



Ozonolysis of α -pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields)

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Received 25 April 2006; revised 31 July 2006; accepted 2 October 2006; published 2 February 2007.

[1] Despite a number of smog chamber studies of the α -pinene/ O_3 system, the effect of temperature on α -pinene secondary organic aerosol (SOA) mass fractions (or yields) remains poorly understood. In this study, the temperature dependence of secondary organic aerosol mass fractions (AMF) during ozonolysis of α -pinene is investigated in a temperature controlled smog chamber. Experiments were performed with and without ammonium sulfate aerosol seeds at RH < 10% and at 0°C, 15°C, 20°C, 30°C and 40°C. The initial α -pinene concentration varied from 3.5 to 50 ppb, and an excess of ozone was used. High time resolution secondary organic AMFs were obtained combining continuous gas-phase concentration measurements (using proton transfer reaction mass spectrometry, PTR-MS) with continuous aerosol concentration measurements (using a scanning mobility particle sizer, SMPS). The presence of inert aerosol seeds is often necessary to minimize experimental errors due to loss of semivolatile vapors to the walls of the chamber. The α -pinene secondary organic AMFs show a weak dependence on temperature in the 15° to 40°C range and stronger temperature dependence in the 0° and 15°C range.

Citation: Pathak, R. K., C. O. Stanier, N. M. Donahue, and S. N. Pandis (2007), Ozonolysis of α -pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), *J. Geophys. Res.*, 112, D03201, doi:10.1029/2006JD007436.

1. Introduction

[2] Oxidation of α -pinene is an important source of secondary organic aerosol (SOA) in the troposphere and plays a significant role in ozone (O_3) chemistry in rural areas [Went, 1960; Trainer *et al.*, 1987; Andreae and Crutzen, 1997]. The global α -pinene emissions are estimated to be around 50 Tg yr⁻¹ [Guenther *et al.*, 1995; Seinfeld and Pankow, 2003]. Ozonolysis is the major α -pinene oxidation pathway in the troposphere, destroying roughly 80% of the emitted α -pinene [Griffin *et al.*, 1999a]. The α -pinene/ O_3 reaction is quite efficient in forming SOA with AMFs (AMF: mass of SOA formed/mass of α -pinene reacted) as high as 0.70 for high α -pinene concentrations [Hoffmann *et al.*, 1997]. A number of smog chamber studies have shown that the α -pinene secondary organic AMF depends upon the α -pinene concentration, on oxidizing agent, e.g., O_3 or OH, and temperature [Odum *et al.*, 1996; Hoffmann *et al.*, 1997; Hallquist *et al.*, 1997, 1999; Griffin *et al.*, 1999b; Jang and Kamens, 1999; Kamens *et al.*, 1999; Yu *et al.*, 1999a, 1999b; Cocker *et al.*, 2001; Gao *et al.*, 2001; Hoppel *et al.*, 2001; Bonn and Moortgat, 2002; Takekawa *et al.*, 2003; Saathoff *et al.*, 2004; Docherty *et al.*,

2005; Kroll and Seinfeld, 2005]. Overall, secondary organic AMF increases with increasing α -pinene concentration rapidly at small values of α -pinene concentrations (<50 ppb) and slowly at higher α -pinene levels [Odum *et al.*, 1996; Hoffmann *et al.*, 1997; Griffin *et al.*, 1999b; Cocker *et al.*, 2001; Hoppel *et al.*, 2001]. This observed behavior is consistent with the predictions of gas/particle partitioning theory [Pankow, 1994a, 1994b; Odum *et al.*, 1996; Pankow *et al.*, 2001; Seinfeld *et al.*, 2001; Seinfeld and Pankow, 2003].

[3] Hoffmann *et al.* [1997] reported α -pinene ozonolysis aerosol mass fraction ranging from 0.14 to 0.23 for initial α -pinene concentrations in the 40–160 ppb range, at 48°C, without OH scavenger. The same authors observed that AMFs are generally higher for experiments in the dark than those in day light. Griffin *et al.* [1999b] found AMF of 0.08–0.19 at 37°C for 17–65 ppb of α -pinene with 2-butanol as OH scavenger. Secondary organic AMFs were relatively lower in the presence of NO_x [Odum *et al.*, 1996]. Cocker *et al.* [2001] reported AMF in the range of 0.02 to 0.26 at various α -pinene concentrations (12–220 ppb at 28°–30°C) and experimental conditions (with or without seeds, variable RH). These authors found that the AMF was not affected by the presence of inorganic salt aerosol seeds and varied little with RH. Saathoff *et al.* [2004] reported strong dependence of the AMF on temperature. For 17 ppb initial α -pinene concentration in the presence of OH scavenger, the AMF was: 0.42 at –20°C, 0.23 at 0°C, 0.17 at 10°C, 0.14 at 20°C and 0.06 at 40°C. In the above studies the ozone concentrations were 200–500 ppb. C. O. Stanier

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et al. (Measurements of the volatility of aerosols from α -pinene ozonolysis, submitted to *Environmental Science and Technology*, 2007, hereinafter referred to as Stanier et al., submitted manuscript, 2007) reported that aerosol volume depends approximately linearly on temperature during ramps with slopes ranging from 0.6 to 2.9% per $^{\circ}\text{C}$. In their experiments, aerosols were generated from reaction of α -pinene (14–150 ppb) and ozone at a constant temperature of $22^{\circ} \pm 2^{\circ}\text{C}$ in the presence of the OH-scavenger 2-butanol. After the reactions were completed at $22^{\circ} \pm 2^{\circ}\text{C}$ the chamber was heated and/or cooled in an operating range from 15° to 40°C .

