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Dear Prof. Nizkorodov:

We are submitting our revised manuscript (acp-2016-301) entitled: "The effect of particle acidity on secondary organic aerosol formation from α-pinene photooxidation under atmospherically relevant conditions" for publication in Atmospheric Chemistry and Physics.

We have revised the manuscript with consideration of all the comments from the reviewers. Please see our response to the reviewers below for details. We also have attached a copy of the manuscript with all the changes tracked for other minor corrections.

We hope that this paper will be accepted in your journal. Thank you very much for editing the paper.

Sincerely yours,

Yuemei Han and coauthors

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

Yuemei Han et al.

(*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

modeling calculations to strengthen their conclusions prior to consideration of being published on

Atmospheric Chemistry and Physics.

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 RO$_2$+NO pathway under 'low NO$_x$ conditions'. As shown in Figure 6, the fraction of these nitrogen-containing organic fragments under low NOx conditions seems comparable with those under high NO$_x$ 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 NO$_x$ 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).
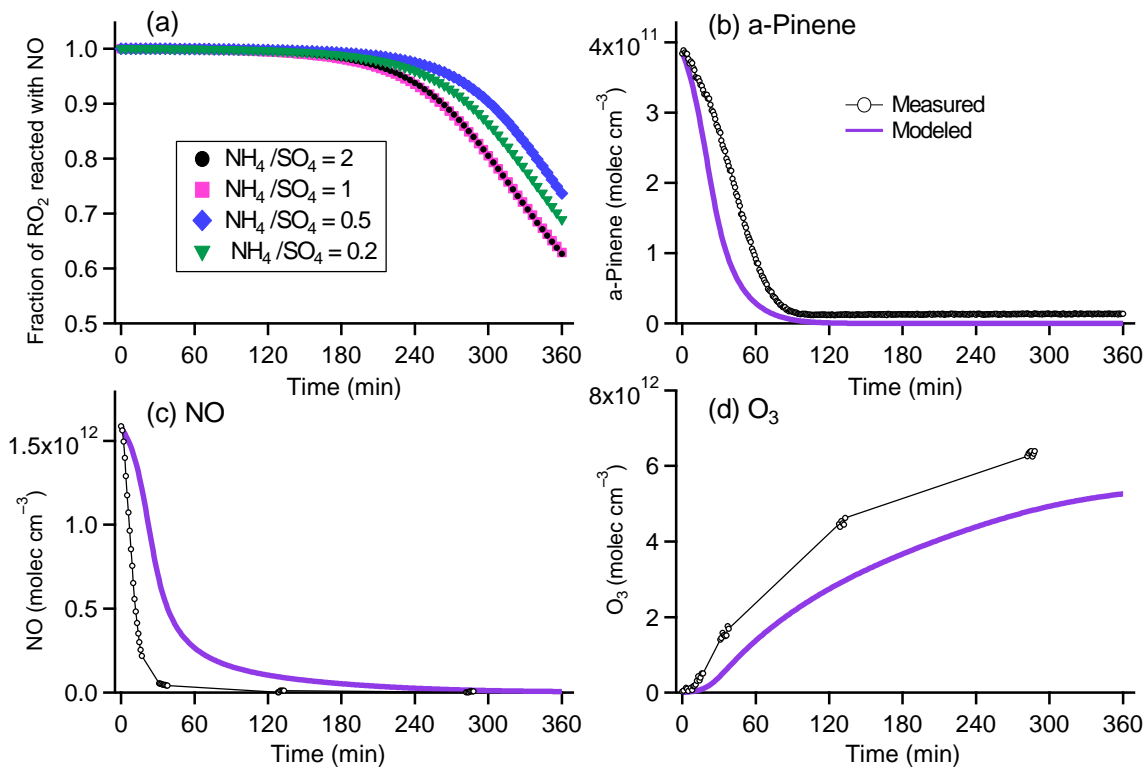
Figure S1. (a) Fraction of RO_2 reacted with NO compared to the total reacted RO_2 radicals for high-NO_x experiments with ammonium sulfate and acidic seed particles. The measured and the modeled time series of the concentrations of (b) α-pinene, (c) NO, and (d) O_3 for the high-NO_x experiment with 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.

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

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 µg 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 µg 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

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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

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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 NO₃ 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)

Response to referee #2: "The effect of particle acidity on secondary organic aerosol formation from α-pinene photooxidation under atmospherically relevant conditions"

Yuemei Han et al.

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

The authors performed laboratory chamber experiments to study the effect of particle acidity on α-pinene SOA. Firstly, the authors found that the particle acidity has small effect on α-pinene SOA yield under low-NOx conditions, but has large effects on α-pinene SOA yield under high-NOx conditions. This has been shown in Eddingsaas et al. (2012a). Secondly, the authors showed that α-pinene SOA formation under low-NO_x conditions is influenced if the particle seed is injected after α-pinene photooxidation. This has also been shown in Eddingsaas et al. (2012a). Thirdly, the authors observed that the fraction of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$ fragments in total organics increases with particle acidity, which is the only new finding in the manuscript. Considering the lack of novel findings in the manuscript, I would not recommend this manuscript for publication in its current state.

Response: We thank reviewer #2 for the comments on our manuscript. The reviewer has proposed some relevant points that could improve the quality of this paper. However, it seems that the reviewer has missed the main concept of our study on some points, as will be expanded upon further below. Regardless, the reviewer's conclusion that this study lacks novelty is inaccurate and it is further

inappropriate to make such a conclusion by simply comparing with Eddingsaas et al. (2012a). However, we agree that perhaps we could have improved the description in the paper of how this current study is different from Eddingsaas et al. (2012a), and specifically what aspects are novel. We assumed that the novelty of the study's results would be apparent, however we admit that additional clarity is warranted. Our study is unique as it investigates the effect of aerosol acidity under conditions more relevant to the ambient atmosphere. The originality and the differences of our paper compared to Eddingsaas et al. (2012a) have been summarized in the response to major comment #1. Clearly there are enough differences and novelty to warrant publication. Moreover, a single study is generally far from enough to demonstrate a scientific fact, especially since some of the current results contradict those of Eddingsaas et al. (2012a). We have addressed all the issues noted by the reviewer and have made the relevant changes in the manuscript.

Major comments:

1.1 This manuscript does not represent a substantial contribution to scientific progress, because most of the findings have been shown in Eddingsaas et al. (2012a). The authors should try to differentiate this study from Eddingsaas et al. (2012a).

Response: We strongly disagree with this viewpoint, although as noted above we could have made the differences more apparent. Our study does not simply replicate or follow the work of Eddingsaas et al. (2012a). Our study was originally designed to investigate the effect of particle acidity on α-pinene SOA formation under relevant ambient conditions as opposed to Eddingsaas et al. Furthermore, there are a number of other substantial differences between our study and Eddingsaas et al. in terms of studied conditions and research focus. The difference in experimental conditions between the two studies is summarized in the table below. The modest relative humidity and the lower initial concentrations of

seed particles and α-pinene applied in our study are more relevant to the atmosphere compared to Eddingsaas et al. (2012a). In fact, one could argue that the experiments of Eddingsaas et al. (2012a) were conducted under conditions that were entirely irrelevant to the atmosphere, as NO_x levels of 800 ppb are never encountered and RH of <10% are similarly rare.

	RH (%)	Seed size (nm)	Seed volume ($\mu m^3\,cm^{-3}$)	α-pinene (ppb)	High-NO_x level (ppb)
Eddingsaas et al. (2012a)	< 10	60	~10–15	19.8–52.4	800
This study	33–67	150	~2.5–7.1	13.6–20.4	66–82

Regarding the research focus, we investigate the effect of particle acidity at four acidic levels; we observed that the acidity effect was stronger in the initial photooxidation period under high-NO_x conditions; we reported the time scale of the acidity effect, the high-resolution organic fragment distributions, the oxidation state of α-pinene SOA in the different experiments, and the potential formation of organic nitrates based on the AMS measurements. In contrast, there is little or no discussion on these topics by Eddingsaas et al. (2012a). In order to highlight the novelty of our study, an explicit research objective has been added in the revised manuscript:

"The yield of α-pinene SOA was obtained at various particle acidity levels under high- and low-NO_x conditions. The dependence of SOA yield on particle acidity and the time scale of the acidity effect are characterized and discussed. The effect of particle acidity on the chemical composition of α-pinene SOA, the fragment distributions of bulk organics, and the oxidation state of organics are examined based on the high-resolution analysis of organic aerosol mass spectra. The possible contribution of particle acidity to the formation of particulate organic nitrates under high-NO_x conditions is also discussed. Finally, the potential significance of the observed acidity effect in the ambient atmosphere is summarized." (Lines 83–89)

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1.2. For example, while the RH was below 10% in Eddingsaas et al. (2012a), the experiments were conducted under humid conditions in this study. Thus, discussions on dry vs. humid could be added.

Response: It is true that RH is an important factor in the formation of α-pinene SOA. However, given that we did not conduct experiments under dry conditions, a direct comparison between the dry and humid conditions are not available from this study. We could roughly compare our results with those from previous studies under dry conditions, but other experimental conditions such as temperature and hydrocarbon loading are generally different as well. Therefore, rather than to discuss the dry and humid condition itself, we have added the following statement to indicate the importance of RH in SOA chamber studies:

"Moreover, we have studied the acidity effect under more realistic RH conditions. While RH is an important factor affecting the concentrations of [H^+], the kinetics of hydrolysis reactions, and the physical properties of SOA such as viscosity, more investigation over a broader RH range are essential to understand the acidity effect in the real atmosphere." (Lines 403–406)

1.3. In addition, the authors should provide more insights into why the effects of acidic seed are different between low-NO_x and high-NO_x conditions.

Response: The acidity effect has been discussed mostly in section 3.2 of the manuscript. The different effects of particle acidity were most likely associated to the distinct reaction mechanisms between high- and low-NO_x conditions, which resulted in the different chemical composition of α-pinene SOA (as seen in Figure 6). It was possible that acid-catalyzed heterogeneous reactions occurred under high-NO_x but not low-NO_x conditions. However, given that the bulk organic aerosol mass was measured by the

AMS (with very strong fragmentation), it is a challenge to provide detailed reaction mechanisms from this study. Therefore, we have proposed this topic to be an open question as follows:

"The potential mechanisms leading to the different acidity effects between high- and low-NO_x conditions warrant further investigation." (Lines 379–380)

2. The authors observed that the mass fraction of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$ in total OA increases with particle acidity under high-NO_x conditions. However, the discussions on this observation are highly speculative.

(1) In order to explain this observation, the authors propose "organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity". line 191-192, the authors suggest that particle acidity can facilitate the gas phase RO2 and NOx reaction and organic nitrate formation. This mechanism is highly speculative. The authors need to provide more evidence and cite related reference to support the proposed mechanism.

