Response to referee #1: "The effect of particle acidity on secondary organic aerosol formation from α-pinene photooxidation under atmospherically relevant conditions"

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(*The blue, green, and black fonts represent the referee's comments, the associated revised text in the manuscript, and the authors' responses, respectively.*)

This work presents laboratory chamber studies on the effect of particle acidity on the secondary organic aerosols (SOA) formation from OH-initiated oxidation of α-pinene, a topic that has received much attention yet still under debate. The authors concentrate their discussions on how seed particle acidity would affect the SOA yield and elemental composition during different stages of photooxidation and under different reaction regimes (high vs. low NO_x). Overall, these experimental observations would certainly contribute a relatively complete dataset to studies that highlight the role of aerosol acidity in SOA production and aging.

Response: We greatly appreciate reviewer #1 for affirming the value of our study and providing thoughtful comments on our manuscript. We have revised the manuscript with careful consideration of all the issues addressed by the reviewer, as described below.

However, the major conclusions are potentially biased by the experimental protocols, in particular, the interference of NO_2 under low NO_x conditions as well as liquid water contents under different particle acidities. The authors are suggested to conduct additional experiments and perform

Response: We have examined the experimental results carefully and added more detailed discussions regarding the interference of NO_2 under low-NO_x conditions and the potential role of liquid water content on the observed acidity effects, as described in the responses to general comments #1 and #3, respectively. We have focused mainly on the further analysis and discussion of the current available experimental data in the revised manuscript, rather than conducting additional experiments proposed by the reviewer. We believe that the proposed experiments will not significantly contribute to the main conclusions of the paper and some of them are likely not appropriate. We have calculated the pH value of seed particles using the Extended Aerosol Inorganic Model (E-AIM) and added more discussions on the relevance of the studied particle acidity to atmospheric conditions, as described in the response to general comment #4.

General Comments

1. Low vs. High NO_x conditions

1.1. The authors observed enhanced nitrogen-containing organic fragments formation with increasing aerosol acidity under high NO_x conditions. However, the fraction of these fragments remains constant at different particle acidities under low NO_x conditions, as shown in Figure 6. By examination of the ozone profile shown in Figure 1, one realizes that moderate ozone production is still occurring under the so-called 'low NO_x conditions', owing to the photolysis of NO_2 that are either released from the chamber wall or penetrated from the enclosure air, which is OK and cannot be completely avoided in most chamber setups. The production of ozone indicates a rapid recycling of the NO-NO_2 chemistry, and thus the active role of NO in the production of the nitrogen-

containing organic fragments via the RO₂+NO pathway under 'low NOₓ conditions'. As shown in Figure 6, the fraction of these nitrogen-containing organic fragments under low NOx conditions seems comparable with those under high NOₓ conditions, indicating that they cannot be simply artifacts in the AMS measurement. But the question is why the dependence of these nitrogen-containing organic fragments on particle acidity is only observed under high NOₓ conditions? The authors need to give a convincing explanation on this inconsistency.

Response: We agree that some organic nitrate species might also be formed under low-NO$_x$ conditions. Given that the NO concentration in the chamber was very low (<0.3 ppb) prior to α-pinene photooxidation (i.e., turned on the lamp) under low-NO$_x$ conditions, the contamination of NO$_2$ from the enclosure air was likely negligible. It is most likely that some NO$_2$ was released from the chamber walls and was involved in the α-pinene photooxidation reactions. These organic nitrate species might have different formation pathways and also different composition compared to those formed under high-NO$_x$ conditions, and therefore the acid-catalyzed reactions for these species were possibly insignificant. We have added the following explanations for the observed organic nitrate fragments (i.e., $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$) under low-NO$_x$ conditions:

"Noted that a small amount of $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ fragments were also observed under low-NO$_x$ conditions, where NO was not added (Figure 6b). This may be contributed by the formation of minor amounts of organic nitrates from the reactions of NO$_2$ released from the chamber walls with α-pinene oxidation products. The average NO^+/NO_2^+ ratio was in the range of 6.92–7.91 for particles with different acidities under low-NO$_x$ conditions, which indicates that some organic nitrate species different from those under high-NO$_x$ conditions might be formed. No apparent changes are observed in the mass fractions of $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ fragments with particle acidity under low-NO$_x$

conditions, suggesting that acid-catalyzed formation and partitioning of those organic nitrate species were possibly insignificant." (Lines 368–374)

1.2. Another issue is that the so-called 'high NO_x condition' does not necessarily lead to the RO_2+NO reaction dominant regime over the entire course of the experiment. As shown in Figure 1, NO concentration seems to be completely depleted after a few min of reaction, which is expected due to the intense formation of nitric acid and its rapid deposition on the wall and particles.

Response: The reviewer could be somewhat correct in terms of "the intense formation of nitric acid and its rapid deposition". However, it is speculative what the nitric acid would do once it deposited on the wall and particles. In order to identify the dominant reaction pathway of organic peroxy radicals (RO_2) under high-NO_x conditions, we have assessed the gas-phase reactions in the chamber using a box model based on the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt) constrained by the initial experimental conditions in this study. The fraction of RO_2 radicals reacted with NO compared to the total reacted RO_2 radicals (with NO, HO_2, and RO_2) was derived from the ratio of $k_{NO}[NO] / (k_{NO}[NO] + k_{HO2}[HO_2] + k_{RO2}[RO_2])$, where k_{NO}, k_{HO2}, and k_{RO2} represent the reaction rates of RO_2+NO, RO_2+HO_2 and RO_2+RO_2, respectively and [NO], [HO_2], and [RO_2] represent the concentration of NO, HO_2, and RO_2, respectively from the MCM model output. The result from the box model demonstrates that more than 99% of RO_2 radicals were reacting with NO in the first 2 hours and at least 62% of RO_2 radicals were reacting with NO by the end of the experiments. This suggests that the RO_2 + NO was the dominant reaction under the high-NO_x conditions in our study. We have added the following statement in the revised manuscript:

"Approximately 62–99% of RO_2 radicals reacted with NO over the entire experimental time (totally 6 hours) under high-NO_x conditions in this study, which was estimated based on the Master Chemical

Mechanism constrained by the initial experimental conditions (S1 and Figure S1 in the Supplement)."

(Lines 192–194)

We have also added the following descriptions regarding the MCM model in the supplement:

S1   High-NO$_x$ regime assessment

The Master Chemical Mechanism (MCM v3.3.1, http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt) was incorporated into a box model to assess the NO$_x$ regime for the gas-phase reactions of α-pinene photooxidation under high-NO$_x$ conditions. The box model was constrained with the initial experimental conditions including temperature, pressure, and the concentrations of α-pinene, NO, water vapor, and H$_2$O$_2$ for the individual chamber experiments in this study. The photooxidation reaction of α-pinene was simulated for 6 hours with the box model. The output of the box model was the time series of the concentrations of α-pinene, NO, O$_3$, HO$_2$, and organic peroxy radicals (RO$_2$) (molecule cm^{-3}) from each time step with a 1-min resolution. The fraction of RO$_2$ radicals reacted with NO compared to the total reacted RO$_2$ radicals (with NO, HO$_2$, and RO$_2$) was calculated by

