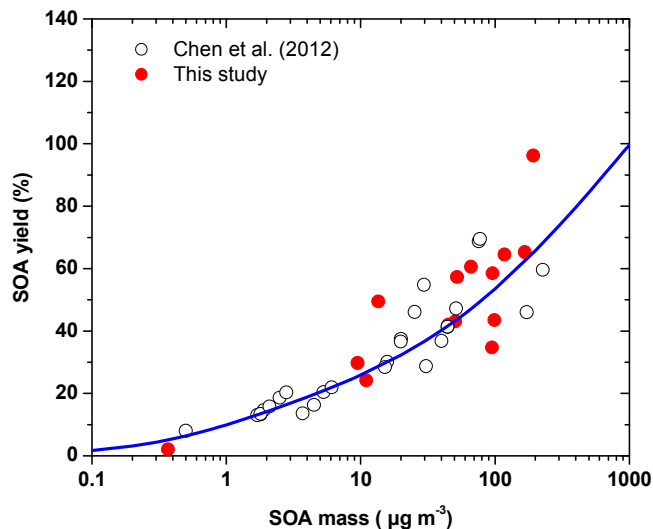


Figure 2. The SOA yield vs. the total mass produced (for $w = 1$). The red dots are the results of this study and the open symbols are the results of Chen et al. (2012). The dashed line is the fitting of the data from both studies using the volatility basis set (VBS) framework.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

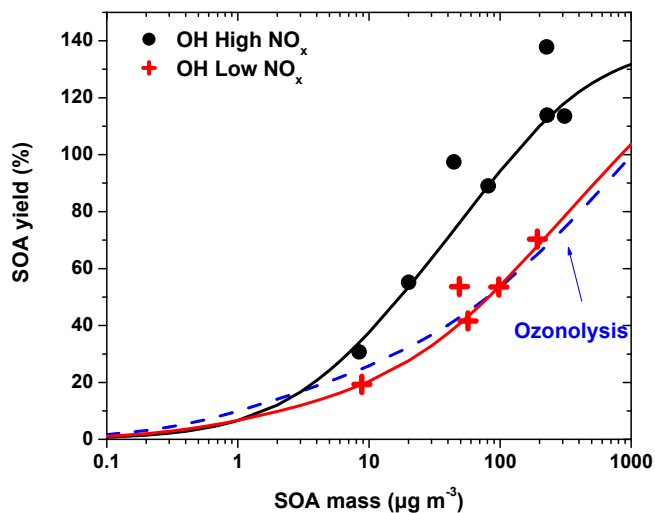


Figure 3. The SOA yield vs. the total mass aerosol produced. The black dots represent the experiments when photolysis of HONO was used as a source of hydroxyl radicals and the red crosses are for the photolysis of H_2O_2 . The dashed line corresponds to the SOA yield from the ozonolysis of β -caryophyllene.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

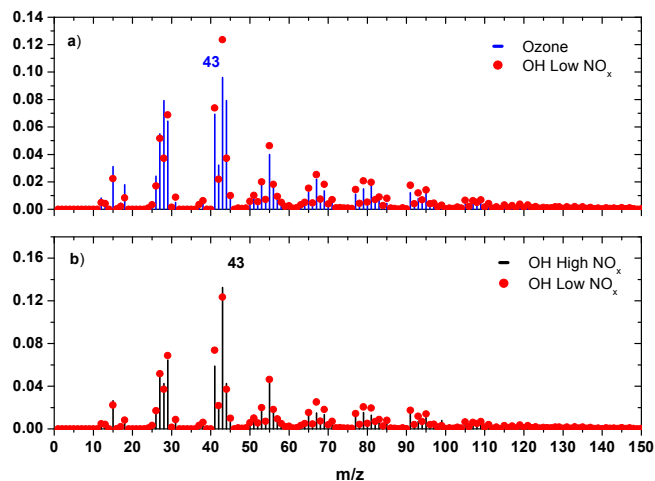


Figure 4. Comparison of the organic mass spectra of the β -caryophyllene SOA produced from the three reaction systems: **(a)** from ozonolysis and OH at low NO_x ($\theta=20.1$) **(b)** from OH at high and low NO_x ($\theta = 8.1$).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