The sentence referred to:

a. "The fraction of nitrogen-containing organic fragments ($C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$) in the total organics was enhanced with the increases in particle acidity under high-NO_x conditions, indicating that organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity."

b. "Clearly, NO_x is most likely involved in the acid-catalyzed reactions during α-pinene photooxidation, such as the formation of organic nitrates from RO_2 reacting with NO_x facilitated by particle acidity (as discussed in Sect. 3.4)."

Response: The acid-catalyzed formation of organic nitrates could indeed occur, although we agree that is rarely reported in literature. We did not intend to say that acidity can facilitate the RO_2 + NO_x reactions in the gas phase, as the reviewer states. Rather, we are saying that the acidity can enhance the

partitioning into the particle phase and there may also be particle phase reactions which are enhanced by acidity leading to nitrates. As there is no detailed information on the exact form of the organic molecules here, it is not possible to provide a mechanism from the available data of this study. However, one example is the formation of sulfated organic nitrates through the further reactions of sulfuric acid with α-pinene oxidation products of nitroxyl alcohols and carbonyls, as proposed by Surratt et al. (2008). We have revised the original sentences as follows (a and b) and also have added a statement (c) for the possible mechanisms:

a. "…, indicating that organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity *or that acidic conditions facilitate the partitioning of gas phase organic nitrates into particle phase.*" (Lines 23–25)

b. "Clearly, the presence of acidic particles promotes the formation of α-pinene SOA under high-NO_x conditions and NO_x is likely involved in the acid-catalyzed reactions during α-pinene photooxidation." (Lines 217–219)

c. "One possible reaction is the acid-catalyzed formation of sulfated organic nitrates through α-pinene oxidation products such as nitroxyl alcohols and carbonyls reacting with sulfuric acid (Surratt et al., 2008). Further investigations on the individual particle phase organic nitrate species at a molecular level combined with gas-particle kinetics are required to elucidate the detailed reaction mechanisms." (Lines 344–348)

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate Formation in Biogenic Secondary Organic Aerosol, J. Phys. Chem. A, 112(36), 8345–8378, doi:10.1021/jp802310p, 2008.

(2) line 322-323. The change in NO^+/NO_2^+ ratio is a reflection of the change in organic nitrate composition, instead of organic nitrate amount. The increasing in NO^+/NO_2^+ ratio with particle acidity likely suggests that particle acidity has different effects on the partition of different organic nitrate species. This is one possible explanation for the observation that the mass fraction of organic nitrates increases with particle acidity under high-NO_x conditions.

The sentence referred: "An increasing NO^+/NO_2^+ ratio again suggests that organic nitrates were enhanced with the increase in particle acidity under high-NO_x conditions."

Response: We agree that the composition of organic nitrate species might be different under various acidic conditions and particle acidity could have different effects on the partitioning of different organic nitrate species. The original sentence has been revised to:

"The increase in NO^+/NO_2^+ ratio with particle acidity suggests that the composition of organic nitrate species might be different under various acidic conditions, which is possibly due to the varied effect of particle acidity on the formation and/or partitioning of different organic nitrate species." (Lines 364–367)

(3) As shown in figure 6b, the mass fractions of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$ under low-NO_x conditions are similar to that under high-NO_x conditions. How are organic nitrates formed under low-NO_x conditions? Why are the mass fractions of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$ under low-NO_x conditions not affected by particle acidity?

Response: A possible explanation is that a small amount of NO_2 released from the chamber walls was involved in the α-pinene photooxidation under low-NO_x conditions. 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, compared to

those of 9.13–10.44 under high-NO_x conditions. This possibly suggests that different organic nitrate species were formed under high- and low-NO_x conditions, and that the particle acidity had different effects on the formation and partitioning of those organic nitrate species. We have added the following statement in the revised manuscript:

"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." (368–374)

(4) line 296. The organic nitrate yield reported in this study is misleading. It is because the fragmentation of organic nitrate in AMS give rise to $C_xH_yO_z^+$, which accounts for a large mass fraction in organic nitrate but not included in the yield calculation in this study. The authors could estimate the organic nitrate yield based on the concentration of the sum of $NO^+ + NO_2^+$ and assumed molecular weight of organic nitrate (A.W.Rollins, 2012; Boyd et al., 2015; Xu et al., 2015a).

Response: We agree that the original method for the calculation of SOA yield is not appropriate. We have estimated the organic nitrates mass and yield using the method suggested by the reviewer and have added the following details in the revised manuscript:

"Assuming an average molecular weight of organic nitrate molecules ranging from 200 to 300 g mol^{-1}, where 62 g mol^{-1} is attributed to the $-ONO_2$ group and the remaining from the organic mass (Boyd et al., 2015), the organic nitrate mass was estimated to be approximately 0.6–1.4 µg m^{-3}. This resulted in a contribution of 17.5–20.5% to total α-pinene SOA and an overall organic nitrate yield of 0.7–1.6% under high-NO$_x$ conditions in this study." (Lines 331–335)

Also, are NO$^+$ and NO$_2^+$ included in the SOA yield and O:C calculation?

Response: As NO$^+$ and NO$_2^+$ were considered to be the fragments from organic nitrates in this study, we have included them in the SOA yield and O/C ratio calculation. The mass concentrations of NO$^+$ and NO$_2^+$ fragments were generally small and the sum of them was in the range of 0–0.3 µg m^{-3}. Therefore, the SOA yield and O/C ratio reported in the revised manuscript only changed very slightly compared to the original values, and these changes did not affect the conclusions in this study.

3. Many results are confusing.

(1) Figure 3: the SOA yield curves under both conditions are not typical and problematic (Griffin et al., 1999). Under low-NO$_x$ conditions, why would SOA yield decrease with delta_Mo at the beginning of the experiments? Under high-NO$_x$ conditions, what causes the SOA yield decrease within the first 30min? If one looks at the figure 1, the yield curve is expected to be monotonic. Is the weird yield curve caused by the SOA wall loss correction? What does the sulfate concentration (measured by AMS) look like over the course of the experiments? Does the sulfate concentration (measured by AMS) change once organics are formed?

Response: We do not regard the results in Figure 3 as problematic. The main difference in Griffin et al. (1999) compared to our study is that they investigated the SOA yield from ozonolysis of α-pinene without the consideration of an acidity effect. We attribute the gradual decrease in the first 30 minutes to the acidity effect, and more specifically, the decrease in the availability of the acidic phase as organics were formed. This is discussed in the manuscript as follows:

"A slight decrease in the SOA yield for acidic particles was also observed after the relatively higher SOA yields within the first 30 min. 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 241–247)

Also, Figure 3 in our study presents the time series of instantaneous SOA yields vs. ΔM_0 for individual experiments, in contrast to the final SOA yield presented in Griffin et al. (1999). The mass concentration of sulfate decreased smoothly over the experiment period due to particle loss on the chamber wall. There was no significant unexpected change in sulfate concentration once organic mass was formed. The calculated α-pinene SOA yield (i.e., the ratio of $\Delta M_0/\Delta HC$) can be affected by both ΔM_0 and ΔHC. The ΔM_0 in individual experiments increased constantly as seen in Figure 1. The high yields at the very beginning are caused mainly by the very low ΔHC. These data points were acquired by the PTR-MS when α-pinene concentration was high at the very beginning, whereas the calculated ΔHC was too low and within the α-pinene detection limit. Therefore, we have removed the initial data points with extremely low ΔHC in Figure 3.

(2) Figure 4: This figure is confusing. Firstly, following the same delta_Mo, the authors are comparing the SOA yield under different NH4/SO4 ratio. The trend shown in figure 4 does not hold if the authors add data points when delta_Mo = ~0.25 ug/m³ (where SOA yield peaks for NH4/SO4 = 0.2). Secondly, many data points are obtained from the period when SOA yield decreases with delta_Mo, the reason for which is not clear yet.

Response: We agree that the data points in the initial period for the experiment with $NH_4/SO_4= 0.5$ was not in line with the other three experiments ($NH_4/SO_4= 2$, 1, and 0.2) when making similar plots for $\Delta M_0= \sim 0.25$ µg m^{-3} in Figure 4a. However, as these are experimental results, it should be acceptable if any of the experiments did not perfectly match the trend. There could be some uncertainty in the SOA yield for the experiment with $NH_4/SO_4= 0.5$ at the very beginning. We therefore have used the ΔM_0 values above 0.7 µg m^{-3} for plotting in Figure 4. As SOA yield depended both on ΔM_0 and ΔHC, a decrease of yield indicates a lower aerosol formation potential, which was possibly due to the reduced acidity effect caused by inaccessibility to the acidic medium as organics were formed. That is in fact the point of choosing the first hour to demonstrate that the acidic effect on the yield does indeed change with organic mass increases. We have provided the reason for the decrease of SOA yield 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)

(3) Figure 5: Firstly, the y-axis scale is misleading. Although it seems that SOA yield increases a lot once injecting seed, the actual enhancement is only on the order of 0.01, which is within measurement uncertainty.

Response: We agree that using "SOA yield" as the label of y-axis is not appropriate here, as this is different from the general definition of SOA yield. The main point of Figure 5 is to show the increase in organic aerosol mass for experiments with acidic particles (high- and low-NO_x) compared to those with ammonium sulfate particles. We have changed the "SOA yield" to "Normalized SOA mass" and also added an additional graph in the revised Figure 5 to show the increased organic aerosol mass for the acidic particles compared to the ammonium sulfate particles. The increase in organic aerosol mass was up to 6 times higher for acidic particles than those of ammonium sulfate particles at the initial stages, as presented in Figure 5b below.
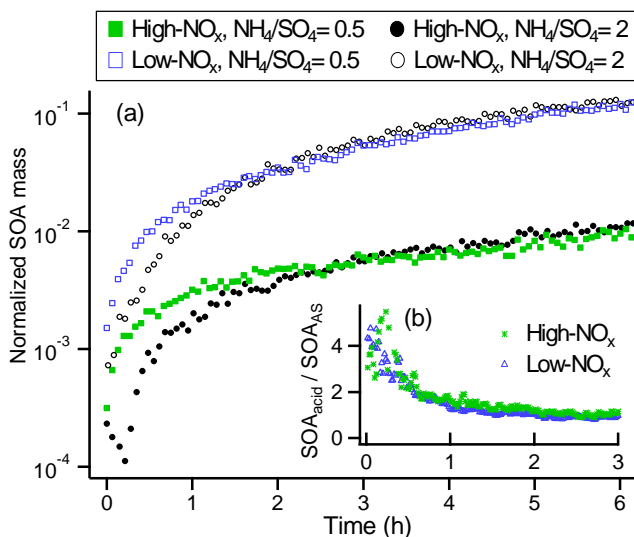

Figure 5. (a) The increase of SOA mass with time for experiments with injecting neutral and acidic seed particles after α-pinene photooxidation for 2 and 4 hours under high- and low-NO_x conditions, respectively (Exp. 9–12 in Table 1). Time= 0 hour represents the beginning of reactive uptake of

oxidation products after seed particles added. The SOA mass was normalized by the reacted α-pinene concentration before adding seed particles. (b) The ratio of SOA mass for acidic particles to that of ammonium sulfate particles.