$$\frac{k_{NO}[NO]}{k_{NO}[NO] + k_{HO_2}[HO_2] + k_{RO_2}[RO_2]}$$

where k_{NO}, k_{HO2}, and k_{RO2} are the reaction rates of RO$_2$ + NO, RO$_2$ + HO$_2$ and RO$_2$ + RO$_2$, respectively and [NO], [HO$_2$], and [RO$_2$] are the concentration of NO, HO$_2$, and RO$_2$, respectively. The results from the box model are presented in Figure S1. At the start of the simulations, more than 99% of the RO$_2$ radicals were reacting with NO; while by the end of the experiments (after 6 hours), at least 62% of the RO$_2$ radicals continued to react with NO (Figure S1a). The time series for α-pinene, NO, and O$_3$ from the measurements were reasonably well captured by the box model (Figure S1b, c, and d).
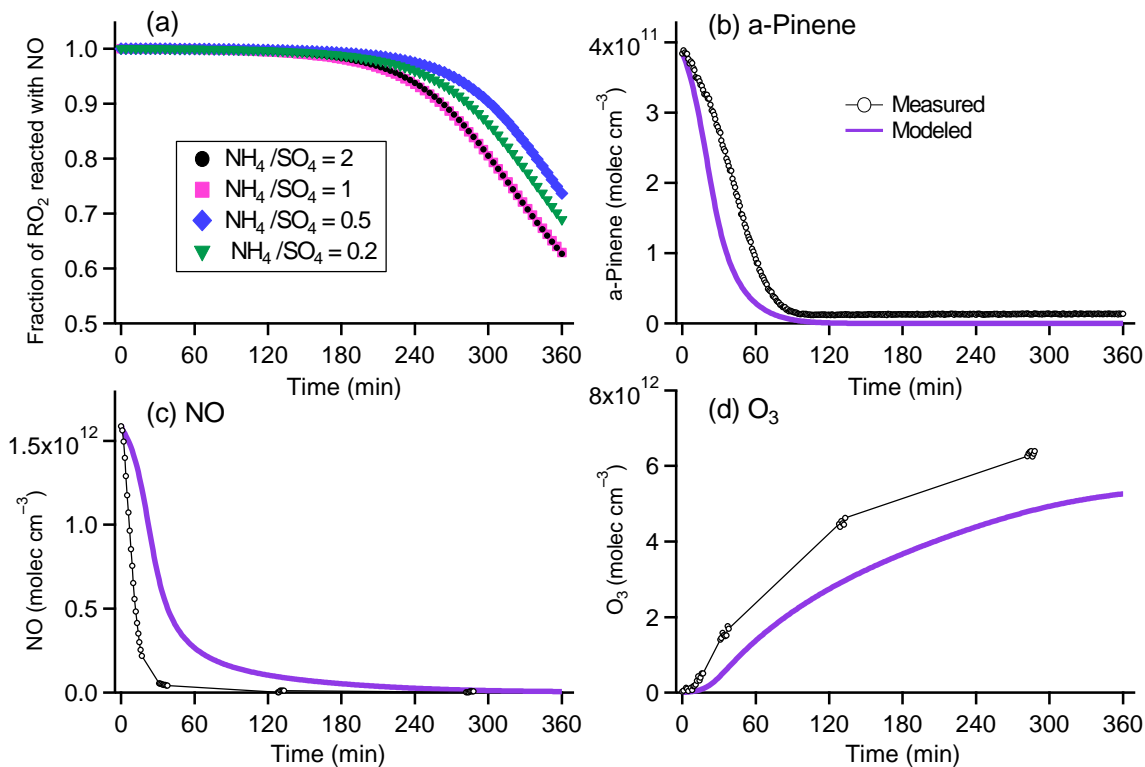
Figure S1. (a) Fraction of RO_2 reacted with NO compared to the total reacted RO_2 radicals for high-NO_x experiments with ammonium sulfate and acidic seed particles. The measured and the modeled time series of the concentrations of (b) α-pinene, (c) NO, and (d) O_3 for the high-NO_x experiment with ammonium sulfate particles (NH_4/SO_4 = 2). The variations in time for each species in all experiments with acidic particles under high-NO_x conditions are similar to (b), (c), and (d)."

1.3. The authors are suggested to carry out continuous NO injection after the initial consumption of NO to truly achieve the 'high NO_x condition'. Alternatively, HONO or CH_3ONO can be used as the OH precursor under high NO_x conditions.

