



Formation and  
chemical aging of  
SOA

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# Formation and chemical aging of secondary organic aerosol during the $\beta$ -caryophyllene oxidation

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## Abstract

The secondary organic aerosol (SOA) production during the oxidation of  $\beta$ -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  $\beta$ -caryophyllene SOA was studied by exposing the fresh SOA to high concentrations ( $10^7$  molecules  $\text{cm}^{-3}$ ) 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  $\beta$ -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  $\beta$ -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  $\beta$ -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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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  $\beta$ -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  $\beta$ -caryophyllene/ $\text{NO}_x$  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  $\text{kJ mol}^{-1}$  for aerosol generated from  $\beta$ -caryophyllene ozonolysis and 41.1  $\text{kJ mol}^{-1}$  for aerosol generated from  $\beta$ -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  $\beta$ -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  $\beta$ -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  $\beta$ -caryophyllene SOA. The volatility and the effective vaporization enthalpy of  $\beta$ -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 m<sup>3</sup> 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.

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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  $\text{H}_2\text{O}_2$  (Sigma-Aldrich, 50–50 % solution) photolysis as the source of OH radicals. HONO was produced by mixing a  $4.9\text{ g L}^{-1}$  sulfuric acid solution with a  $6.9\text{ g L}^{-1}$  sodium nitrite with a volumetric ratio of 2 : 1. HONO or  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  photolysis. We did not add any  $\text{NO}_x$  in the chamber for the ozonolysis experiments and the low  $\text{NO}_x$  experiments. The measured  $\text{NO}_x$  level was of the order of a few ppb for these experiments. For the high  $\text{NO}_x$  experiments the corresponding  $\text{NO}_x$  concentrations due to the dissociation of HONO were more than 1 ppm.

$\beta$ -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 ( $5\text{ L min}^{-1}$ ) for 1 h after the injection. The concentration of the  $\beta$ -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  $\beta$ -caryophyllene (Lee et al., 2006a, b). During the tests the initial signal of  $m/z$  81 was zero and after

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yield increases with increasing  $\text{NO}_x$  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  $0.15 \pm 0.04$  at the high  $\text{NO}_x$  experiments, while at the low  $\text{NO}_x$  experiments the ratio was  $0.01 \pm 0.00$ . The formation of organonitrates at the high  $\text{NO}_x$  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  $\text{H}_2\text{O}_2$  photolysis. We estimate that the exposure of the organics to OH was 10 times higher in the HONO experiments compared to the  $\text{H}_2\text{O}_2$  ones for the period until the maximum yield was achieved.

Our results suggest that there are substantial differences in  $\beta$ -caryophyllene SOA produced under different  $\text{NO}_x$  conditions. The density of the SOA produced under high  
15  $\text{NO}_x$  conditions is approximately 20% higher than the one produced under low  $\text{NO}_x$  conditions. Furthermore, during the oxidation of  $\beta$ -caryophyllene under high  $\text{NO}_x$  conditions less volatile compounds are produced (Table 2). In Fig. 4 we compare the mass spectra of the  $\beta$ -caryophyllene SOA produced by ozonolysis (Exp. 8), reaction with OH at high  $\text{NO}_x$  (Exp. 15), and low  $\text{NO}_x$  (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  $\theta$  angles of  $19.5^\circ$  with the high  $\text{NO}_x$  SOA and  $20.1^\circ$  for the low  $\text{NO}_x$  case. The high and low  $\text{NO}_x$  spectra (without accounting for the nitrate) were quite similar to each other ( $\theta = 8.1^\circ$ ).

### 3.3 Chemical aging of fresh $\beta$ -caryophyllene SOA

25 In another series of experiments we studied the chemical aging of the  $\beta$ -caryophyllene SOA produced in this first set of reactions. The formed SOA in these experiments was produced by the oxidation of the  $\beta$ -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  $\beta$ -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  $\beta$ -caryophyllene.