Secondly, is there organics associated with sulfate seed in the atomizing solution? Based on some tests in our lab, the injection of sulfate would introduce organics, which comes from the atomizing solution, even if HPLC-grade DI water is used to make solution. Actually, the organics associated with sulfate seed may explain the immediate OA increase after adding seed particles (line 239).

The sentence referred: "Organic aerosol mass increased immediately after adding seed particles for all experiments.

Response: The reviewer is correct in terms of the potential organic contamination during the atomization procedure. We also have noticed that the organic concentration was increased slightly when adding acidic seed particles. However, the organics associated with sulfate seed is not a concern here, as we are discussing the generated organic aerosol mass (ΔM_0), which was obtained by subtracting the initial organic mass from the total organic mass measured in real-time. We have clarified the meaning of the original sentence:

"The *generated* organic aerosol mass increased immediately after adding seed particles for all experiments." (Line 277)

Thirdly, how is the increase of SOA yields calculated? What's the reference?

Response: We calculated the SOA yields for the four experiments in Figure 5 using the ratios of $\Delta M_0/\Delta HC$ in the original manuscript. However, as described in the response to the first question, we

believe that it is not appropriate to use "SOA yield" as the label of the y-axis in Figure 5. Therefore, the "SOA yield" has been replaced by the "Normalized SOA mass".

Fourthly, the results are not consistent with Eddingsaas et al. (2012a) (figure 7), who showed that AS particles have no effect on for both low and high NO_x conditions.

Response: It is not clear why there was no additional SOA was formed after introducing ammonium sulfate particles in Eddingsaas et al. (2012a). In contrast, the increase of particulate organic aerosol mass in our study can be explained by the reactive uptake of the gas-phase α-pinene oxidation products formed in the early stage by the acidic and ammonium sulfate seed particles. The point here is that the increase of particulate organic aerosol mass was stronger for acidic particles than for ammonium sulfate particles. The results of our study are also not necessary to be consistent with those of Eddingsaas et al. (2012a), considering the different initial conditions. We have added this statement in the revised manuscript:

"This can be explained by the reactive uptake of the gas-phase α-pinene oxidation products formed in the early stages onto the acidic and ammonium sulfate seed particles." (Lines 277–279)

Minor comments:

1. Table 1: (1) Since both H^+ and LWC are modeled by E-AIM in the study, I suggest the authors to replace NH_4/SO_4 by particle pH, because NH_4/SO_4 or ion balance is not a good proxy for particle pH (Guo et al., 2015; Hennigan et al., 2015). (2) Are the $[NH_4]$ and $[SO_4]$ input for E-AIM obtained from aqueous solution or AMS measurements? The latter should be used, because the NH_3/NH_4^+ partitioning would cause the real $[NH_4]/[SO_4]$ ratio different from that in aqueous solution.

Response: We have added the aerosol pH value calculated from the E-AIM II in Table 1, as presented below. The mass concentrations of NH_4^+ and SO_4^{2-} measured by the AMS have been used as inputs in the E-AIM. The initial seed composition also has been updated accordingly. We still kept the initial NH_4/SO_4 molar ratios in Table 1, because they are important references for making ammonium sulfate/sulfuric acid aqueous solution.

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.

2. Figure 1: (1) The legend "OH consumed a-pinene" is confusing because cumulative a-pinene consumed by OH should increase with time instead of decreasing as shown in the figure. I suggest to change the y-axis to "Δa-pinene consumed by OH". (2) Is SOA mass concentration shown in this figure corrected for wall loss?

Response: (1) As the y-axis is scaled both for total α-pinene concentration and α-pinene consumed by OH, it is not appropriate to change the y-axis to "Δα-pinene consumed by OH". Therefore, in order to avoid confusion, we have changed the "OH consumed α-pinene" to "α-Pinene decay by OH" in the legend of Figure 1.

(2) The SOA mass concentrations were corrected for particle wall loss using the method described in the manuscript. We have added the following statement in the caption of Figure 1: "The presented SOA mass concentrations have been corrected for particle wall loss according to the decay of sulfate mass." (Lines 664–665)
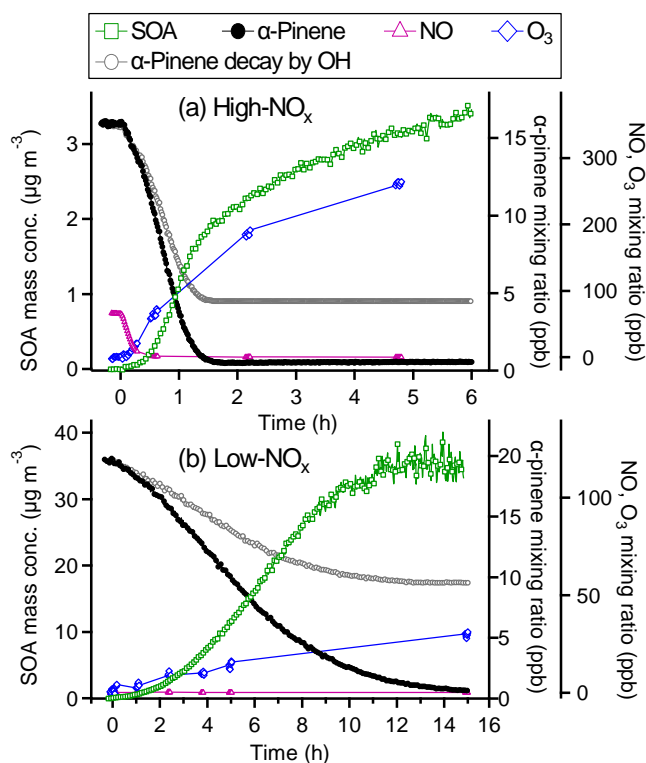
Figure 1. Time series of the mass concentrations of generated SOA and the mixing ratios of NO, O$_3$, total α-pinene decay, and OH consumed α-pinene in (a) high- and (b) low-NO$_x$ experiments using ammonium sulfate as seed particles. Time = 0 hour is defined as α-pinene photooxidation initiated when the lamps were turned on. The presented SOA mass concentrations have been corrected for particle wall loss according to the decay of sulfate particles.

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3. line 15. The core-shell model contradicts with literature. For example, Renbaum-Wolff et al. (2013) measured the viscosity of a-pinene SOA and calculated that the mixing time is on the order of 10-100s under 40-50% RH.

The sentence referred to: "The SOA yield decreased gradually with the increase in organic mass under high-NO$_x$ conditions, which is likely due to the inaccessibility of the acidity over time with the coating of α-pinene SOA."

Response: The reviewer's comment is not accurate in this case. According to Figure 2 in Renbaum-Wolff et al. (2013), the viscosity of α-pinene SOA varied up to 5 orders of magnitude at 40–50% RH, and the mixing time due to bulk diffusion was in the range of several seconds to 2×10^4 seconds (i.e., approximately 5.6 hours). As a result, the proposed core-shell model in this study is reasonable at the studied final RH of approximately 29–43%. Nevertheless, this assumption is based on the upper limit of the estimated viscosity. We have revised the original sentence to:

"The SOA yield decreased gradually with the increase in organic mass **in the initial stage (approximately 0–1 hour)** under high-NO$_x$ conditions, which is likely due to the inaccessibility to the acidity over time with the coating of α-pinene SOA **assuming a slow particle-phase diffusion of organic molecules into the inorganic seeds**." (Lines 14–17)

4. line 18-20. The authors found that the SOA is more oxidized under low-NO$_x$ conditions than high-NO$_x$ conditions. However, Chhabra et al. (2011) figure 2c showed that the O:C of a-pinene SOA under low-NO$_x$ (using H$_2$O$_2$) and high-NO$_x$ conditions (using CH$_3$ONO) are similar.

The sentence referred to: "The fraction of oxygen-containing organic fragments ($C_xH_yO_1^+$ 33–35% and $C_xH_yO_2^+$ 16–17%) in the total organics and the O/C ratio (0.49–0.54) of α-pinene SOA were lower

under high-NO$_x$ conditions than those under low-NO$_x$ conditions (39–40%, 17–19%, and 0.60–0.62), suggesting that α-pinene SOA was less oxygenated in the studied high-NO$_x$ conditions."

Response: The different results between the two studies are most likely due to the distinct experimental conditions. Chhabra et al. (2011) performed their α-pinene photooxidation experiments at lower RHs (4.2% and 4.9%), higher initial α-pinene concentrations (46 and 47 ppb), and generated higher α-pinene SOA loadings (63.9 and 53.7 μg m^{-3}), and eventually they obtained lower O/C ratios of 0.40 and 0.42 under low- and high-NO$_x$ conditions, respectively. In contrast, the higher O/C ratios observed in our study (0.52–0.56 and 0.61–0.64 under high and low-NO$_x$ conditions, respectively) suggest that α-pinene SOA was more oxygenated, which is most likely associated to the lower initial α-pinene concentrations used in our reaction system (approximately 14–20 ppb). This is consistent with the following statement in our manuscript:

"Laboratory studies were usually performed with relatively high loadings of hydrocarbons (e.g., from tens of ppb to several ppm), which would result in higher yield and lower oxidation state of laboratory SOA compared to ambient SOA (Ng et al., 2010; Odum Jay et al., 1996; Pfaffenberger et al., 2013; Shilling et al., 2009)." (Lines 70–73)

5. line 35. It should be "enhance the reactive uptake of gas phase organics", instead of "particle phase".

The sentence referred to: "The presence of acidic aerosol particles has been shown to enhance the reactive uptake of particle phase organics and increase SOA yields due to acid-catalyzed reactions (i.e., Garland et al., 2006; Jang et al., 2004; Liggio and Li, 2006; Northcross and Jang, 2007)."

Response: The "particle phase organics" has been changed to "gas phase organic species" in the revised manuscript.

6. line 37. Cite Surratt et al. (2010) and Xu et al. (2015a), who showed the effect of sulfate on the reactive uptake of IEPOX.

Response: The two references have been cited as below and also listed in the References.

"The presence of acidic aerosol particles has been shown to enhance the reactive uptake of gas phase organic species and increase SOA yields due to acid-catalyzed reactions (i.e., Garland et al., 2006; Jang et al., 2004; Liggio and Li, 2006; Northcross and Jang, 2007; Surratt et al., 2010; Xu et al., 2015a)." (Lines 37–39)

7. line 43. It is not accurate to state that atmospheric chemistry models do not consider the dependence of SOA formation on aerosol acidity. Large efforts have been devoted to consider the effect of particle acidity for SOA through IEPOX uptake (Marais et al., 2016; McNeill et al., 2012; Pye et al., 2013). Please rephrase this sentence.