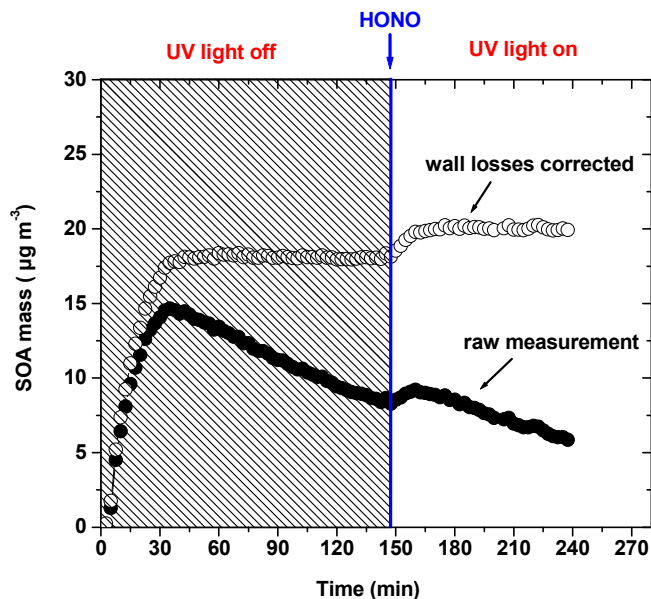
Formation and
chemical aging of
SOAA. Tasoglou and
S. N. Pandis

Figure 5. The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for $w = 1$) (Exp. 27). The shaded part indicates the period where the UV light was off and the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

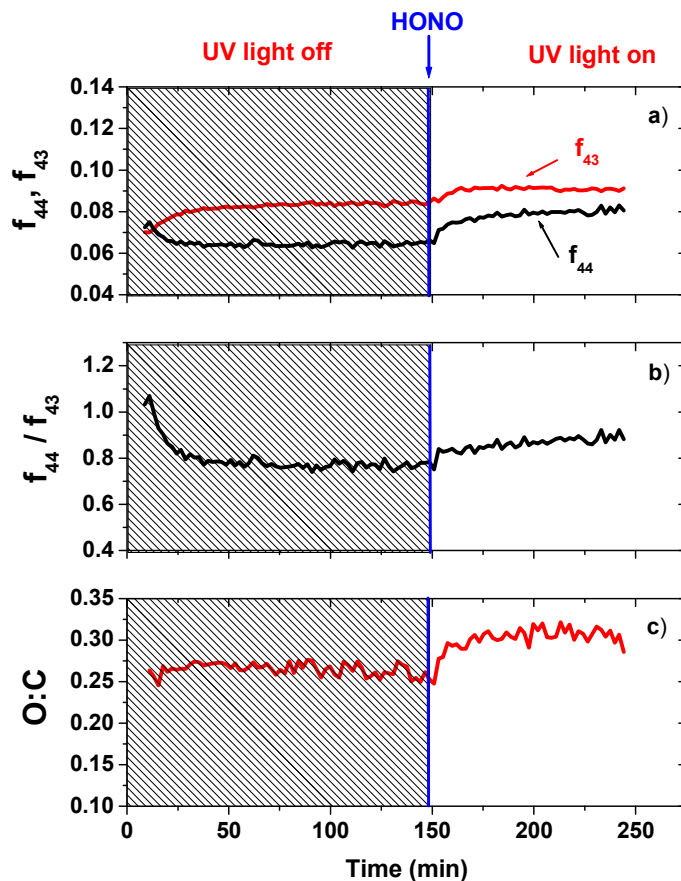
Formation and
chemical aging of
SOAA. Tasoglou and
S. N. Pandis