[4] It has been shown that the distribution of SOA products from ozonolysis of α -pinene changes in the presence of water [Jang and Kamens, 1998; Fick et al., 2003]. Jang and Kamens [1998] reported that the SOA formation was reduced in wet conditions. Although Cocker et al. [2001] found that the α -pinene secondary organic AMF varies little with RH in seed free or dry seed conditions, the presence of aqueous salt seeds reduced the AMF compared to dry seed conditions.

[5] Secondary organic AMF from α -pinene decreases in the presence of both UV light and high concentrations of NO_x [Presto et al., 2005a, 2005b]. These studies suggest that SOA formation may depend significantly on actinic flux, and that the final products of ozonolysis depend on NO_x concentration (i.e., $[\text{VOC}]/[\text{NO}_x]$).

[6] Despite these significant efforts a number of issues related to the formation of SOA by α -pinene are yet to be elucidated. These include the AMFs at low α -pinene concentrations (<10 ppb) and the temperature dependence of AMF. The effects of the presence of inert seeds, low or high ozone, and temperature, on both the real time and the final secondary organic AMF are explored in this study.

2. Experimental Methods

[7] Experiments were performed in the Carnegie Mellon University smog chamber using a 10 m^3 Teflon reactor (Welch Fluorocarbons). Concentrations of ozone and particles were measured using a continuous ozone analyzer (Dasibi 1008-PC) and a scanning mobility particle sizer (SPMS, TSI 3936), respectively. The gas phase concentration of α -pinene was monitored by gas chromatography (Perkin Elmer AutoSystem XL with FID and J&W Scientific DB-624 capillary column, $30\text{ m} \times 0.530\text{ mm}$). A 3-stage preconcentrator (Entech 7100A) was used upstream of the gas chromatograph for improved VOC quantification. Gas phase concentrations were measured using proton transfer reaction mass spectrometry (PTR-MS) with a resolution of 20 s. The PTR-MS operation details are described elsewhere [Presto et al., 2006].

[8] Most experiments were conducted at constant temperatures (0°C , 15°C , 20°C , 30°C or 40°C). The temperature control in all the 0°C experiments was performed manually using liquid nitrogen as a cooling medium. The temperature variability in these 0°C experiments is in the range of $\pm 5^{\circ}\text{C}$. However, in all other experiments temperature control was automated with little variability, $\pm 0.5^{\circ}\text{C}$, throughout the experiment. These were complemented with temperature ramp experiments (Stanier et al., submitted manuscript, 2007), in which the ozonolysis reaction was carried out to

completion at one temperature and then the temperature was varied. Experiments were carried out at initial α -pinene concentration of 3.5 ± 0.4 ppb, 7.3 ± 0.7 ppb, 14.3 ± 0.8 ppb, 38.5 ± 1.5 ppb and 50 ± 2.0 ppb. The experiments were carried out with an excess of ozone (Table 1) produced from an ozone generator (Azco HTU500ACPS). Reactions were carried out in the presence of an OH-scavenger (2-butanol) in excess (0.5 ml, which is 500–2000 times the initial α -pinene concentration). Reagents were HPLC or ACS purity from Sigma Aldrich. Reactions were carried out under dry conditions ($<10\%$ RH) and with or without polydisperse seed aerosols, generated from 7 mM (0.9 g/L) ammonium sulfate aqueous solutions. The seed aerosol concentrations were usually between 4000 and 6000 particle cm^{-3} . The particle density of SOA was assumed to be 1 g cm^{-3} for all calculations in the paper; therefore the aerosol mass fractions (AMFs) are normalized to unity density. The detailed experimental conditions are listed in Table 1.

2.1. Corrections for Aerosol Mass Loss on Smog Chamber Walls

[9] Aerosol is lost to the walls of the reactor during smog chamber experiments. If $M(t)$ is the aerosol mass measured in the reactor at time t . Let us assume that the wall loss rate is first order and that the loss rate constant is independent of size. We will investigate these assumptions in a subsequent section. The rate constant, k , of aerosol mass loss to walls after aerosol chemical production has stopped is given by:

$$\ln[M(t)] = -kt + C, \quad (1)$$

where C is a constant. The plot of $\ln[M(t)]$ against time after the SOA production has stopped provides the mass loss rate constant k (hr^{-1}), as the slope of the corresponding line (Figure 1). The values of k were estimated for each experiment using the measurements after more than 90% of the initial α -pinene had reacted in the chamber. The fits were excellent (usually $R^2 = 0.99$) suggesting that our assumptions were valid. After the calculation of k , the produced SOA can be calculated subtracting the mass concentration of the seeds from the total mass.

$$\text{SOA}(t) = M(t) + k \int_0^t M(t) dt - M_S \quad (2)$$

where M_S is the seed concentration at the time when the SOA formation begins. The integral in equation (2) was calculated numerically using the measurements. Values of k ranged from 0.07 to 0.48 hr^{-1} depending on the air circulation around the Teflon reactor due to the temperature control system. The application of the wall loss correction for an experiment is illustrated in Figure 2.