The sentence referred to: "The dependence of SOA formation on aerosol acidity has not been considered in most atmospheric chemistry models thus far due to the large uncertainties associated with its quantification."

Response: The original sentence has been reworded to:

"The dependence of SOA formation on aerosol acidity generally has not been incorporated in many atmospheric chemistry models thus far due to the large uncertainties associated with the quantification

of acidity effects, with the exception of the acidity effect for SOA via isoprene epoxydiol uptake (Marais et al., 2016; Pye et al., 2013)." (Lines 45–48)

8. line 50-52 and line 63-66. I don't agree with the authors that "large discrepancies among experiments remain with respect to the effects of aerosol acidity on SOA formation". The seemingly "contradictory" observations among studies listed in the manuscript are just due to the difference in experimental conditions. For example, the effects of particle acidity on α-pinene SOA formation are different for low-NO$_x$ and high-NO$_x$ conditions. Thus, the previous studies cited in the manuscript only show the complexity of this scientific question, instead of the discrepancy.

The sentence referred to:

a. "Despite the efforts of previous laboratory studies, large discrepancies among experiments remain with respect to the effect of aerosol acidity on SOA formation from individual hydrocarbons."

b. "The large discrepancy regarding the previously reported acidity effect on α-pinene SOA is most likely attributed to the varied experimental parameters such as particle acidity, initial hydrocarbon concentration, oxidant type and level, NO$_x$ level, temperature, and relative humidity (RH)."

Response: The "discrepancies" in the above two sentences are actually more close to "dissimilarities", instead of "contradictory". We agree that different results in previous studies show the complexity of this scientific question. To clarify these points, we have revised the original sentences to:

a. "Despite the efforts of previous laboratory studies under various experimental conditions, the effect of aerosol acidity on SOA formation from individual hydrocarbons remains unclear due to the complexity of this scientific question." (Lines 55–57)

b. "These inconsistent results reported previously are most likely attributed to the varied experimental parameters such as particle acidity, initial hydrocarbon concentration, oxidant type and level, NO_x level, temperature, and relative humidity (RH)." (Lines 67–69)

9. line 124. The collection efficiency of AMS. Was a dryer deployed upstream of AMS and SMPS? If not, considering the high RH in this study, the particle water could affect the comparison between AMS and SMPS.

The sentence referred to: "A collection efficiency value of 0.7 was applied for the AMS data analysis based upon the comparison of the volume concentrations derived from AMS and SMPS measurements, assuming that particles are spherical and the densities of organics, sulfate, ammonium, and nitrate are 1.4, 1.77, 1.77, and 1.725 g cm^{-3}, respectively."

Response: We did not use a dryer upstream of AMS and SMPS during the experiments. As a result, the particle volume concentrations derived from the SMPS could have a contribution by aerosol water, whereas those derived from the AMS does not include water. This is an uncertainty for the collection efficiency estimation. We have added the following statement to demonstrate this uncertainty in the revised manuscript:

"Note that aerosol particles were not dried upstream of the AMS and SMPS measurements, and thus particle water content might have contributed to the SMPS-derived volume concentrations. This was not taken into account for the AMS-derived volume concentration." (Lines 134–136)

10. line 133-134. How do the authors estimate the concentration of organics from self-nucleation? Is the particle size distribution bimodal? Please show the particle size distribution measured by SMPS.

The sentence 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 is same as minor comment #4 from reviewer #1. 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 particle size distribution measured by SMPS. We observed less than 50 cm^{-3} particles contributed by self-nucleation and also no obvious increase in organic mass concentration by the AMS measurement in 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 particle size. We have therefore replaced the estimated value with the observed experimental results as follows:

"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)

11. line 166-167. The lower SOA yield under high-NO$_x$ conditions is due to RO$_2$ reacts with NO and likely undergo fragmentation to produce volatile species, not due to the formation of organic nitrates. According to group contribution method by Pankow and Asher (2008), the reduction in vapor pressure by adding of one nitrate functional group is similar to that of adding one hydroxyl group.

The sentence referred to: "RO$_2$ reacted primarily with NO and NO$_2$ under high-NO$_x$ conditions, which would result in the formation of relatively volatile species such as organic nitrates and reduce the overall SOA yield; …"

Response: We agree that using organic nitrates as an example here is inappropriate, as some organic nitrates are less- or non-volatile. The original sentence has been reworded to:

"RO$_2$ reacted primarily with NO under high-NO$_x$ conditions and generated relatively more volatile products that reduced the overall SOA yield, …" (Lines 189–190)

12. line 246-247. Eddingsaas et al. (2012a) is not properly cited. Section 3.3 in Eddingsaas et al. (2012a) stated that "Under high-NO2 conditions, no additional SOA is formed after the addition of either neutral or acidic seed particles in the dark". Thus, the finding in this study is not consistent with Eddingsaas et al. (2012a).

The sentence referred to: "Eddingsaas et al. (2012) similarly reported that α-pinene photooxidation products preferentially partition to highly acidic aerosols when introducing seed particles after OH oxidation under both low-NO$_x$ and high-NO$_2$ conditions."

Response: We agree that this effect was not observed under high-NO$_2$ conditions by Eddingsaas et al. (2012a). The original sentence has been rephrased to:

"Eddingsaas et al. (2012) also reported that α-pinene photooxidation products preferentially partition to highly acidic aerosols when introducing seed particles after OH oxidation under low-NO$_x$ conditions." (Lines 285–287)

13. line 249-250. The authors propose that the early generation products don't participate in acid catalysis. This is not consistent with Eddingsaas et al. (2012a) (figure 8), who showed that the first generation products can partition to acidic particles.

The sentence referred to: "The results of Figure 5 also indicate that early α-pinene oxidation products under low-NO$_x$ condition did not participate in acid catalysis, whereas the later products did."

Response: This conclusion is not in conflict with Eddingsaas et al. (2012a). Indeed, the increase of organic mass was only observed when introduced seed particles after photooxidation under low-NO_x conditions. We therefore concluded that early α-pinene oxidation products under low-NO_x condition did not participate in acid catalysis. Note that here the "early α-pinene oxidation products" in our study are not necessary the "first generation products". Figure 8 in Eddingsaas et al. (2012a) presents the time series of CIMS traces in experiments with adding seed particles after 4-hour α-pinene photooxidation under low-NO_x condition, where the products are similar to "the later products" defined in our study. We have rephrased the original sentence to make it more clear:

"The results in Figure 5 also indicate that later products of α-pinene oxidation were more likely to be acid-catalyzed than the early products under low-NO_x conditions." (Lines 287–288)

14. line 267-270. The authors need to cite previous studies which discussed the gas phase products from a-pinene oxidation. Especially, Eddingsaas et al. (2012b) showed that pinonaldehyde is important intermediate under both low and high-NO_x conditions.

The sentence referred to: "The dependence of chemical composition and oxidation state of α-pinene SOA on NO_x level is most likely associated with the gas-phase chemistry of RO_2. For instance, peroxynitrates and organic nitrates formed from the chemical reaction of RO_2 and NO_x are the dominant products under high-NO_x conditions, whereas organic peroxides and acids formed from RO_2 with HO_2 are dominant under low-NO_x conditions (Xia et al., 2008)."

Response: We intended to address the different final oxidation products from the gas-phase chemistry of RO_2 rather than to refer to the detailed gas-phase chemistry here. Therefore, we have rephrased the first sentence slightly as follows:

"The dependence of chemical composition and oxidation state of α-pinene SOA on NO_x level is most likely associated with the different oxidation products from gas-phase chemistry of RO_2." (Lines 305–306)

15. line 270-272. Xu et al. (2014) is not properly cited. Instead of showing that isoprene SOA is more oxidized under low-NO_x conditions, Xu et al. (2014) showed that the oxidation state of isoprene SOA shows a non-linear dependence on NO_x level.

The sentence referred to: "SOA formed from photooxidation of isoprene has also been reported to become more oxidized under low-NO_x conditions, which is contrary to those under high-NO_x conditions (Xu et al., 2014)."

Response: As stated by Xu et al. (2014), "SOA becomes less volatile and more oxidized as oxidation progresses in HO_2-dominant experiments, while the volatility of SOA in mixed experiments does not change substantially over time". Therefore, this sentence itself is correct, but it was not appropriate to be cited here and also it distracted our major focus on α-pinene. We have removed this sentence in the manuscript.

16. line 318. Please cite Boyd et al. (2015) and Xu et al. (2015b).

Response: These two references have been cited as follows and also listed in the section of References:
"Large relative contribution of organic nitrates to the nominal inorganic nitrate fragments is demonstrated by a higher NO^+/NO_2^+ ratio than those of pure ammonium nitrate (Bae et al., 2007; Boyd et al., 2015; Farmer et al., 2010; Fry et al., 2009; Xu et al., 2015b)." (Lines 359–361)

17. line 331. What's the Org/SO₄ ratio in this study? Is it atmospherically relevant?

The sentence referred to: "Given that the α-pinene loading used in this study was low, similar phenomenon may also occur in the atmosphere."

Response: The final ratio of organics to sulfate at the end of each experiment was in the range of 0.6–0.8 and 1.7–2.8 under high- and low-NO_x conditions, respectively. These are relevant to atmospheric levels. We have added this information to the original sentence as follows:

"Given that the α-pinene loading used in this study was low **and the generated organic aerosol mass was relevant to ambient levels (e.g., the final ratio of organic/sulfate was 0.6–0.8 and 1.7–2.8 under high- and low-NO_x conditions, respectively)**, similar process may also occur in the atmosphere." (Lines 382–385)

18. line 342. The authors have already ruled out the mechanism "acidic seed facilitates the partitioning of gas phase organic nitrate" (line 308-310). Please rephrase this sentence.

The sentence referred to:

a. "This is inconsistent with the observed increase in organic nitrate fragments with increasing acidity. Therefore, acid-catalyzed formation of organic nitrates also very likely contributed to the observed enhancement of N-containing organic fragments with particle acidity."

b. "Organic nitrates in these experiments may be formed heterogeneously through a mechanism catalyzed by particle acidity and/or the acidic conditions facilitate the partitioning of gas phase nitrates into the particle phase under high-NO_x conditions."