Initially, we studied the effect of UV light on the SOA. In Exp. 2 the  $\beta$ -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  $\beta$ -caryophyllene SOA. In experiments 27–31 the OH radicals were produced by HONO photolysis while in experiments 32–33 they were produced by  $\text{H}_2\text{O}_2$  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  $\beta$ -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  $10^7$  molecules  $\text{cm}^{-3}$ ). 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  $\beta$ -caryophyllene SOA (Fig. 6c). The results of all aging experiments

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

The reaction of  $\beta$ -caryophyllene with OH at low  $\text{NO}_x$  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  $0.24 \pm 0.02$ .

The SOA yield at the reaction of  $\beta$ -caryophyllene with OH at high  $\text{NO}_x$ , 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  $\text{NO}_x$  experiments. The average O : C ratio was  $0.33 \pm 0.06$ . While the reactions under low  $\text{NO}_x$  conditions had similar SOA yields, the presence of high  $\text{NO}_x$  concentration during the reaction seems to benefit the production of  $\beta$ -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  $\beta$ -caryophyllene and ozone in the presence of hydroxyl radicals. The addition of hydroxyl radicals into the system of  $\beta$ -caryophyllene SOA, under high  $\text{NO}_x$  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  $\beta$ -caryophyllene SOA in UV light and in hydroxyl radicals under low  $\text{NO}_x$  conditions had no effect in the SOA.

Experiments at 50 and 90 % relative humidity were conducted in which  $\beta$ -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  $\beta$ -caryophyllene SOA. The exposure of the SOA to hydroxyl radicals under high  $\text{NO}_x$  and

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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  $\beta$ -caryophyllene the calculated effective enthalpy of vaporization was  $70 \text{ kJ mol}^{-1}$ , while for the experiments that  $\beta$ -caryophyllene reacted with OH at low  $\text{NO}_x$  conditions was  $56 \text{ kJ mol}^{-1}$ , and at high  $\text{NO}_x$  conditions  $44 \text{ kJ mol}^{-1}$ . In all cases there was evidence of moderate resistances to mass transfer (mass accommodation coefficient 0.04–0.08).

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**Table 1.** Initial conditions and results of the  $\beta$ -caryophyllene oxidation experiments.

Experiment	$\beta$ -caryophyllene (ppb) <sup>a</sup>	Ozone (ppb)	SOA density (g cm <sup>-3</sup> )	SOA concentration ( $\mu\text{g m}^{-3}$ ) <sup>b</sup>		SOA yield (%) <sup>c</sup>
				$w = 0$	$w = 1$	
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 <sub>x</sub>						
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 <sub>x</sub>						
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

<sup>a</sup> This concentration is calculated based on the amount of  $\beta$ -caryophyllene injected into the chamber.

<sup>b</sup> Wall losses corrected mass concentration measured by the SMPS using the corresponding density.

<sup>c</sup> The SOA yields are calculated using the wall losses corrected SOA mass concentration for  $w = 1$ .

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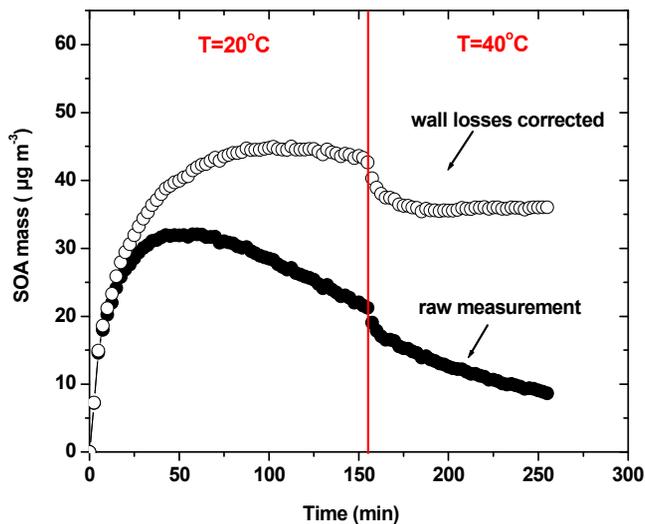
**Table 2.** Product mass yields for the three different reactions using a four product volatility basis set.