2.2. Secondary Organic AMF Calculation From GC/FID Measurements Coupled With PTR-MS

[10] For each experiment, AMF is calculated in two separate ways. First, the final AMF is calculated by:

$$\text{Aerosol Mass Fraction(AMF)} = \frac{[\text{SOA}]}{\Delta[\alpha\text{-pinene}]} \quad (3)$$

Table 1. Summary of α -Pinene Ozonolysis Experiments

Experiment	Initial α -Pinene, ^a ppb	Ozone, ppb	Temperature, °C	Seed Concentration, cm ⁻³	Initial Mass, $\mu\text{g}/\text{m}^3$	Final Mass, $\mu\text{g}/\text{m}^3$	Net SOA Mass, $\mu\text{g}/\text{m}^3$	Secondary Organic AMF
1	14.3	250	40	0	0	7	7.0	0.09
2	42	250	15	0	0	50.7	50.7	0.21
3	38.3	250	20	0	0	33.7	33.7	0.16
4	50	250	30	0	0	48.7	48.7	0.18
5	50	250	40	0	0	34.7	34.7	0.13
6 ^b	7.3	50	20	0	0	0.08	0.08	0.00
7	7.3	1500	20	0	0	2.8	2.8	0.07
8 ^b	7.3	750	20	0	0	1.4	1.4	0.03
9	3.7	3100	20	0	0	0.7	0.7	0.03
10	7.3	1500	40	0	0	2.1	2.1	0.05
11	7.3	1500	15	0	0	2.6	2.6	0.06
12	7.3	1500	30	0	0	2.5	2.47	0.06
13	38.3	250	20	6000	6.27	43.85	37.58	0.17
14	7.3	1500	20	5000	6.1	8.96	2.86	0.07
15	8	280	20	6000	5.9	8.45	2.55	0.06
16 ^b	3.7	250	20	5000	4.7	4.95	0.25	0.01
17 ^b	8	50	20	5500	5.8	7.3	1.5	0.03
18 ^b	7.3	250	20	0	0	0.007	0.01	0.00
19	8	1500	15	4000	3.8	7.5	3.7	0.08
20	7.3	1500	40	5000	4.99	6.41	1.42	0.04
21	8.5	1500	30	5000	4.82	8.21	3.39	0.07
22	14.3	250	15	4000	4.65	11.83	7.18	0.09
23	14.3	300	15	4000	5.28	14.56	9.28	0.11
24	14.3	250	20	0	0	9.81	9.81	0.12
25	14.3	250	30	0	0	10.02	10.02	0.13
26 ^c	38.3	250	15	5500	5.5	38.8	33.3	0.15
27	38.3	250	40	3500	0.5	37.5	37	0.18
28	29	250	15	4000	2.27	20.5	18.23	0.11
29	7.3	750	20	4500	3.73	6.78	3.05	0.07
30	33	250	30	3500	2.8	29.3	26.5	0.15
31	14.3	250	30	3500	2.87	10.5	7.63	0.10
32 ^d	15	250	0 \pm 5	9000	5.66	21.77	16.11	0.18
33 ^d	17	250	15	12000	8.34	18.82	10.48	0.11
34	14.3	250	30	7000	4.19	14.96	10.77	0.14
35 ^d	24	250	40	3000	2.47	18.51	16.04	0.13
36 ^d	42	250	0 \pm 5	4000	3.34	99.5	96.16	0.38
37	115	300	15	0	0	293	293	0.44

^aThe standard deviations of the α -pinene concentrations in different experiments are provided with their initial concentrations: 3.5 ± 0.4 ppb, 7.3 ± 0.7 ppb, 14.3 ± 0.8 ppb, 38.5 ± 1.5 ppb and 50 ± 2.0 ppb.

^bIn these experiments, there was a significant loss of semivolatile compounds to the wall of the chamber and they are not used for secondary organic AMF analysis.

^cAfter completion of the α -pinene reactions at 15°C the temperature was changed to 20°C, 30°C and 40°C.

^dIn these experiments, proton transfer reaction mass spectrometry coupled with gas chromatography was used to measure α -pinene gas phase concentration.

where [SOA] is the organic aerosol mass concentrations ($\mu\text{g m}^{-3}$) produced at the end of experiment after a concentration $\Delta[\alpha\text{-pinene}]$ has reacted. The reacted α -pinene concentration is practically equal to the initial α -pinene concentration in the chamber. One such AMF can be calculated for each experiment.

[11] The real-time AMF is the AMF measured continuously during an experiment, from the SOA produced and α -pinene reacted at that point of time, while only a fraction of the initial α -pinene has reacted. To calculate it we use once more equation (3) with SOA(t) calculated from equation (2) and $\Delta[\alpha\text{-pinene}]$ calculated from the PTR-MS and GC/FID data. PTR-MS and/or GC/FID data are fitted using an exponential function ($\Delta[\alpha\text{-pinene}] = [\alpha\text{-pinene}]_0(1 - e^{-qt})$), as shown in Figure 3.

[12] PTR-MS permits direct observations of AMF during the initial phase of oxidation experiments. In contrast, GC/FID measurements require 25–30 min between samples. In the experiments where both PTR-MS and GC/FID measurements were available measurements and exponential fits were consistent (Figure 3). In the experiments where only GC/FID measurements were available the corresponding

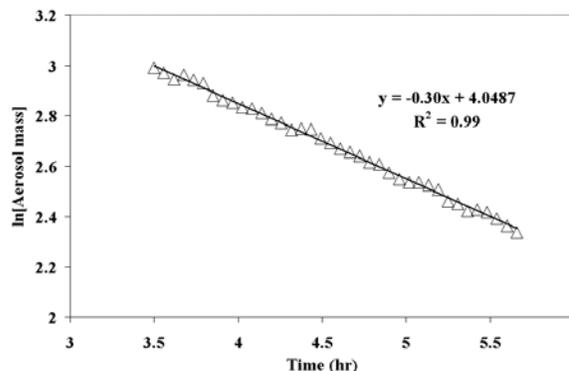


Figure 1. Logarithm of measured aerosol mass concentration as a function of time in smog chamber experiment 13 (38.3 ppb α -pinene, 250 ppb O_3 , 20°C, ammonium sulfate seeds). The wall loss rate constant is given by the slope of the line.