Response: We did not rule out the partitioning mechanism from the original line 308–310. We meant that the partitioning mechanism cannot solely explain the enhanced N-containing organic fragments. We have added the following explanations to clarify the meaning:

"Moreover, it has been demonstrated that acid-catalyzed hydrolysis is an important removal process for organic nitrates in the particle phase, from which organic nitrates can be converted to alcohols and nitric acid (Day et al., 2010; Hu et al., 2011; Liu et al., 2012; Rindelaub et al., 2015). This process would also enhance the partitioning of gaseous organic nitrates into the particle phase due to the perturbation in gas/particle partitioning, and therefore decrease the organic nitrate yields both in the gas and particle phases (Rindelaub et al., 2015). The observed increase in N-containing organic fragments with particle acidity under high-NO_x conditions suggests that the production of organic nitrates generally exceeded their removal rates in this reaction system." (Lines 348–354)

19. line 495. The author list of this citation is wrong.

Response: The author list of this citation was correct. Please find the entire author lists from the original line 494.

"Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, a. C., Sueper, D., Jimenez, J. L. and Martin, S. T.: Loading-dependent elemental composition of α-pinene SOA particles, Atmos. Chem. Phys., 9, 771–782, doi:10.5194/acp-9-771-2009, 2009." (Lines 583–585)

The effect of particle acidity on secondary organic aerosol formation from α-pinene photooxidation under atmospherically relevant conditions

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Abstract. Secondary organic aerosol (SOA) formation from ~~OH initiated~~ photooxidation of α-pinene has been investigated in a photochemical reaction chamber under varied _inorganic seed_ particle acidity levels _at moderate relative humidity_. The effect of particle acidity on SOA yield and chemical composition was examined under high- and low-NO_x conditions. The SOA yield (4.~~0~~2%–7.~~3~~6%) increased nearly linearly with the increase in particle acidity under high-NO_x conditions. In contrast, the SOA yield (~~27.9%–35~~28.6%–36.3%) was substantially higher under low-NO_x conditions, but its dependency on particle acidity was insignificant. A relatively strong increase in SOA yield (up to 220%) was observed in the first hour of α-pinene photooxidation under high-NO_x conditions, suggesting that SOA formation was more effective for early α-pinene oxidation products in the presence of fresh acidic particles. The SOA yield decreased gradually with the increase in organic mass _in the initial stage (approximately 0–1 hour)_ under high-NO_x conditions, which is likely due to the inaccessibility ~~of~~to the acidity over time with the coating of α-pinene SOA _assuming a slow particle-phase diffusion of organic molecules into the inorganic seeds_. The formation of later-generation SOA was enhanced by particle acidity even under low-NO_x conditions when introducing acidic seed particles after α-pinene photooxidation~~.~~, _suggesting a different acidity effect exists for α-pinene SOA derived from later oxidation stages._ The fraction of oxygen-containing organic fragments ($C_xH_yO_1^+$ 33–35% and $C_xH_yO_2^+$ 16–17%) in the total organics and the O/C ratio (0.~~49~~52–0.~~54~~56) of α-pinene SOA were lower under high-NO_x conditions than those under low-NO_x conditions (39–40%, 17–19%, and 0.~~60~~61–0.~~62~~64), suggesting that α-pinene SOA was less oxygenated in the studied high-NO_x conditions. The fraction of nitrogen-containing organic fragments ($C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$) in the total organics was enhanced with the increases in particle acidity under high-NO_x conditions, indicating that organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity~~.~~ _or that acidic conditions facilitate the partitioning of gas phase organic nitrates into particle phase._ The results of this study suggest that inorganic acidity ~~have~~has a significant role to play in determining various organic aerosol chemical properties such as _mass yields,_ oxidation state, ~~mass yields,~~ and organic nitrate content. ~~It~~The acidity effect being further dependent on the time scale of SOA formation is also an important parameter in the modeling of SOA~~, which is further dependent on the time scale of SOA formation. Additional research is required to understand the complex physical and chemical interactions facilitated by aerosol acidity.~~.

1 Introduction

Secondary organic aerosols (SOA) formed by oxidation of biogenic and anthropogenic volatile organic compounds ~~(VOCs)~~ comprise a substantial portion of submicron aerosol particles in the atmosphere (Kanakidou et al., 2005; Zhang et al., 2007a). Understanding the physical and chemical properties associated with SOA formation and transformation is important to adequately assess aerosol impacts on climate and human health (Hallquist et al., 2009). The effect of aerosol acidity on SOA formation is one of the scientific questions currently under open debate~~, as results obtained from both laboratory and field studies tend to be inconsistent.~~. Acid-catalyzed heterogeneous reactions such as hydration, hemiacetal/acetal formation, polymerization, and aldol condensation have been proposed to form SOA (Jang et al., 2002). The presence of acidic aerosol particles has been ~~shown~~reported to enhance the reactive uptake of ~~particle~~gas phase ~~organics~~organic species and increase SOA yields due to acid-catalyzed reactions (i.e., Garland et al., 2006; Jang et al., 2004; Liggio and Li, 2006; Northcross and Jang, 2007~~).~~; Surratt et al., 2010; Xu et al., 2015a). However, other studies have suggested that those reactions may be thermodynamically or kinetically unfavorable and are possibly insignificant in the real atmosphere (Barsanti and Pankow, 2004; Casale et al., 2007; Kroll et al., 2005; Li et al., 2008). Furthermore, the enhanced formation of SOA, organic sulfates, and epoxide compounds has been reported in ambient environments with an abundance of acidic aerosol particles (Hawkins et al., 2010; Lin et al., 2012; Rengarajan et al., 2011; Zhang et al., 2012; Zhou et al., 2012), which is contrary to other field studies showing no apparent evidence of acid-catalyzed SOA formation (Peltier et al., 2007; Takahama et al., 2006; Tanner et al., 2009; Zhang et al., 2007b). The dependence of SOA formation on aerosol acidity generally has not been ~~considered~~incorporated in ~~most~~many atmospheric chemistry models thus far due to the large uncertainties associated with ~~its~~the quantification~~.~~ of acidity effects, with the exception of the acidity effect for SOA via isoprene epoxydiol uptake (Marais et al., 2016; Pye et al., 2013).

A number of laboratory studies have investigated the effect of particle acidity on SOA formation from oxidation of various precursor hydrocarbons such as isoprene, terpenes, toluene, m-xylene, and 1, 3-butadiene (e.g., Kristensen et al., 2014; Lewandowski et al., 2015; Ng et al., 2007a; Offenberg et al., 2009; Song et al., 2013; Surratt et al., 2007b). α-Pinene is the most abundant biogenic monoterpene emitted from terrestrial vegetation (Guenther et al., 2012). 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). Despite the efforts of previous laboratory studies~~, large discrepancies among experiments remain with respect to the~~ under various experimental conditions, the effect of aerosol acidity on SOA formation from individual hydrocarbons remains unclear due to the complexity of this scientific question. In particular, the magnitude of the acidic effect on SOA yields for α-pinene has been found to vary significantly. For instance, a nearly 40% increase in organic carbon (OC) was observed for the ozonolysis of α-pinene in the presence of acidic seed particles without NO$_x$, and aerosol acidity played an important role in the formation of high molecular weight organic molecules in particles (Iinuma et al., 2004). ~~Enhanced aerosol acidity led to the formation of sulfate esters that contributed to a large fraction of~~

65 ~~SOA mass from photooxidation of α-pinene under high-NO~~x~~ conditions (Surratt et al., 2007a, 2008).~~ A linear increase of 0.04% <ins>in OC mass</ins> per nmol H^+ m^{-3} ~~in OC mass~~ was reported from the photooxidation of α-pinene with NO_x, and this effect was independent of initial hydrocarbon concentration or the generated organic mass (Offenberg et al., 2009). In contrast, Eddingsaas et al. (2012) reported a relatively small increase of SOA yield (approximately 22%) for OH photooxidation of α-pinene under high-NO_x conditions, and no effect of aerosol acidity on SOA yield under low-NO_x conditions~~.~~ <ins>when</ins>

70 <ins>introducing acidic seeds before photooxidation.</ins> Kristensen et al. (2014) similarly found that the increase of aerosol acidity has a negligible effect on SOA formation from ozonolysis of α-pinene under low-NO_x conditions.

~~The large discrepancy regarding the previously reported acidity effect on α-pinene SOA is~~<ins>These inconsistent results</ins> <ins>reported previously are</ins> most likely attributed to the varied experimental parameters such as particle acidity, initial hydrocarbon concentration, oxidant type and level, NO_x level, temperature, and relative humidity (RH). Most previous

75 studies were conducted with different acidity levels, and therefore a quantitative comparison of the acidity effect among various studies is ~~problematic~~<ins>difficult</ins>. Laboratory studies were usually performed with relatively high ~~loading~~<ins>loadings</ins> of hydrocarbons (e.g., from tens of ppb to several ppm ~~level~~), which would result in higher yield and lower oxidation state of laboratory SOA compared to ambient SOA (Ng et al., 2010; Odum Jay et al., 1996; Pfaffenberger et al., 2013; Shilling et al., 2009). In addition, the presence of NO_x during α-pinene oxidation may change the reaction chemistry and lead to ~~different~~

80 ~~oxidation products by introducing~~<ins>the formation of</ins> relatively volatile ~~nitrogen-containing organic species~~<ins>oxidation products</ins>, and hence decrease α-pinene SOA yields (Eddingsaas et al., 2012; Ng et al., 2007a). Moreover, temperature is an important factor in SOA formation; higher SOA yields may be obtained at lower temperature (Saathoff et al., 2009; Takekawa et al., 2003). RH is another important factor, the decrease of which may lead to an increase in α-pinene SOA yields (Jonsson et al., 2006~~). However~~<ins>); however</ins>, many previous studies have been performed at very low RH (e.g., less than 10%) or even dry

85 conditions. As a result of the above issues, it is highly important for laboratory studies to investigate the acidity effect on SOA formation under more realistic conditions approaching those of the ambient atmosphere. This would facilitate an accurate parameterization of the acidity effect for incorporation into air quality models.

This study aims to improve our current understanding of the effect of particle acidity on SOA formation from ~~OH-~~ ~~initiated~~ photooxidation of α-pinene. <ins>Photochemical chamber experiments were performed</ins> under conditions ~~of~~<ins>with</ins> relatively

90 low α-pinene loadings and moderate RH, which are more representative of the ambient atmosphere. <ins>The yield of α-pinene</ins> <ins>SOA was obtained at various particle acidity levels under high- and low-NO_x conditions.</ins> The dependence of ~~α-pinene~~ SOA yield on particle acidity ~~is~~ <ins>and the time scale of the acidity effect are</ins> characterized ~~under high~~ <ins>and</ins> ~~low NO~~x ~~conditions.~~<ins>discussed.</ins> The ~~changes in~~<ins>effect of particle acidity on</ins> the chemical composition of α-pinene SOA ~~with particle~~ ~~acidity and NO~~x ~~level are also~~<ins>, the fragment distributions of bulk organics, and the oxidation state of organics are</ins> examined~~.~~

95 ~~Finally,~~ <ins>based on</ins> the ~~potential significance~~<ins>high-resolution analysis</ins> of organic <ins>aerosol</ins> ~~acidity in~~<ins>mass spectra. The possible</ins> <ins>contribution of particle acidity to</ins> the formation of <ins>particulate</ins> organic nitrates under high-NO_x conditions is ~~discussed.~~<ins>also</ins> <ins>discussed. Finally, the potential significance of the observed acidity effect in the ambient atmosphere is summarized.</ins>

2 Experimental methods

100   Photooxidation experiments were performed in a 2 m^3 Teflon chamber (Whelch Flurocarbon) enclosed in an aluminum support (Liggio and Li, 2006; Liggio et al., 2005). Twelve black light lamps (model F32T8/350BL, Sylvania) were used as the irradiation source with intensity peaking at approximately 350 nm. The chamber was flushed by zero air with the lamps turned on for more than 20 hours before each experiment to avoid contamination from previous experiments. Hydrogen peroxide (H$_2$O$_2$) vapor was introduced into the chamber to produce OH radicals during the first 6 hours of flushing.