Figure 6. (a) The time series of fragments 43 and 44. (b) The ratio of the two fragments as a function of time. (c) The oxygen over carbon ratio of the particles as a function of time for Exp. 26. The shaded part indicates the period where the UV light was off and the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

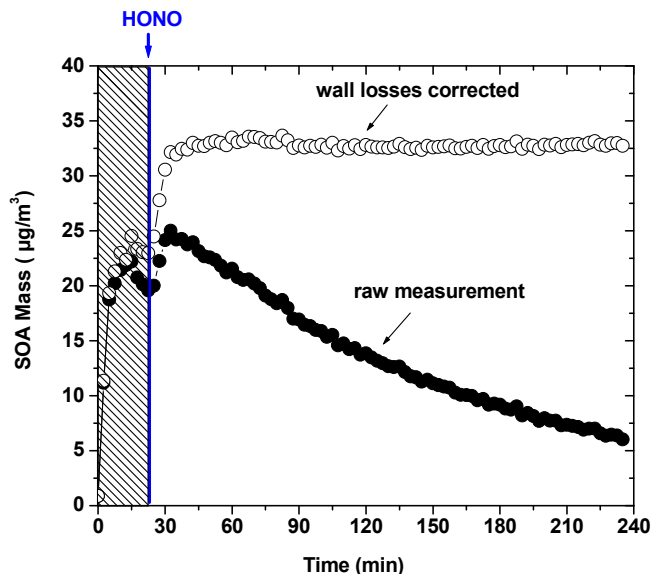


Figure 7. The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for $w = 1$) (Exp. 31). The shaded part indicates the period where the UV light was off and the with the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

Formation and chemical aging of SOA

A. Tasoglou and
S. N. Pandis

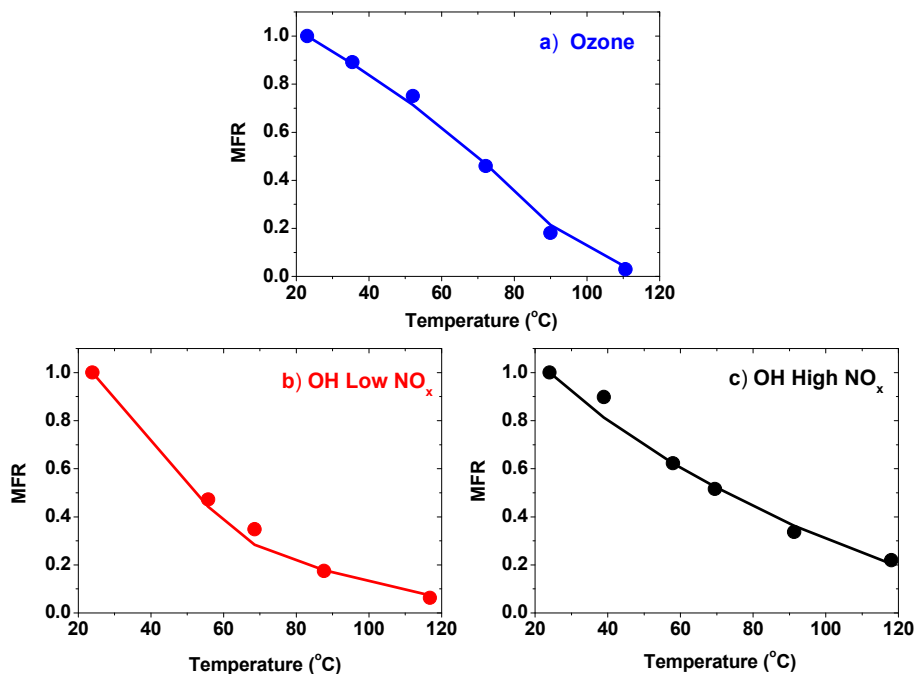


Figure 8. The thermograms (mass fraction remaining, MFR as a function of temperature) of the three different reaction systems. The circles represent the experimental data while the lines are the fitting of the model.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)