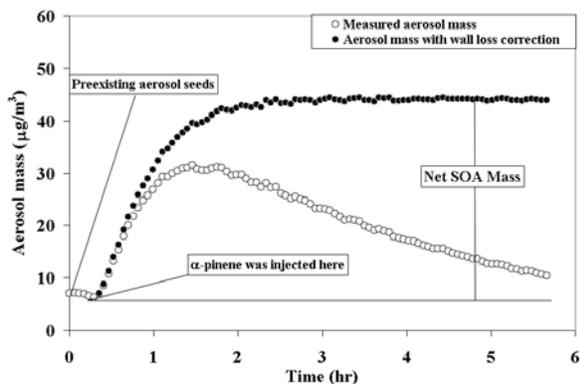


Figure 2. Wall loss correction using equation (2) for smog chamber experiment 13. This is the same experiment as that of Figure 1.

fits relied only on them. We used the PTR-MS or GC/FID first-order fit, as shown in Figure 3 ($\Delta[\alpha\text{-pinene}] = [\alpha\text{-pinene}]_0(1 - e^{-qt})$) to estimate the amount of α -pinene reacted at the time of each SOA mass measurement by the SMPS (Figure 3). α -pinene concentrations were calculated every 3.5 min, that is the same interval for which SMPS measurements are available.

[13] Results from smog chamber experiments are subject to a range of errors including concentration measurements but also artifacts caused by the chamber walls. These errors are, at least partially, reflected in the reproducibility of the experiments. We use as an estimate of the experimental errors the standard deviation in similar experiments at four temperatures (15° , 20° , 30° and 40°C) and three concentration levels of α -pinene (7.3–8.5 ppb, 14.3–17 ppb and 38.3–50 ppb). The average standard deviation was approximately 10% of the AMF and therefore we assume an experimental error of $\pm 10\%$ in AMF throughout this paper.

3. Results

3.1. Role of Ozone and Seeds

[14] For a concentration of α -pinene equal to 7.3 ppb, experiments were carried out with 50, 250, 750 and 1500 ppb initial ozone concentrations at 20°C without

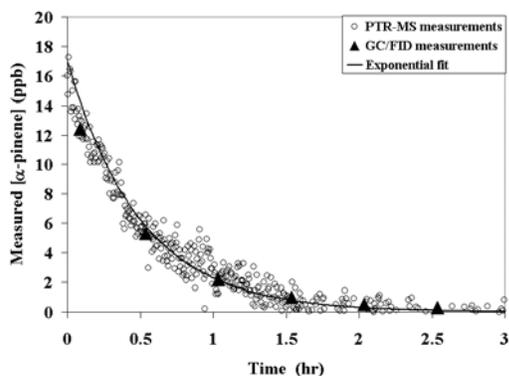


Figure 3. Comparison of gas phase α -pinene concentration measurements by GC/FID and PTR-MS. The experiment was carried out for 17 ± 0.8 ppb of α -pinene concentration and 250 ppb ozone in the presence of ammonium sulfate seeds at 15°C (experiment 34).

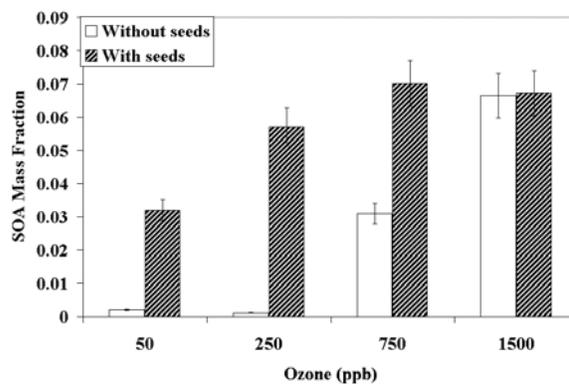


Figure 4. Comparison of SOA mass fraction with and without seeds for 7.3 ± 0.7 ppb of α -pinene at 20°C and 50, 250, 750 and 1500 ppb ozone.

seeds. The measured AMFs were suspiciously low for O_3 less than 250 ppb (Figure 4). The secondary organic AMF increased dramatically as ozone concentration was increased further to 750 ppb and 1500 ppb. Few particles (number concentrations $< 100 \text{ cm}^{-3}$) were formed in the low O_3 experiments (Figure 5) and there was little surface area available for condensation of the semivolatile vapors other than the walls. Even if all the α -pinene eventually reacted with O_3 only a small fraction of its semivolatile products was still available in the gas phase for transfer to the particle phase. These results suggest that significant losses of the semivolatile vapors to the smog chamber walls can take place during experiments where both of the reactants are at low concentrations. However, large numbers of particles were formed in the experiments with high ozone concentrations. The high initial reaction rates lead to a rapid saturation of the gas phase with semivolatile vapors, nucleation, and then condensation of the remaining semivolatile material on the newly created particle surface area. To minimize these losses of condensable vapors to the walls we used two approaches: higher O_3 initial concentrations and use of $(\text{NH}_4)_2\text{SO}_4$ seeds to provide the necessary surface area for concentration in the first stages of the experiment. Use of seeds and O_3 concentrations above 250 ppb or no seeds and O_3 levels of 1500 ppb minimizes

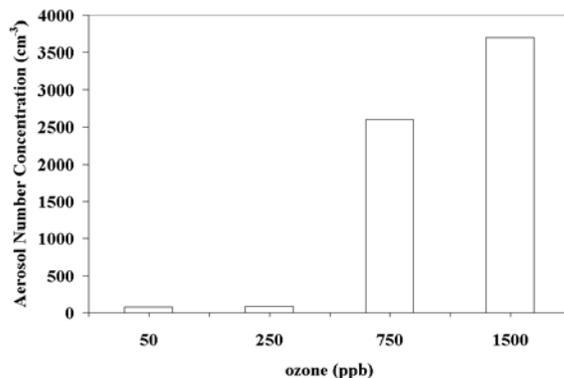


Figure 5. Aerosol number concentrations during ozonolysis of α -pinene (without seeds) for 7.3 ± 0.7 ppb and 50, 250, 750 and 1500 ppb ozone.