105   Temperature and RH inside the chamber were monitored continually using a temperature and humidity probe (model HMP 60, Vaisala). Temperature was not controlled during the experiments, but it was relatively constant at 25 °C before experiments began and increased to a stable value (approximately 30–34 °C) after the lamps were turned on. RH was maintained manually by adding water vapors generated from a bubbler with zero air as a carrier gas (15 L min^{-1}). Other chamber inputs (e.g., H$_2$O$_2$ vapor, NO, seed particles, and α-pinene) were conducted after the RH reached approximately

110   60%. RH inside the chamber stabilized at approximately 29–43% after the lamps were turned on for about 1 hour due to the increase in temperature.

      H$_2$O$_2$ vapor, as the source of OH radical, was introduced into chamber using a bubbler with a flow of zero air (0.09 L min^{-1}) passing through H$_2$O$_2$ aqueous solution (30 weight % in water, Sigma-Aldrich) for 1 hour. Ammonium sulfate (AS)/sulfuric acid (SA) solutions with varied NH$_4$/SO$_4$ molar ratios were used to provide various acidities in seed particles.

115   A complete list of the composition of the seed particles and other initial conditions in all experiments is given in Table 1. The seed particles were generated by atomizing AS/SA aqueous solution using an aerosol generator (model 3706, TSI), dried in a silica gel diffusion dryer, and then size-selected at 150 nm in mobility diameter using a differential mobility analyzer (DMA, model 3081, TSI). Nitric oxide (NO) was added into the chamber from a compressed gas cylinder (9.1 ppm NO in nitrogen) in high-NO$_x$ experiments, in contrast to low-NO$_x$ experiments where NO was not added. A micro-syringe was used

120   to inject approximately 0.25 µL liquid α-pinene (99+%, Sigma-Aldrich) into the chamber through a stainless steel tube with a zero air at 3 L min^{-1}. After achieving the desired experimental conditions for a stable 30 min period, photooxidation reactions were initiated by turning on the lamps. The typical photooxidation time was 6 and 15 hours for high- and low-NO$_x$ experiments, respectively.

      Four experiments were also performed to investigate the effect of aerosol acidity on α-pinene oxidation products at

125   different photooxidation stages (Exp. 9–12; Table 1). Photooxidation of α-pinene was conducted without seed particles in the reaction chamber for 2 and 4 hours under high- and low-NO$_x$ conditions, respectively. This was followed by turning off the lamps and adding neutral/acidic seed particles into the chamber within 1 hour. The experiments continued for another 6 hours on the reactive uptake of the α-pinene oxidation products by the newly introduced seed particles in the dark.

      The concentration of α-pinene in the chamber was measured in real-time using a proton-transfer-reaction time-of-flight

130   mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH) (Hansel et al., 1999; Lindinger and Jordan, 1998). The mixing

ratios of NO and O_3 were monitored using a NO analyzer (model 42i-Y, Thermo Scientific) and an O_3 monitor (model 202, 2B Technologies), respectively. The particle number size distribution was measured using a scanning mobility particle sizer (SMPS) consisting of a DMA (model 3081, TSI) and a condensation particle counter (model 3776, TSI). The non-refractory chemical composition of the submicron aerosol particles, including organics, sulfate, ammonium, nitrate, and chloride, was

135 measured using a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research) (DeCarlo et al., 2006). The AMS instrument was operated in a high-sensitivity mode (V-mode) with the data stored at 1 min intervals. The AMS data were processed using the standard ToF-AMS data analysis software (SQUIRREL v1.56D and PIKA v1.15D, http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/). The mass concentrations of aerosol species were generated from the PIKA analysis of raw mass spectral data. A collection efficiency value of 0.7 was applied for the AMS

140 data analysis based upon the comparison of the volume concentrations derived from AMS and SMPS measurements, assuming that particles are spherical and the densities of organics, sulfate, ammonium, and nitrate are 1.4, 1.77, 1.77, and 1.725 g cm^{-3}, respectively. Note that aerosol particles were not dried upstream of the AMS and SMPS measurements, and thus particle water content might have contributed to the SMPS-derived volume concentrations. This was not taken into account for the AMS-derived volume concentration. The detection limits of organics, sulfate, nitrate, and ammonium,

145 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.

SOA yield, which represents the aerosol formation potential of precursor hydrocarbon, was calculated from the ratio of generated SOA mass (ΔM_0) to the reacted α-pinene mass (ΔHC). The SOA yields and ΔM_0 presented in Table 1 correspond to the maximum values at the end of each experiment. Organic mass concentrations derived from AMS measurement were

150 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. This correction assumed that α-pinene oxidation products condensed on the sulfate particles instead of their self-nucleation. This assumption is appropriate given that ~~organics~~ less than 50 particles cm^{-3} were contributed by self-nucleation and that an obvious increase in organic mass concentration was ~~estimated~~not observed from the AMS measurement in the experiments without adding seed particles. The

155 decay rate of particles coated with organics was assumed to be ~~less than 0.1 μg cm^{-3} in the studied system~~same as that of pure sulfate particles, although the later could be slightly higher due to the larger Brownian diffusion rate of smaller particles. The calculated SOA yield could have been affected by the wall loss of semi-volatile vapors at low α-pinene loadings, whereas this effect was not taken into account herein.

The initial seed composition in each experiment was predicted using the Extended Aerosol Inorganic Thermodynamic

160 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. OH concentration in each experiment was estimated from a linear fitting of the first order decay of gaseous α-pinene by OH

165 radicals, i.e., the difference between the total α-pinene decay and the α-pinene consumed by O₃, as described by Liu et al. (2015). The OH concentrations were calculated to be approximately $4.3\text{–}5.9 \times 10^6$ and $0.8\text{–}1.1 \times 10^6$ molecules cm^{-3} for experiments under high- and low-NO_x conditions, respectively. 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.

170

3   Results and discussion

3.1   α-Pinene SOA formation under high- and low-NO_x conditions

An increase of α-pinene SOA mass concentration with the decay of α-pinene mixing ratio in high- and low-NO_x experiments using $(NH_4)_2SO_4$ seed particles (Exp. 1 and 5 in Table 1) is shown in Figure 1. Under the high-NO_x condition,
175   the increase of α-pinene SOA mass was observed shortly after the irradiation started until the end of the experiment (Figure 1a). Gaseous α-pinene was mostly consumed within approximately 1.5 hours. NO (66 ppbv initially) was consumed in the first 30 min of the irradiation. The formation of O_3 was not suppressed over the experiment. O_3 increased to more than 200 ppb at the end of the experiments, and therefore ozonolysis reactions would have contributed to the formation of α-pinene SOA. A rough estimation shows that α-pinene consumed by ozonolysis accounted for in the range of 0–28% of the total α-
180   pinene decay, as seen from the difference between the total α-pinene decay and OH consumed α-pinene in Figure 1a. Nitrate radicals may also have been generated from NO_x reactions and have contributed to α-pinene SOA formation, whereas its direct measurement was not available in this study.

In contrast, under the low-NO_x condition, the increase of SOA mass concentration and the decay of α-pinene were relatively slower (Figure 1b). This is most likely due to the ~~low~~lower production of OH radicals from H_2O_2 photolysis under
185   low-NO_x condition, that is, 1.1×10^6 molecules cm^{-3} compared to that of 5.3×10^6 molecules cm^{-3} under high-NO_x conditions. A plateau of the generated SOA mass was observed after approximately 12 hours of irradiation, suggesting that SOA formation reached equilibrium after α-pinene was consumed completely, if the gas-particle partitioning was reversible (Grieshop et al., 2007). NO was less than 0.3 ppbv through the entire experiment. A slight increase of O_3 (up to 30 ppb) was also observed under low-NO_x conditions, which might have resulted from the photolysis of a small amount of NO_2 ~~that~~
190   ~~deposited on~~released from the chamber ~~wall. Approximately less~~walls. Less than approximately 47% of α-pinene was consumed by ozonolysis.

The α-pinene SOA yield was 4.~~0~~2% when using $(NH_4)_2SO_4$ seed particles under high-NO_x condition, which is a factor of 8.~~7~~4 lower than that under low-NO_x condition (~~34.6~~35.2%) (Table 1). The relatively lower SOA yield under higher NO_x levels is consistent with those reported previously for the photooxidation and ozonolysis of α-pinene (Eddingsaas et al.,
195   2012; Ng et al., 2007a; Presto et al., 2005). Similar relationships are also observed in the photooxidation of isoprene and aromatic hydrocarbons such as benzene, toluene, and *m*-xylene (Kroll et al., 2006; Ng et al., 2007b). The dependence of α-

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pinene SOA yield on NO_x level is possibly due to the different gas-phase chemical reactions of the intermediate organic peroxy radicals (RO_2) formed in the initial photooxidation stage. RO_2 reacted primarily with NO ~~and NO_2~~ under high-NO_x conditions~~, which would result in the formation of~~ and generated relatively more volatile ~~species such as organic nitrates and reduce~~products that reduced the overall SOA yield~~;~~, whereas the reactions of RO_2 with other peroxy radicals (e.g., RO_2 and HO_2) were dominant under low-NO_x conditions (Kroll et al., 2006; Presto et al., 2005; Xu et al., 2014). ~~Note that the~~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). The observed difference in SOA yields might also be affected to some extent by other experimental conditions such as the initial α-pinene concentration, seed loading, and temperature, but NO_x level was most likely the primary cause, given that other factors did not vary as much as NO_x in these experiments (Table 1).