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 $\text{NO}_x$	0.01	0.59	0.79	0.01
OH radicals at low $\text{NO}_x$	0.1	0.11	0.57	0.62



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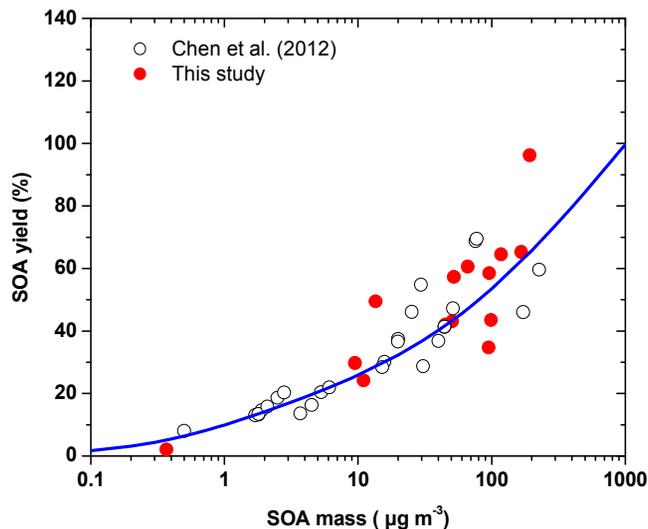


**Figure 1.** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w = 1$ ) for Exp. 1. Also shown, the time when the temperature inside the chamber room was increased.

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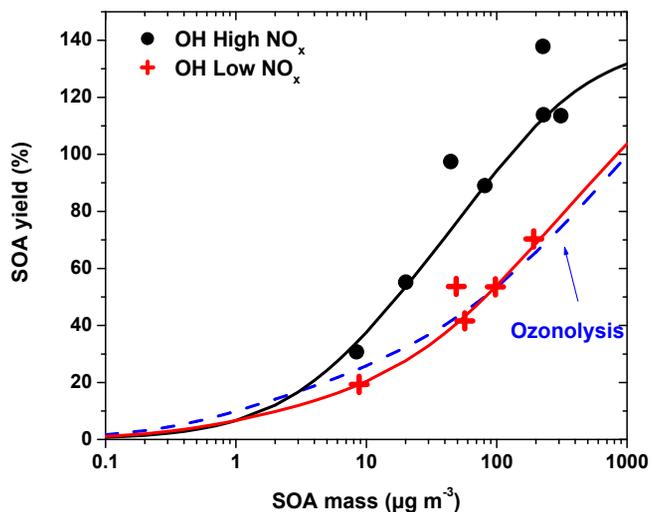


**Figure 2.** The SOA yield vs. the total mass produced (for  $w = 1$ ). The red dots are the results of this study and the open symbols are the results of Chen et al. (2012). The dashed line is the fitting of the data from both studies using the volatility basis set (VBS) framework.