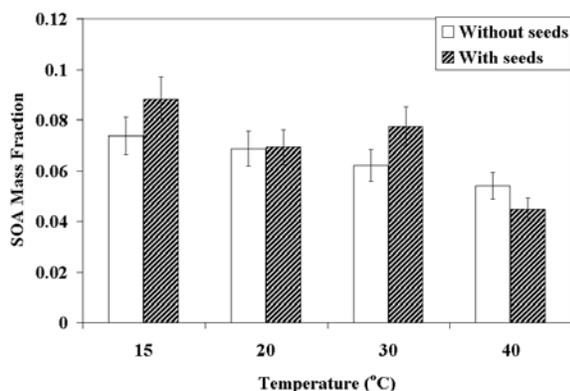


Figure 6. Comparison of the α -pinene secondary organic AMFs with and without seeds for 7.3 ± 0.7 ppb initial concentration and 1500 ppb ozone.

the losses to walls in our system (Figure 4). For the high O_3 concentrations the final AMFs do not depend on the presence of seeds, in agreement with the work of *Cocker et al.* [2001]. In all the seeded experiments, there was no formation of new particles due to homogeneous nucleation.

[15] Figure 6 shows the final α -pinene secondary organic AMFs measured with and without seeds for 7.3 ppb α -pinene and 1500 ppb ozone at 15°C, 20°C, 30°C and 40°C. At all four temperatures, AMFs with and without seeds were the same within experimental error (two standard deviations). This suggests that when nucleation is rapid and produces a high concentration of nuclei, the addition of seeds does not affect the final AMF. For smog chambers of modest size, like the one in Carnegie Mellon University, and rapid mixing (due to the vigorous air circulation outside the reactor by the temperature control system) use of inert seeds is recommended for secondary organic AMF experiments. For the rest of our discussion on final AMFs, we will use the results of the experiments with seeds and/or the moderate to high O_3 concentrations for our analysis.

[16] The lack of seeds can introduce experimental errors to the real time AMFs even at high ozone concentrations. Figure 7 illustrates this point for the experiments with 1500 ppb of O_3 with and without ammonium sulfate seeds.

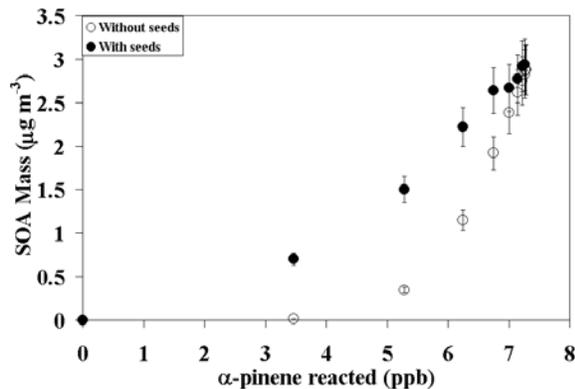


Figure 7. Role of seeds on the real time secondary organic AMFs: comparison of SOA mass as a function of α -pinene reacted, in the seeded and nonseeded experiments for 7.3 ± 0.7 ppb of α -pinene and 1500 ppb ozone at 20°C.

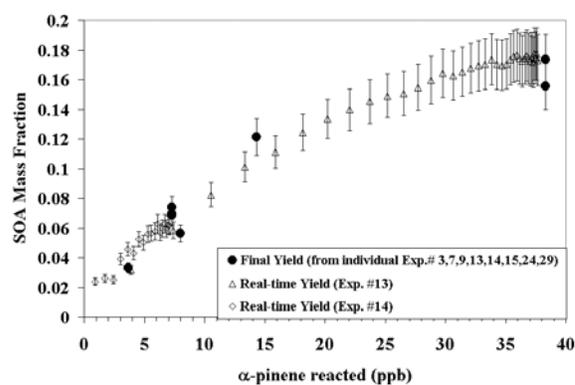


Figure 8. Comparison of final AMFs and real-time AMFs in seeded experiments at 20°C for various amount of α -pinene reacted.

Even if the final AMFs are practically the same for the two experiments (see also the high ozone experiments in Figure 4) the real time AMFs for $\Delta[\alpha\text{-pinene}]$ less than 6 ppb are significantly smaller in the nonseeded experiment. In these conditions, the formation of SOA is limited by the mass transfer of organic vapors to the newly formed particles. Even if little semivolatile material is lost to the chamber walls during the first few minutes of reaction the system is out of equilibrium. The gas phase is supersaturated with semivolatile material and the AMF is low during the initial stages of the nonseeded experiments. The small losses of vapors to the walls during these few minutes allow the system to eventually reach a similar final AMF with the seeded experiments.

[17] Mass transfer limitation can, in principle, affect the seeded experiment too resulting in lower real time AMFs. To investigate this we compare the final AMF, which corresponds to equilibrium conditions, with real time AMFs (Figure 8) measured at 20°C. The good agreement of the results suggests that the system is close to equilibrium in the seeded experiments. These results strongly support the presence of seeds in all similar chamber experiments to minimize the corresponding experimental artifacts (losses of semivolatile vapors to the walls and mass transfer limitations).