A comparison of SOA yields as a function of the generated SOA mass (ΔM_0) in this study and previous studies of α-pinene photooxidation is shown in Figure 2. The experimental parameters and SOA yields from previous studies are summarized in Table 2. SOA yields in these studies varied in the range of approximately 1.3–24% in the presence of NO_x, in contrast to those of 26–46% without NO_x. The SOA yields observed in our study are generally comparable to those reported from previous studies despite ~~with~~the different experimental parameters. The SOA yield under high-NO_x condition in our study is in particular closest to those with lower α-pinene level (Ng et al., 2007a; Odum et al., 1996) and at higher temperature (Takekawa et al., 2003). It has been established that low α-pinene level and high temperature can lead to relatively low SOA yields, which is possibly due to the changes of gas/particle partitioning thermodynamics in the reaction system (Odum et al., 1996; Pankow, 2007; Takekawa et al., 2003). The SOA yield under low-NO_x conditions here is similar to those reported by Eddingsaas et al. (2012) but lower than those reported by Ng et al. (2007a). The varied SOA ~~yield~~yields among these studies most likely depend on different experimental conditions~~, suggesting that~~. Therefore, laboratory studies performed under conditions ~~near~~relevant to the atmosphere are important for an ~~intercomparison~~inter-comparison among studies and for ultimately using those results in air quality models ~~ultimately~~.

3.2 Effect of particle acidity on α-pinene SOA yield

3.2.1 Dependence of SOA yield on particle acidity

The initial pH value of aerosol particles calculated from the E-AIM was in the range of −0.93 to −1.66 in the high- and low-NO_x experiments (see Table 1). An increase of the α-pinene SOA yield with an increase of particle acidity was observed under high-NO_x conditions. The final SOA yields were 5.~~4%, 6.3~~%, 6.6%, and 7.~~3~~6% for acidic particles with the initial NH_4/SO_4 molar ratios of 1.0, 0.5, and 0.2, respectively (Table 1). This corresponds to 1.~~4~~3, 1.6, and 1.8 times the SOA yield for neutral particles (i.e., 4.~~0~~2%). Conversely, the final SOA yields for acidic particles varied from ~~27.9~~28.6% to ~~35.6~~36.3% under low-NO_x conditions, from which a systematic increase in SOA yield with particle acidity was not observed. Clearly, the presence of acidic particles promotes the formation of α-pinene SOA under high-NO_x conditions and NO_x is ~~most~~ likely

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involved in the acid-catalyzed reactions during α-pinene photooxidation~~, such as the formation of organic nitrates from RO₂ reacting with NOₓ facilitated by particle acidity (as discussed in Sect. 3.4).~~. The dependence of α-pinene SOA yield on particle acidity under only high-NOₓ conditions in this study is similar to those reported by Eddingsaas et al. (2012), whereas they observed a smaller increase of SOA yield (approximately 22% compared to ~~40~~30–80% here) when using acidic particles. The effect of particle acidity on SOA formed from α-pinene has been reported to be much lower than that for isoprene, e.g., the former one was 8 times lower than the later one (Offenberg et al., 2009).

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 µg m^{-3} for high-NOₓ 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-NOₓ 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-NOₓ conditions.

3.2.2 Time scale of acidity effect

SOA yield is found to be a strong function of the generated SOA mass (ΔM_0) (Odum et al., 1996). The time-dependent SOA yield as a function of ΔM_0 for ~~acid~~acidic and neutral particles under high- and low-NOₓ conditions is shown in Figure 3. Under high-NOₓ conditions, the increase of SOA yield with particle acidity (black through green points in Figure 3a) was much stronger in the first hour of photooxidation than in the later period ~~(Figure 3a),~~. suggesting that the acidity effect was more significant in the initial period of photooxidation in this reaction system. This is possibly due to ~~that~~ fresh acidic particles ~~were~~being more accessible for acid-catalyzed reactions by early α-pinene oxidation products in the initial stage. A slight decrease in the SOA yield for acidic particles was also observed after the relatively higher SOA yields within the first 30 min. A possible interpretation for such a decrease in yield is that acidic particles (i.e., the inorganic core) were gradually less accessible ~~gradually~~ with increased organic coating ~~of~~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). This indicates that the acidity effect is particularly important in ~~particular in~~ the initial ~~stage~~stages of α-pinene oxidation in the presence of acidic particles ~~being introduced~~. The SOA yields increased nearly linearly with ΔM_0 after 2 hours of irradiation, suggesting that the growth of SOA mass continued after the complete consumption of the α-pinene. This is possibly due to the further oxidation of early-generation products such as carbonyls, hydrocarbonyls, and organic nitrates, and/or the continued partitioning of gas-phase

oxidation products into particle-phase. In contrast, the growth curves of SOA yields for acidic particles under low-NO$_x$

265 conditions were quite similar to that for neutral particles over the irradiation time (Figure 3b), which again suggests that acidity effect is insignificant under the studied low-NO$_x$ conditions.

The acidity effect on α-pinene SOA yield was relatively strong in the first hour of irradiation under high-NO$_x$ conditions, as illustrated above. This effect was characterized more quantitatively as a function of NH$_4$/SO$_4$ molar ratio, a proxy of particle acidity, in Figure 4. Here, the SOA yields at several specific ΔM$_0$ values from 0.7 to 1.9 µg m^{-3} (within the

270 first hour in Figure 3a) are used as it represents the strongest acidity effect observed. As seen in Figure 4, the SOA yield increased nearly linearly with the decrease in the NH$_4$/SO$_4$ molar ratio. A maximum increase of 220% in SOA yield was observed for the most acidic particles (i.e., NH$_4$/SO$_4$ molar ratio = 0.2) with the ΔM$_0$ of 0.~~5~~7 µg m^{-3} at the irradiation time of approximately 20 min compared to those for neutral particles (NH$_4$/SO$_4$ molar ratio = 2.0) (Figure 4). This increase is much higher than the increase in the final SOA yield with particle acidity (i.e., 80% at 6 hours) in the same experiments.

275 Furthermore, the increase in the SOA yield gradually slowed with the increase in organic mass, which is evident by the decreased trend of the slope curve derived from the fitting of SOA yield with NH$_4$/SO$_4$ molar ratios (Figure 4b). This could be again explained, at least in part, by acidic particles ~~became~~being less accessible over time with the coating of α-pinene SOA. Another possible cause is the consumption of sulfate due to the formation of organic sulfates (Surratt et al., 2007a, 2008). However, we cannot identify organic sulfates clearly based upon the AMS measurement, since their fragmentation

280 results mainly in inorganic sulfate fragments (Farmer et al., 2010).

3.2.3 Acidity effect on later-generation SOA

Due to ~~organics coating~~organic coatings on acidic particles, the effect of particle acidity on SOA formation in ~~the~~a later experimental stage may be underestimated when introducing seed particles before α-pinene photooxidation, in particular

285 under low-NO$_x$ conditions with higher SOA yield. ~~The SOA yield~~Figure 5 presents the growth curves ~~from~~of the generated organic aerosol mass for experiments with seed particles injected after 2 and 4 hours α-pinene photooxidation under high- and low-NO$_x$ conditions, respectively~~, are shown in Figure 5. Here the SOA yield was derived using the same method as that for other experiments (Exp. 1–8 in Table 1), that is, the ratio of ΔM$_0$/ΔHC.~~. The organic aerosol mass was normalized by the reacted α-pinene concentration before adding seed particles. Aerosol particles from the nucleation of gas molecules were not

290 significant in these experiments (less than 50 particles cm^{-3}), and thus the oxidation products were likely present mainly in the gas phase ~~or on the chamber wall~~ prior to adding seed particles.

~~Organic~~The generated organic aerosol mass increased immediately after adding seed particles for all experiments. ~~A slightly~~This can be explained by the reactive uptake of the gas-phase α-pinene oxidation products formed in the early stages onto the acidic and ammonium sulfate seed particles. A higher ~~SOA yield~~increase in organic aerosol mass (up to 6 times)

295 was observed for acidic particles than that for neutral particles in the first 2 hours under both high- and low-NO$_x$ conditions (Figure 5). This suggests that the formation and/or partitioning of organic aerosols, possibly the mixture of early- and later-generation SOA (although their proportions are unknown based on the available data), were enhanced in the presence of

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acidic particles even under low-NO$_x$ conditions, where ~~this~~no discernable acidity effect was ~~not~~ observed previously (as seen in Figure 3b). It is postulated that this effect is apparent here since the acidic particles had not been coated previously with
300   early-generation products of α-pinene photooxidation, which makes the acidic particles accessible to further acid-catalyzed chemistry. Eddingsaas et al. (2012) ~~similarly~~also reported that α-pinene photooxidation products preferentially partition to highly acidic aerosols when introducing seed particles after OH oxidation under ~~both~~ low-NO$_x$ ~~and high NO$_2$~~ conditions. ~~Considering there is no discernable acidity effect observed for the low-NO$_x$ cases previously, it is expected that the actual yield~~ The results in Figure 5 ~~could be even higher. The results of Figure 5~~ also indicate that ~~early~~later products of α-pinene
305   oxidation were more likely to be acid-catalyzed than the early products under low-NO$_x$ ~~condition did not participate in acid catalysis, whereas the later products did.~~conditions. Therefore, acidity ~~effect could~~effects may be different for α-pinene SOA products formed from multiple oxidation steps. ~~Detailed~~A detailed analysis of those products ~~in~~at the molecular level is essential to fully understand ~~the acidity~~this effect.

3.3   Chemical composition of SOA

310   The effect of particle acidity on the chemical composition of α-pinene SOA in high- and low-NO$_x$ experiments is examined from the distribution of organic fragments in the high-resolution organic aerosol mass spectra. The average fractions of organic fragment groups in the organic aerosol mass spectra for particles of different acidity are shown in Figure 6. $C_xH_y^+$ fragments (accounted for 41–44% of total signal) dominated the organic aerosol mass spectra, followed by $C_xH_yO_1^+$ (33–35%) and $C_xH_yO_2^+$ (16–17%) fragments for experiments with varied particle acidity under high-NO$_x$ conditions (Figure
315   6a). In contrast, $C_xH_yO_1^+$ (39–40%) was the most dominant organic fragment, followed by $C_xH_y^+$ (33–36%) and $C_xH_yO_2^+$ (17–19%) fragments under low-NO$_x$ conditions (Figure 6b). An increase in the fractions of oxygenated fragments ($C_xH_yO_1^+$ and $C_xH_yO_2^+$) and a decrease in the fraction of hydrocarbon fragments ($C_xH_y^+$) were observed under low-NO$_x$ conditions compared to those ~~under~~of high-NO$_x$ conditions. Also, lower O/C ratios of α-pinene SOA were observed under high-NO$_x$ conditions (0.~~49~~52–0.~~54~~56, averaged at the irradiation time of 1–6 hours) compared to those under low-NO$_x$ conditions
320   (0.~~60~~61–0.~~62~~64, averaged at the irradiation time of 2–12 hours). This indicates that less oxygenated α-pinene SOA was formed in the presence of high NO$_x$ despite the fact that oxidants (i.e., OH and O$_3$) levels were higher during the high NO$_x$ containing experiments (see Table 1 and Figure 1).