Response: The reviewer's proposed experiments may in fact achieve the high-NO_x conditions for long periods of time with an additional NO source. However, as described above, the high-NO_x experiments

in our study were also dominated by the reactions of RO_2 with NO over the entire experimental course. Therefore, we believe it is not necessary to perform the proposed experiments for this study.

2. First vs. later generation SOA products

2.1. The strong dependence of SOA yield on particle acidities under high NOx conditions was only observed during the initial photooxidation stage, where the total SOA mass concentration is less than 2 ug/m^3. As the reaction proceeds, SOA yields are eventually comparable at different particle acidities and the authors explained this phenomenon as the unavailability of free H$^+$ due to thick organic coatings. Note that this argument is established under the assumption that the core of the particles are (semi)-solid and there is no particle-phase diffusion over the entire course of several hours of reaction, which is doubtful considering the moderate RH conditions employed in the experiments. One suspects that if the observed SOA yield dependence at the initial particle growth period on the acidity can be simply attributed to the uncertainties in the AMS measurement when the overall organic loadings are extremely low (< 2 ug/m^3).

Response: We have calculated the detection limits of individual species to estimate the uncertainties of the AMS measurement using data acquired from particle-free periods. The detection limits for organics, sulfate, nitrate, and ammonium were 34, 4, 1, and 5 ng m^{-3}, respectively. Given that the measured organic aerosol mass was far above the AMS detection limit, the observed acidity effect in the initial photooxidation stage should not be simply attributed to the uncertainties from the AMS measurement. We have added the following statement in the revised manuscript:

"The detection limits of organics, sulfate, nitrate, and ammonium, defined as 3 times the standard deviations of the mass concentrations of individual species (1-min average) in particle-free air, were 34, 4, 1, and 5 ng m^{-3}, respectively." (Lines 136–138)

Furthermore, the core-shell theory assumes that the inorganic core was liquid or solid and the organic coating might be semisolid, instead of "the core of the particles are semisolid" as the reviewer stated. The occurrence of particle-phase diffusion has not been ruled out in our study, although we did not discuss this topic in the original manuscript. The generated α-pinene SOA could be in semisolid or in an amorphous solid state and highly viscous over a range of moderate RH (approximately 29–43% in this study). This could easily slow down the diffusion rate of organic molecules. Considering the large uncertainties in the quantification of SOA viscosity, the mixing time of the organic coating with the inorganic core can vary from seconds to days (Renbaum-Wolff et al., 2013). Therefore, the core-shell assumption is indeed possible. We have added the following explanations in the revised manuscript:

"A possible interpretation for such a decrease in yield is that acidic particles (i.e., the inorganic core) were gradually less accessible with increased organic coating on acidic particles, assuming that the diffusion of organic molecules into the inorganic seeds was considerably slowed. This process was indeed possible at the studied final RH (approximately 29–43%), given that SOA could be in an amorphous solid or semisolid state with high viscosity at low to moderate RH (e.g., ≤ 30%) (Renbaum-Wolff et al., 2013; Virtanen et al., 2010)." (Lines 242–247)

2.2. The authors are suggested to perform additional calibration experiments:

1) Prepare a mixture of pinonic acid (a surrogate for α-pinene photo-oxidation products) and ammonium sulfate salt under different acidities, atomize the mixtures into the chamber under controlled RH and T conditions, and sample the suspended particles by AMS. The authors need to verify if AMS measured organic loadings are identical under different seed acidities even at low organic levels. This calibration experiments can also be used as a means to correct the AMS collection efficiency, if different from the default value used.

2) Alternatively, the authors could repeat experiments # 9-12, but adding seed particles after only 30 min of reaction. Would the dependence of SOA yield on the organic loadings still be observed?