3.2. Temperature Dependence of Secondary Organic AMFs

[18] The final α -pinene secondary organic AMFs obtained at the different constant temperature experiments are shown in Figure 9. A weak dependence of AMF on temperature was observed at all three α -pinene concentrations between 15° and 40°C. On average, the AMF decreased slightly (~ 10 – 20%) when temperatures were increased from 15° to 40°C. However, a strong temperature dependence of AMF on temperature was observed between 0° and 15°C. The secondary organic AMFs almost decreased two fold, when temperature was raised from 0° to 15°C. The results from four experiments of *Saathoff et al.* [2004] are also shown. These experiments at 17 ppb of α -pinene are relatively consistent with our experiments at 15 ppb, but suggest a little stronger temperature dependence in the 10°–40°C range. The real time AMFs can be used to provide additional information about the temperature dependence of

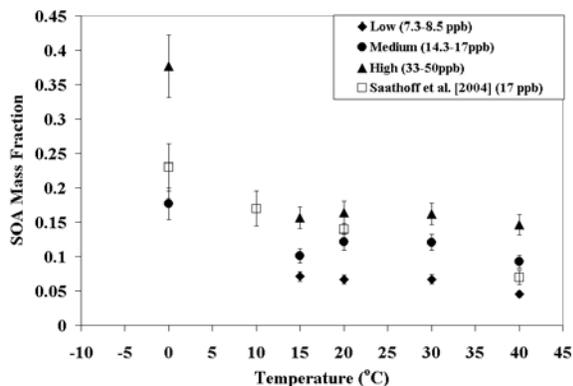


Figure 9. Comparison of the secondary organic AMFs for low, medium and high concentrations of α -pinene at $0^\circ \pm 5^\circ\text{C}$, $15^\circ \pm 0.5^\circ\text{C}$, $20^\circ \pm 0.5^\circ\text{C}$, $30^\circ \pm 0.5^\circ\text{C}$ and $40^\circ \pm 0.5^\circ\text{C}$. The results of *Saathoff et al.* [2004] are also shown.

the SOA formation at concentration smaller than 7 ppb. For example, for 5 ppb of reacted α -pinene $1.7 \mu\text{g m}^{-3}$ of SOA were formed at 0°C , $1.3 \mu\text{g m}^{-3}$ at 20°C , $0.7 \mu\text{g m}^{-3}$ at 40°C . The aerosol AMFs showed once more a rather weak dependence on temperature in the $15^\circ\text{--}30^\circ\text{C}$ range. Also for reacted α -pinene concentrations less than 3 ppb the real time AMFs were the same for all temperatures within at least the experimental error (Figure 10). Real time secondary organic AMF analysis suggests that there is little temperature dependence of AMFs at ambient level concentrations of α -pinene (<3 ppb). This suggests that at these conditions the SOA composition may be dominated by the species of low volatility that remain in the particulate phase even at the higher temperatures.

3.3. Thermodynamics Versus Kinetics

[19] The temperature dependence of α -pinene secondary organic AMF may be thermodynamically or kinetically driven. Thermodynamics controls the equilibrium partitioning of the semivolatile products of the reaction between the gas and particulate phases. Lower temperature leads to lower vapor phase concentrations and higher SOA concentrations. The change of the rates of the numerous reactions with temperature can lead to different production

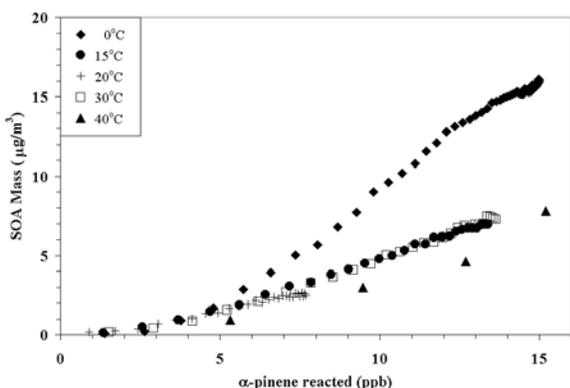


Figure 10. SOA mass produced during the ozonolysis of α -pinene as a function of amount of α -pinene reacted at different temperatures.

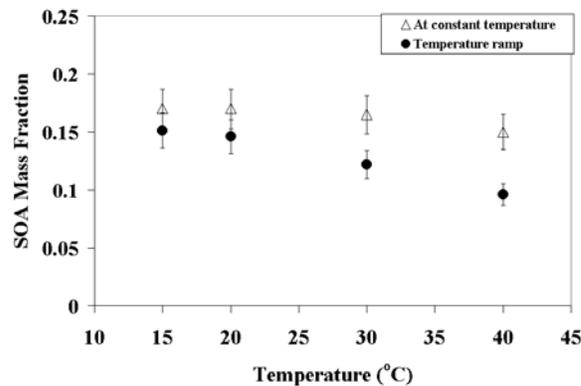


Figure 11. Comparison of α -pinene secondary organic average AMF measured for 38.3 ± 1.5 ppb α -pinene and 250 ppb ozone concentrations at constant temperature and secondary organic AMFs which were first obtained at 15°C and then later temperature ramp was carried out and secondary organic AMF were obtained at 20°C , 30°C and 40°C .

rates of the various products and therefore different composition of the particulate phase. The change of the kinetics with temperature may increase or decrease the AMF after the complete reaction of the same α -pinene at different temperatures.

[20] To investigate the role of thermodynamics versus kinetics in SOA formation a few experiments were conducted at one reaction temperature and later, after the complete α -pinene ozonolysis, the temperature was altered using the approach of Stanier et al. (submitted manuscript, 2007). Figure 11 shows the comparison of α -pinene secondary organic AMFs each measured at constant temperature and secondary organic AMFs first obtained with reaction at one temperature (15°C) and then later temperature ramp to 20°C , 30°C and 40°C .