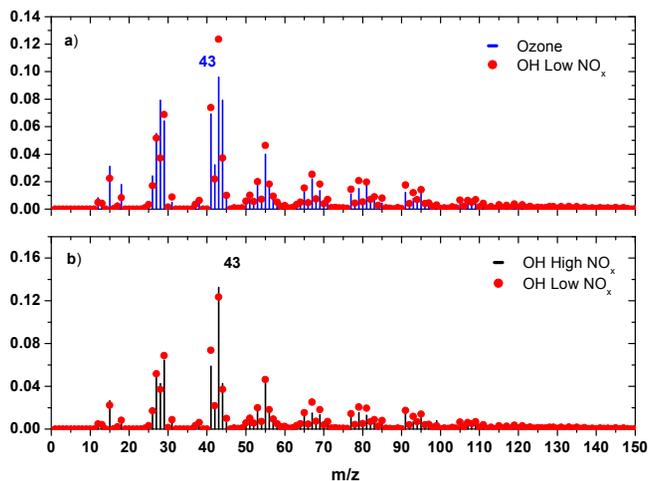
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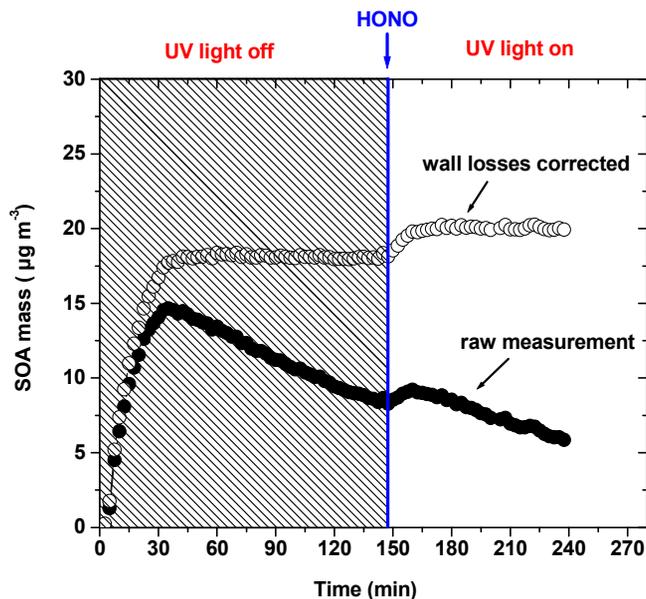


**Figure 3.** The SOA yield vs. the total mass aerosol produced. The black dots represent the experiments when photolysis of HONO was used as a source of hydroxyl radicals and the red crosses are for the photolysis of  $\text{H}_2\text{O}_2$ . The dashed line corresponds to the SOA yield from the ozonolysis of  $\beta$ -caryophyllene.

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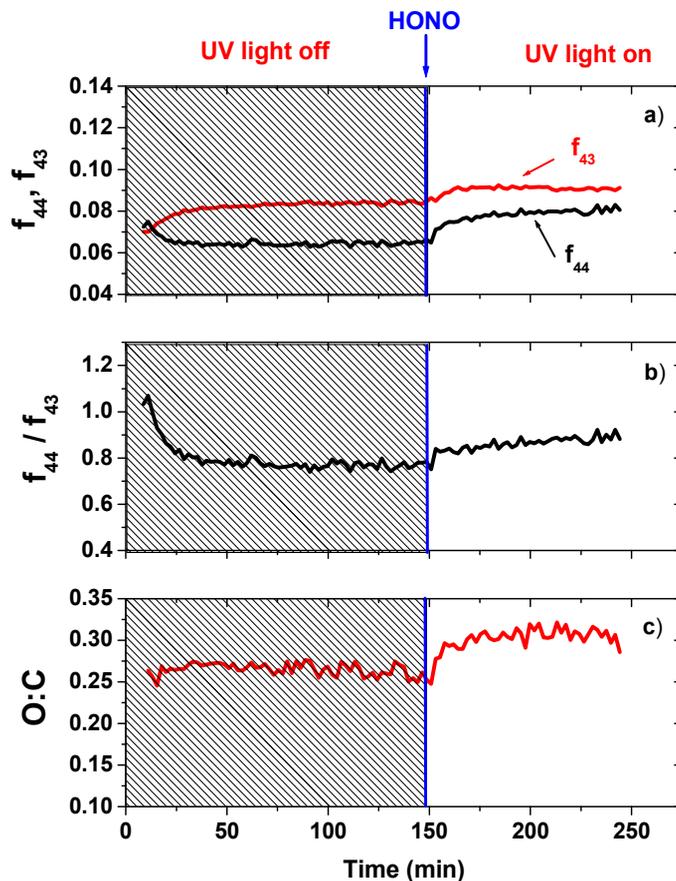
**Figure 4.** Comparison of the organic mass spectra of the  $\beta$ -caryophyllene SOA produced from the three reaction systems: **(a)** from ozonolysis and OH at low NO<sub>x</sub> ( $\theta=20.1$ ) **(b)** from OH at high and low NO<sub>x</sub> ( $\theta = 8.1$ ).