Response: These two proposed experiments are associated with the detection limits of the AMS instrument and potential changes in sensitivity and/or collection efficiency of the organics with particle acidity. As explained above, the measured organic mass concentration was much larger than the organic detection limits of the AMS and thus they are reliable despite being low (note that 2 µg m^{-3} is not too low and it is in fact similar to many ambient atmosphere studies). Regarding the AMS collection efficiency issue, we agree that the CE may change with particle acidity, however it is not a concern in our study. This is mainly because we calculated the generated organic aerosol mass using the following method as given in the manuscript:

"Organic mass concentrations derived from AMS measurement were wall-loss corrected according to the decay of sulfate particles in the chamber, i.e., by multiplying the ratios of the initial sulfate concentrations to the instantaneously measured sulfate concentrations." (Lines 141–143).

Consequently, the real-time measured organic mass was normalized by the sulfate mass and thus the CE has been factored out from this calculation. Therefore, the observed acidity effect is not likely caused by any uncertainties associated with the AMS measurement or the CE issue. As a result, we believe there is no need to perform these two proposed calibration experiments. Additionally, there is no evidence that the ionization efficiency (IE) of organics in the AMS is variable with other factors such as acidity, and a constant IE over the course of days is standard practice in the AMS community.

3. Aerosol liquid water content

3.1. The hygroscopic growth curves for ammonium sulfate seed at different acidities are significantly different. At ~50% RH, diameter changes of $(NH_4)_2SO_4$ and NH_4HSO_4 are 0% and 20% at

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equilibrium, respectively, due to water uptake (Seinfeld and Pandis, 2008). For the experimental conditions in this study, i.e., dry seed particles with different acidities at 50-70% RH, the water content would vary significantly from zero to several tens of percentage in mass, depending the amount of sulfuric acid in the particle phase. As a result, the observed 'acidity effect', if any, should really be the coupled effect of both acidities and water content in aerosols.

Response: We agree that water content in the particles could increase particle diffusivity and thus affect SOA yield, as the aerosol water may serve as a medium to dissolve gas-phase water-soluble organic species, and/or that the observed acidity effect could be a coupled effect of acidity and water content. In our study, the initial liquid water content estimated by the E-AIM were in the same order of magnitude for individual experiments under high-NO_x conditions, that is, on average 5.2, 6.3, and 10.3 $\mu g\ m^{-3}$ for experiments with NH_4/SO_4 molar ratios of 1.0, 0.5, and 0.2, respectively. Higher SOA yield seem to correspond with higher particle water content. However, changes in SOA yield were not observed for experiments with similarly varied water content but under low-NO_x conditions (Exp. 5–8; Table 1), despite the measured O/C ratio being higher and presumably associated with more oxidized (and thus soluble) species. We therefore conclude that the particle water content likely played a minor role in the observed increase in SOA yield under high-NO_x conditions, particularly since the O/C ratio and organic fragments under these conditions indicated the potential for a less soluble organic fraction. We have added the following discussions in the revised manuscript:

"In addition to the effect of particle acidity, the α-pinene SOA yield was also possibly influenced by the liquid water content in the particles. The initial water content in the seed particles estimated by the E-AIM was on average 5.2, 6.3, and 10.3 $\mu g\ m^{-3}$ for high-NO_x experiments with NH_4/SO_4 molar ratios of 1.0, 0.5, and 0.2, respectively. Therefore, more water was present in the particles with higher acidity. The higher particle water content could prompt the partitioning of gas-phase water-soluble organic

species by providing a larger medium for their dissolution and therefore potentially increase the SOA yield (Carlton and Turpin, 2013). However, there was no apparent increase in the SOA yield under low-NO$_x$ conditions, even though seed particles with similarly varied water content were used (Exp. 5–8; Table 1) and despite the fact that products with higher O/C (hence higher solubility) were formed (section 3.3). This suggests that the particle water content likely did not contribute substantially to the observed increase in α-pinene SOA yield with acidity under high-NO$_x$ conditions." (Lines 224–233)

3.2. Another concern is the different phase states of particles could potentially lead to different bouncing effect on the AMS vaporizer, thus changing the collection efficiency for different seed particles.