[21] The secondary organic AMFs differ for the two methods at 30°C and 40°C and the discrepancies cannot be explained by experimental error (Figure 11). This suggests that the chemistry of SOA formation (e.g., the relative AMFs of condensable organic compounds formed at various temperatures) is sensitive to temperature change in the 15°C to 40°C range. Therefore the observed weak temperature dependence of the AMF, between 15°C and 40°C , is due to changes in the kinetics of SOA formation at different temperatures; offsetting partially the change in partitioning of the α -pinene SOA products.

[22] The results of the temperature ramp experiment correspond to an AMF change of approximately 1.6% per $^\circ\text{C}$. This value is consistent with the results of Stanier et al. (submitted manuscript, 2007) in temperature ramping experiments in similar (but not exactly the same) conditions.

4. Comparison With Other Studies

[23] Although a number of α -pinene ozonolysis secondary organic AMF studies have been conducted previously, most of them used higher α -pinene concentrations making a direct comparison difficult. Additional differences include temperature, the lack of an OH scavenger, use of NO_x and dark or light conditions [*Odum et al.*, 1996; *Hoffmann et al.*,

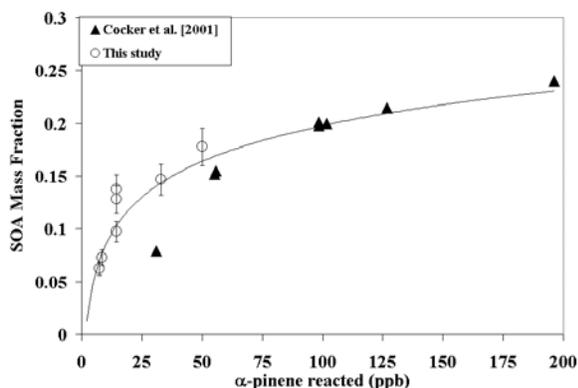


Figure 12. Comparison of SOA α -pinene AMFs as a function of α -pinene reacted in the smog chamber experiments of this study and Cocker *et al.* [2001] at 30°C.

1997; Griffin *et al.*, 1999b]. The α -pinene secondary organic AMF measured in this study can be compared with Cocker *et al.* [2001] as they used similar experimental conditions as ours, e.g., seeds, OH scavenger. The Cocker *et al.* [2001] experiments were performed at 28 to 30°C and in this study, data, shown in Figure 12, was obtained at 30°C. Although there was a little overlap in α -pinene concentrations the results of the two studies appear to be relatively consistent with tendency of higher AMFs measured in this study. The AMF curve shown in Figure 12 is based on both data sets. Two different curves can be obtained if the fits are obtained separately for the two data sets. However, the differences will be due to only one data point of the Cocker *et al.* [2001] study, obtained at the lower α -pinene concentration level.

[24] Our AMF measurements were generally consistent with those of Saathoff *et al.* [2004] (Figure 9). They measured AMF about 0.22 at 0°C and 17 ppb of α -pinene, which is similar to that, was measured in this study (~ 0.18) at $0 \pm 5^\circ\text{C}$ and 15 ppb of α -pinene concentration. The secondary organic AMFs measured at 20°C and 40°C by the two studies were also comparable within experimental error. However, the Saathoff *et al.* [2004] results suggest a stronger temperature dependence of the AMF than our study.

5. Conclusions

[25] In total, we carried out 37 smog chamber experiments in the α -pinene/O₃ system providing new information of secondary organic AMFs at low α -pinene concentrations (1 ppb to 50 ppb) in the temperature range of 0°C to 40°C. The new data can be used in secondary organic AMF parameterizations for air quality models. The secondary organic AMFs increase with increasing α -pinene concentration was quite similar to that of Cocker *et al.* [2001].

[26] The presence of inert seeds in smog chamber secondary organic AMF measurements is recommended to minimize experimental artifacts. PTR-MS or GC/FID measurements can be used to estimate the real-time AMF, which may provide information relevant to secondary organic AMF at ambient level low concentrations of α -pinene. Although at high reactant concentrations, the addition of

seeds does not affect the final secondary organic AMF, seeds are essential in real time AMF measurements.

[27] The α -pinene secondary organic AMF shows strong dependence on temperature at low temperatures (between 0° and 15°C) and a weaker dependence at higher temperatures (15° and 40°C). This weaker dependence appears to be due to the interactions of the kinetics and thermodynamics of SOA formation at different temperatures. Real time secondary organic AMFs show little temperature dependence of AMFs at ambient level concentrations of α -pinene (<3 ppb). The role of relative humidity (RH), NO_x and sunlight on α -pinene SOA formation were not investigated in this study, although they may affect the secondary organic AMF.

[28] **Acknowledgment.** Financial support by USEPA (STAR-831081) is gratefully acknowledged.