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**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.

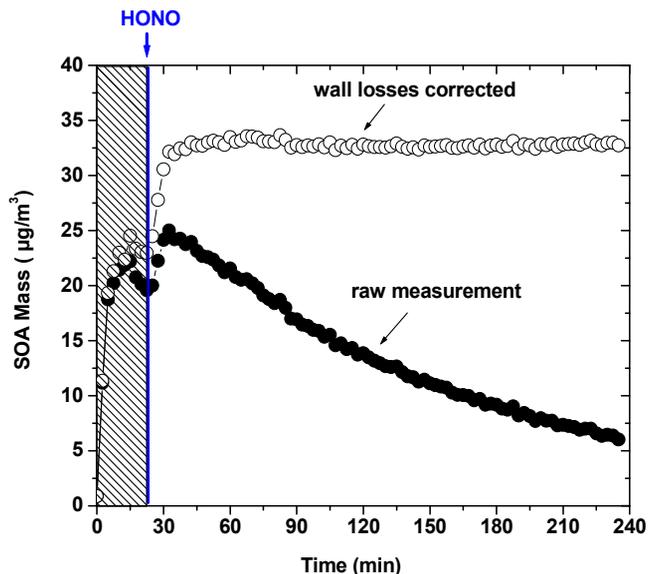
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**Figure 6.** (a) The time series of fragments 43 and 44. (b) The ratio of the two fragments as a function of time. (c) The oxygen over carbon ratio of the particles as a function of time for Exp. 26. The shaded part indicates the period where the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

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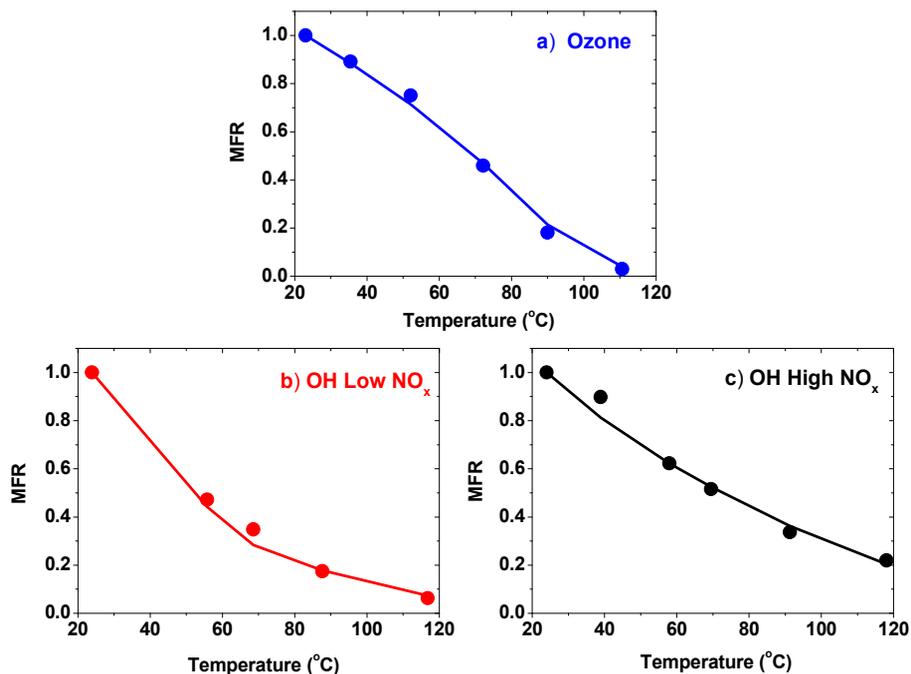


**Figure 7.** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w = 1$ ) (Exp. 31). The shaded part indicates the period where the UV light was off and the with the period when the UV light was on. Also shown, the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

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**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.