Response: We agree that the phase state of particles being sampled into the AMS may affect the CE. However, as explained in the response to general comment #2, the real-time CE has been factored out in the calculation of organic mass concentration. Therefore, only the initial sulfate mass concentration was relevant to the calculated organic mass concentration. The CE for ammonium sulfate particles at moderate RH (approximately 30–80%) did not vary significantly (Matthew et al., 2008). Therefore, the results of our study would not be affected significantly by the CE issue.

(Matthew, B. M., Middlebrook, A. M. and Onasch, T. B.: Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols, Aerosol Sci. Technol., 42(917683900), 884–898, doi:10.1080/02786820802356797, 2008.)

3.3. In view of these uncertainties, the authors are suggested to conduct a series of experiments using hydrated seed particles to begin with.

Response: Based on the above discussion, the observed acidity effect in our study was not likely caused by the different particle water content in individual experiments or AMS collection efficiency that was factored out in the final calculation of organic mass. Therefore, the proposed experiments are not relevant or warranted.

4. Particle acidity and atmospheric relevant conditions

4.1. In view of the main focus of this study, the seed particle acidities need to be estimated based on the AMS measured inorganic composition and thermodynamic models such as E-AIM (http://www.aim.env.uea.ac.uk/aim/aim.php).

Response: We have calculated the seed particle acidity, i.e., the pH value of aerosols in the aqueous phase, using the outputs from E-AIM, as summarized in Table 1 below. The mass concentrations of NH_4^+ and SO_4^{2-} measured by the AMS have been used as the inputs for the E-AIM. The following explanation has been added to the revised manuscript:

"The initial seed composition in each experiment was predicted using the Extended Aerosol Inorganic Thermodynamic Model (E-AIM) II (http://www.aim.env.uea.ac.uk/aim/aim.php) (Clegg et al., 1998). The concentrations of inorganic sulfate, nitrate, and ammonium derived from the AMS measurement as well as the temperature and RH in the chamber were input parameters. The pH of aerosol particles was calculated by $-\log(\gamma \times [H^+])$ using the model outputs, where γ and $[H^+]$ are the activity coefficient of H^+ and the molar concentration of dissociated H^+ (mol L^{-1}) in the aqueous phase, respectively." (Lines 151–155)

Table 1. Experimental conditions and SOA yields from OH-initiated photooxidation of α-pinene under high- and low-NO$_x$ conditions.

Exp.	NH$_4$/SO$_4$ ratio [a]	Initial seed composition, [b] molality (mole kg^{-1})	Aerosol pH [c]	Temp. [d] (°C)	RH [e] (%)	Seed (µg m^{-3})	NO (ppb)	α-pinene (ppb)	ΔHC (µg m^{-3})	ΔM$_0$ (µg m^{-3})	Yield (%)
High-NO$_x$ conditions											
1	2	(NH$_4$)$_2$SO$_4$ (no liquid phase)		24–31	47–29	4.4	66	15.9	84.2	3.5	4.2±0.1
2	1	H$^+$=3.2, NH$_4^+$=15.3, HSO$_4^-$=11.2, SO$_4^{2-}$=3.7	−1.31	23–30	58–34	8.4	69	17.6	93.4	5.2	5.6±0.1
3	0.5	H$^+$=5.0, NH$_4^+$=7.0, HSO$_4^-$=7.5, SO$_4^{2-}$=2.3	−1.50	24–30	61–38	6.3	68	13.6	71.8	4.7	6.6±0.1
4	0.2	H$^+$=7.2, NH$_4^+$=2.7, HSO$_4^-$=6.2, SO$_4^{2-}$=1.9	−1.66	26–34	58–33	7.9	72	17.0	89.9	6.8	7.6±0.2
Low-NO$_x$ conditions											
5	2	(NH$_4$)$_2$SO$_4$ (no liquid phase)		25–32	67–43	12.6	<0.3	19.6	96.7	34.1	35.2±1.1
6	1	H$^+$=1.9, NH$_4^+$=14.8, HSO$_4^-$=8.5, SO$_4^{2-}$=4.1	−0.93	25–32	64–37	12.6	<0.3	17.4	79.1	22.6	28.6±1.5
7	0.5	H$^+$=3.2, NH$_4^+$=10.6, HSO$_4^-$=8.0, SO$_4^{2-}$=2.9	−1.22	26–33	64–38	11.9	<0.3	19.3	92.6	33.7	36.3±1.5
8	0.2	H$^+$=5.3, NH$_4^+$=4.1, HSO$_4^-$=5.6, SO$_4^{2-}$=1.9	−1.35	24–33	66–36	11.4	<0.3	19.5	88.6	28.4	32.0±1.9
Adding seeds after photooxidation											
9	2	(NH$_4$)$_2$SO$_4$ (no liquid phase)		23–31	57–34	9.7	82	20.4			
10	0.5	H$^+$=5.9, NH$_4^+$=7.0, HSO$_4^-$=8.4, SO$_4^{2-}$=2.3	−1.72	24–31	56–33	12.2	72	18.5			
11	2	(NH$_4$)$_2$SO$_4$ (no liquid phase)		25–33	68–42	7.4	<0.3	16.1			
12	0.5	H$^+$=4.9, NH$_4^+$=9.6, HSO$_4^-$=9.3, SO$_4^{2-}$=2.6	−1.64	25–33	57–33	11.4	<0.3	17.3			