References

- Andreae, M. O., and P. J. Crutzen (1997), Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, 276, 1052–1058.
- Bonn, B., and G. K. Moortgat (2002), New particle formation during α - and β -pinene oxidation by O₃, OH and NO₃, and the influence of water vapor: Particle size, *Atmos. Chem. Phys.*, 2, 183–196.
- Cocker, D. R., S. L. Clegg, R. C. Flagan, and J. H. Seinfeld (2001), The effect of water on gas-particle partitioning of secondary organic aerosol. Part I: Alpha-pinene/ozone system, *Atmos. Environ.*, 35, 6049–6072.
- Docherty, K. S., W. Wu, Y. B. Lim, and P. J. Ziemann (2005), Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O₃, *Environ. Sci. Technol.*, 39, 4049–4059.
- Fick, J., L. Pommer, C. Nilsson, and B. Andersson (2003), Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of alpha-pinene, *Atmos. Environ.*, 37, 4087–4096.
- Gao, S., D. A. Hegg, G. Frick, P. F. Caffrey, L. Pasternack, C. Cantrell, W. Sullivan, J. Ambrusko, T. Albrechtski, and T. W. Kirchstetter (2001), Experimental and modeling studies of secondary organic aerosol formation and some applications to the marine boundary layer, *J. Geophys. Res.*, 106, 27,619–27,634.
- Griffin, R. J., D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (1999a), Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104, 3555–3567.
- Griffin, R. J., D. R. Cocker, and J. H. Seinfeld (1999b), Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 2721–2724.
- Guenther, A., et al. (1995), A global-model of natural volatile organic-compound emissions, *J. Geophys. Res.*, 100, 8873–8892.
- Hallquist, M., I. Wangberg, and E. Ljungstrom (1997), Atmospheric fate of carbonyl oxidation products originating from alpha-pinene and delta (3)-carene: Determination of rate of reaction with OH and NO₃ radicals, UV absorption cross sections, and vapor pressures, *Environ. Sci. Technol.*, 31, 3166–3172.
- Hallquist, M., I. Wangberg, E. Ljungstrom, I. Barnes, and K. H. Becker (1999), Aerosol and product AMFs from NO₃ radical-initiated oxidation of selected monoterpenes, *Environ. Sci. Technol.*, 33, 553–559.
- Hoffmann, T., J. R. Odum, F. A. Bowman, D. Collins, D. Klockow, R. C. Flagan, and J. H. Seinfeld (1997), Formation of organic aerosol from the oxidation of biogenic hydrocarbon, *J. Atmos. Chem.*, 26, 189–222.
- Hoppel, W., J. Fitzgerald, and G. Frick (2001), Particle formation and growth from ozonolysis of alpha-pinene, *J. Geophys. Res.*, 106, 27,603–27,618.
- Jang, M., and R. M. Kamens (1998), A thermodynamic approach for modeling partitioning of semivolatile organic compounds on atmospheric particulate matter: Humidity effects, *Environ. Sci. Technol.*, 32, 1237–1243.
- Jang, M., and R. M. Kamens (1999), Newly characterized products and composition of secondary aerosols from the reaction of alpha-pinene with ozone, *Atmos. Environ.*, 33, 459–474.
- Kamens, R., M. Jang, C. J. Chien, and K. Leach (1999), Aerosol formation from the reaction of alpha-pinene and ozone using a gas-phase kinetics aerosol partitioning model, *Environ. Sci. Technol.*, 33, 1430–1438.
- Kroll, J. H., and J. H. Seinfeld (2005), Representation of secondary organic aerosol laboratory chamber data for the interpretation of mechanisms of particle growth, *Environ. Sci. Technol.*, 39, 4159–4165.

- Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld (1996), Gas/particle partitioning and secondary organic aerosol AMFs, *Environ. Sci. Technol.*, *30*, 2580–2585.
- Pankow, J. F. (1994a), An absorption model of gas/particle partitioning of organic compounds in the atmosphere, *Atmos. Environ.*, *28*, 185–188.
- Pankow, J. F. (1994b), An absorption-model of the gas aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, *28*, 189–193.
- Pankow, J. F., J. H. Seinfeld, and W. E. Asher (2001), Modeling the formation of secondary organic aerosol. 1. Application of theoretical principles to measurements obtained in the alpha-pinene/, beta-pinene/, sabinene/, Delta (3)-carene/, and cyclohexene/ozone systems, *Environ. Sci. Technol.*, *35*, 1164–1172.
- Presto, A. A., K. E. H. Hartz, and N. M. Donahue (2005a), Secondary organic aerosol production from terpene ozonolysis. 1. Effect of UV radiation, *Environ. Sci. Technol.*, *39*, 7036–7045.
- Presto, A. A., K. E. H. Hartz, and N. M. Donahue (2005b), Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NOx concentration, *Environ. Sci. Technol.*, *39*, 7046–7054.
- Presto, A. A., K. E. H. Hartz, and N. M. Donahue (2006), The measurement of secondary organic aerosol yield at low total organic aerosol concentration, *Environ. Sci. Technol.*, *40*, 3536–3543.
- Saathoff, H., C. Linke, K. H. Naumann, R. Wagner, E. Weingartner, and U. Schurath (2004), Temperature dependence of the yield of secondary organic aerosol from the ozonolysis of α -pinene and limonene, paper presented at the European Aerosol Conference, Budapest, 6–10 Sept.
- Seinfeld, J. H., and J. F. Pankow (2003), Organic atmospheric particulate material, *Annu. Rev. Phys. Chem.*, *54*, 121–140.
- Seinfeld, J. H., G. B. Erdaos, and W. E. Asher (2001), Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the alpha-pinene-, beta-pinene-, sabinene-, delta(3)-carene-, and cyclohexene-ozone systems, *Environ. Sci. Technol.*, *35*, 1806–1817.
- Takekawa, H., H. Minoura, and S. Yamazaki (2003), Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, *Atmos. Environ.*, *37*, 3413–3424.
- Trainer, M., E. J. Williams, D. D. Parrish, M. P. Burhr, E. J. Allwine, H. H. Westberg, F. C. Fehsenfeld, and S. S. Liu (1987), Models and observations of the impact of natural hydrocarbons on rural ozone, *Nature*, *705–707*.
- Went, F. W. (1960), Blue hazes in the atmosphere, *Nature*, *187*, 641–643.
- Yu, J., D. R. Cocker, R. J. Griffin, R. C. Flagan, and J. H. Seinfeld (1999a), Gas phase ozone oxidation of monoterpenes: Gaseous and particulate products, *J. Atmos. Chem.*, *34*, 207–258.
- Yu, J., D. R. Cocker, R. J. Griffin, R. C. Flagan, and J. H. Seinfeld (1999b), Observation of gaseous and particulate products of mono-terpene oxidation in forest atmospheres, *Geophys. Res. Lett.*, *26*, 1145–1148.

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