[a] NH$_4$/SO$_4$ molar ratios of ammonium sulfate/sulfuric acid aqueous solution used for atomizing seed particles. [b] Initial seed composition was estimated using the E-AIM II. [c] Aerosol pH was calculated with the E-AIM output. [d] Initial and final temperature inside the chamber. [e] Initial and final RH inside the chamber.

4.2. The authors are also suggested to discuss how relevant the acidities used in the chamber experiments with atmospheric conditions.

Response: We have added the following discussions and one reference regarding the relevance of the studied particle acidity to atmospheric conditions:

"Despite the initial pH value of aerosol particles investigated in this study (−0.93 to −1.72) being in the higher acidity range relative to that generally observed for ambient aerosols, pH values less than −2.0 have been reported for atmospheric aerosol particles and haze droplets (Herrmann et al., 2015). It is therefore expected that the effect of particle acidity observed in this study is relevant to the ambient atmosphere, especially in regions enriched with acidic aerosols, and possibly during initial particle growth via sulfuric acid." (Lines 399–403)

"Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, Chem. Rev., 115, 4259–4334, doi:10.1021/cr500447k, 2015." (Lines 481–483)

Minor Comments

1. Page 2, Line 50: Ester dimers are observed as an important class of products from the ozonolysis of α-pinene (e.g., Zhang et al., PNAS, 2015). Epoxides are certainly produced, but from a minor pathway (e.g., Eddingsaas et al., ACP, 2012), and ring-opening reactions proceed rapidly following the reactive uptake of epoxides.

The sentence referred to: "The oxidation of α-pinene by hydroxyl radicals (OH), ozone (O_3), and nitrate radicals produces a variety of multifunctional organic compounds such as carboxylic acids, carbonyls, peroxides, epoxides, alcohols, and organic nitrates (Yasmeen et al., 2012)."

Response: We have added "ester dimers" as one of the possible α-pinene oxidation products. We kept "epoxides" despite it being a minor product, because the listed examples here are not necessary intended to be for major products only. The original sentence has been revised to:

"The oxidation of α-pinene by hydroxyl radicals (OH), ozone (O_3), and nitrate radicals produces a variety of multifunctional organic compounds such as carboxylic acids, carbonyls, peroxides, ester dimers, epoxides, alcohols, and organic nitrates (Calogirou et al., 1999; Yasmeen et al., 2012; Zhang et al., 2015)." (Lines 52–55)

2. Page 2, Line 57: It has been well recognized that sulfate esters contribute to a large fraction of SOA mass via reactive uptake of IEPOX, a second generation oxidation products from isoprene photooxidation under low NO conditions, onto acidified aerosols. However, the exact mass fraction

of sulfate esters in the α-pinene system has not yet been determined. Surratt et al. (2007) and (2008) report for the first time the evidence of organosulfate in α-pinene derived SOA, but not quantification.

The sentence referred to: "Enhanced aerosol acidity led to the formation of sulfate esters that contributed to a large fraction of SOA mass from photooxidation of α-pinene under high-NO_x conditions (Surratt et al., 2007a, 2008)."

Response: We agree that the mass fraction of sulfate esters derived from α-pinene photooxidation has not been quantified exactly, although sulfate esters from isoprene photooxidation and in the ambient atmosphere may contribute to a large fraction of SOA mass. As this entire paragraph is intended to quantitatively characterize the acidity effect, we have removed this sentence from the revised manuscript.

3. Page 5, Line 132: Have the authors performed experiments monitoring the decay of pure sulfate particles? How was the decay rate compared with particles coated with organics?

The sentence referred to: "Organic mass concentrations derived from AMS measurement were wall-loss corrected according to the decay of sulfate particles in the chamber, i.e., by multiplying the ratios of the initial sulfate concentrations to the instantaneously measured sulfate concentrations."

Response: We did not perform specific experiments monitoring the decay of pure sulfate particles. Particle wall loss rates generally depend on particle size, electrical charge, and turbulence level inside the chamber. With the coating of organics on sulfate particles, the particle size increased less than 100 nm in mobility diameter during the experiments in our reaction system. The decay rate of particles coated with organics could be slightly lower than pure sulfate particles, because larger particles usually

have smaller Brownian diffusion rates. We assumed that particles coated with organics have same deposition rate as pure sulfate particles in this study. This assumption should not contribute significant uncertainty or change the conclusion of the paper. We have added the following statement in the revised manuscript:

"The decay rate of particles coated with organics was assumed to be same as that of pure sulfate particles, although the later could be slightly higher due to the larger Brownian diffusion rate of smaller particles." (Lines 146–148)

4. Page 5, Line 134: How was the 0.1 ug/cm^{-3} mass from self-nucleation estimated?

The sentences referred to: "This assumption is appropriate given that organics contributed by self-nucleation was estimated to be less than 0.1 µg cm^{-3} in the studied system."

Response: This estimation is based on the particle number concentration measured by the CPC and the organic mass concentration measured by the AMS, not obtained from the SMPS measured particle size distribution. We observed less than 50 cm^{-3} particles from self-nucleation and also no obvious increase in organic mass concentration by the AMS measurement during the experiments without adding seed particles. We therefore estimated a maximum concentration of 0.1 µg cm^{-3} for self-nucleated organic aerosols by using a particle number concentration of 50 cm^{-3} and a particle diameter of 70 nm. However, this estimation may have some uncertainties in terms of the assumed particle size. We have replaced the estimated value with the observed experimental results:

"This assumption is appropriate given that less than 50 particles cm^{-3} were contributed by self-nucleation and that an obvious increase in organic mass concentration was not observed from the AMS measurement in the experiments without adding seed particles." (Lines 144–146)

5. Page 5, Line 139: What is the estimated NO_3 photolysis rate?

The sentences referred to: "The OH concentrations were calculated to be approximately $4.3–5.9 \times 10^6$ and $0.8–1.1 \times 10^6$ molecules cm^{-3} for experiments under high- and low-NO_x conditions, respectively."

Response: We agree that the photolysis rate of NO_3 radicals is an uncertainty in this estimation, since any NO_3 present can react with α-pinene and affect subsequent estimations of the OH radical levels. However, the estimated OH concentration was not used for any quantitative analysis in this study. We therefore have added the following explanation regarding this uncertainty in the revised manuscript:

"Nitrate radical (NO_3) generated from the reactions such as NO_2 with O_3 might also affect the α-pinene decay (and hence the estimated OH), whereas it was not taken into account here because NO_3 levels were likely to be small under the studied irradiation conditions." (Lines 159–161)