The dependence of chemical composition and oxidation state of α-pinene SOA on NO$_x$ level is most likely associated with the different oxidation products from gas-phase chemistry of RO$_2$. For instance, peroxynitrates and organic nitrates
325   formed from the chemical reaction of RO$_2$ and NO$_x$ are the dominant products under high-NO$_x$ conditions, whereas organic peroxides and acids formed from RO$_2$ with HO$_2$ are dominant under low-NO$_x$ conditions (Xia et al., 2008). ~~SOA formed from photooxidation of isoprene has also been reported to become more oxidized under low-NO$_x$ conditions, which is contrary to those under high-NO$_x$ conditions (Xu et al., 2014).~~ Note that the observed variations in organic fragments in Figure 6 generally represent those over the whole photooxidation period in each experiment, since the individual mass

spectrum of α-pinene SOA did not change significantly with irradiation time, as illustrated by the small standard deviations of individual fragment groups.

With the increase in particle acidity (i.e., NH_4/SO_4 molar ratio from 2.0 to 0.2) under high-NO_x conditions (Figure 6a), the fractions of major fragment ions ($C_xH_y^+$ and $C_xH_yO_1^+$) decreased gradually while $C_xH_yO_2^+$ fractions increased; a slight increase in the O/C ratio from 0.4952 to 0.5456 was also observed. This suggests that more oxygenated SOA was possibly formed in the presence of acidic particles under high-NO_x conditions. A possible interpretation is that particle acidity enhances the formation of more oxygenated SOA in particles such as larger oligomers via acid-catalyzed reactions (Gao et al., 2004), and/or ~~prompts~~promotes the partitioning of those oxidation products into particle-phase (Healy et al., 2008), or particle acidity may also help to hydrolyze unsaturated organic molecules. Conversely, there is no systematic change in the chemical composition of α-pinene SOA with particle acidity under low-NO_x conditions. Therefore, the effect of particle acidity on the chemical composition of α-pinene SOA may be important only under the studied high-NO_x conditions when introducing acidic seed particles before photooxidation, which is consistent with the acidity effect on the yield of α-pinene SOA (Sect. 3.2). It is likely that acidic particles coated rapidly by earlier-generation α-pinene SOA due to the higher SOA yield under low-NO_x conditions, or the reactions of RO_2 with HO_2 and RO_2 were dominated by termination products that were less affected by particle acidity.

3.4 ~~Acid-catalyzed~~Acidity effect on organic nitrate formation ~~of organic nitrates~~

The formation of organic nitrates from α-pinene oxidation has been reported previously in the presence of NO_x (e.g., Atkinson et al., 2000; Albert et al., 2005). Nitrogen (N)-containing organic fragments ($C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$) accounted for less than 10% of total organic signal in our studied conditions. These fragments were most likely contributed by organic nitrates generated from the reactions of early α-pinene oxidation intermediate (RO_2) with NO and NO_2. Organic nitrates likely account for an even higher fraction of the total organic aerosols, since their fragmentation would primarily contribute to inorganic nitrate fragments (NO^+~~/NO_2^+) (Farmer et al., 2010). Organic nitrates yields have been reported to range from~~ and NO_2^+) and other organic groups (Farmer et al., 2010). Assuming an average molecular weight of organic nitrate molecules ranging from 200 to 300 g mol^{-1}, where 62 g mol^{-1} is attributed to the $-ONO_2$ group and the remaining from the organic mass (Boyd et al., 2015), the organic nitrate mass was estimated to be approximately 0.6–1.4 μg m^{-3}. This resulted in a contribution of 17.5–20.5% to total α-pinene SOA and an overall organic nitrate yield of 0.7–1.6% under high-NO_x conditions in this study. Organic nitrates yield has been reported to be in the range of approximately 1% up to more than 20% for α-pinene oxidation (Aschmann et al., 2002; Nozière et al., 1999; Rindelaub et al., ~~2015). The organic nitrates yield in our study was roughly estimated to be in the range of 0.5–1.4%, which was calculated from the ratio of the summed inorganic and organic N-containing fragments ($NO^+ + NO_2^+ + C_xH_yN_p^+ + C_xH_yO_zN_p^+$) mass to ΔHC.~~2015).

Interestingly, both the fractions of $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ fragments increased gradually with the increase in particle acidity under high-NO_x conditions (Figure 6a), which is distinct from those without an apparent change under low-NO_x conditions (Figure 6b). The growth curves of the total N-containing organic fragments (sum of $C_xH_yN_x^+$ and $C_xH_yO_zN_p^+$) for

different acidic particles under high-NO$_x$ conditions are shown in Figure 7a. The absolute mass concentrations of total N-containing organic fragments were also enhanced with particle acidity over the irradiation period. These results indicate that organic nitrates were formed heterogeneously through a mechanism catalyzed by aerosol acidity or that acidic conditions facilitate the partitioning of gas phase nitrates into particle phase under high-NO$_x$ conditions. One possible reaction is the acid-catalyzed formation of sulfated organic nitrates through α-pinene oxidation products such as nitroxyl alcohols and carbonyls reacting with sulfuric acid (Surratt et al., 2008). It has been reported that particle acidity may enhance the partitioning of gaseous organic nitrates into the particle phase due to the Further investigations on the individual particle phase organic nitrate species at a molecular level combined with gas-particle kinetics are required to elucidate the detailed reaction mechanisms. Moreover, it has been demonstrated that acid-catalyzed hydrolysis of particle phaseis an important removal process for organic nitrates, especially under high RH in the particle phase, from which organic nitrates can be converted to alcohols and aqueous conditionsnitric acid (Day et al., 2010; Hu et al., 2011; Liu et al., 2012; Rindelaub et al., 2015). However, the hydrolysis of organic nitrates in the particle phase results in their conversion to alcohols and nitric acid, which This process would lead toalso enhance the partitioning of gaseous organic nitrates into the particle phase due to the perturbation in gas/particle partitioning, and therefore decrease in the organic nitrate yields both theirin the gas and particle phase amountsphases (Rindelaub et al., 2015). This is inconsistent with theThe observed increase in organic nitrate fragments with increasing acidity. Therefore, acid-catalyzed formation of organic nitrates also very likely contributed to the observed enhancement of N-containing organic fragments with particle acidity under high-NO$_x$ conditions suggests that the production of organic nitrates generally exceeded their removal rates in this reaction system.

The time-dependent mass concentrations of NO$^+$ and NO$_2^+$ fragments for variedvarious acidic particles under high-NO conditions are also shown in Figure 7b. The mass concentrations of the NO$^+$ fragment for acidic particles were higher than those of neutral particles, whereas no apparentobvious difference in the NO$_2^+$ fragment was observed for particles with varied acidity. Therefore, the enhanced organic nitrates by particle acidity might contribute mainly to the increase in the NO$^+$ fragment. Large relative contribution of organic nitrates to the nominal inorganic nitrate fragments is demonstrated by a higher NO$^+$/NO$_2^+$ ratio than those of pure ammonium nitrate (Bae et al., 2007; Boyd et al., 2015; Farmer et al., 2010; Fry et al., 2009).; Xu et al., 2015b). The average NO$^+$/NO$_2^+$ ratio was 9.13 $\pm$ 4.24, 9.28 $\pm$ 5.19, 9.31 $\pm$ 4.27, and 10.44 $\pm$ 5.48 for particles with initial NH$_4$/SO$_4$ molar ratio of 2.0, 1.0, 0.5, and 0.2, respectively. These values are significantly higher than 2.6 $\pm$ 0.2 from the current AMS measurement of pure ammonium nitrate, but very similarclose to that of 11 $\pm$ 8 reported for NO$_3$ oxidation of α-pinene, from which organic nitrates were likely the dominant aerosol component (Bruns et al., 2010). An increasing The increase in NO$^+$/NO$_2^+$ ratio again suggests that organic nitrates were enhanced with the increase in particle acidity suggests that the composition of organic nitrate species might be different under high NO$_x$various acidic conditions, which is possibly due to the varied effect of particle acidity on the formation and/or partitioning of different organic nitrate species.

Noted that a small amount of C$_x$H$_y$N$_p^+$ and C$_x$H$_y$O$_z$N$_p^+$ 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.

4 Implications

This study investigated the effect of particle acidity on the yield and chemical composition of α-pinene SOA from ~~OH-initiated~~ photooxidation in a photochemical reaction chamber. A nearly linear increase of α-pinene SOA yield with the increase in particle acidity was observed under high-NO_x conditions, which is contrary to the insignificant acidity effect under low-NO_x conditions. The potential mechanisms leading to the different acidity effects between high- and low-NO_x conditions warrant further investigation. The acidity effect was relatively strong in the early photooxidation stages under high-NO_x conditions, and this effect decreased gradually with the growth of SOA mass. This may be explained by a reduced accessibility of the SOA partitioning species to the acidic particles for acid-catalyzed chemistry, possibly as a result of the SOA coating. Given that the α-pinene loading used in this study was low~~, similar phenomenon~~ and the generated organic aerosol mass was relevant to ambient levels (e.g., the final ratio of organic/sulfate was 0.6–0.8 and 1.7–2.8 under high- and low-NO_x conditions, respectively), similar process may also occur in the atmosphere. Consequently, an ambient acidity effect is likely stronger for newly formed particles and/or freshly formed sulfate coating. Therefore, the time scale of SOA formation with respect to acidity effects is expected to be an important factor for field studies measuring acidity effect in the atmosphere.

More oxygenated SOA was formed with the increase of particle acidity under high-NO_x conditions. Since aerosol acidity could affect the oxidation state of aerosol particles and alter their chemical composition and other properties as demonstrated here, this may be an important process in the atmosphere and deserve further investigation. The formation of SOA from later-generation gas phase products was enhanced by particle acidity even under low-NO_x conditions when introducing acidic seed particles after α-pinene photooxidation. This suggests that the overall acidity effect on the formation of SOA could be underestimated, and that more systematic studies are necessary to evaluate the acidity effect on SOA generated from multiple oxidation steps. Organic nitrates in these experiments may be formed heterogeneously through a mechanism catalyzed by particle acidity and/or the acidic conditions facilitate the partitioning of gas phase nitrates into the particle phase under high-NO_x conditions. This implies that aerosol acidity could also be of importance in the atmosphere by altering the deposition patterns~~/~~ and rates of gas phase NO_x via its conversion to particle nitrates with differing atmospheric lifetimes.

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

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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. Moreover, we have studied the acidity effect under more realistic RH conditions. While RH is an important factor affecting the concentrations of [H$^+$], the kinetics of hydrolysis reactions, and the physical properties of SOA such as viscosity, more investigation over a broader RH range are essential to understand the acidity effect in the real atmosphere. Finally, further studies on SOA formation from various other hydrocarbons under conditions near ambient atmospheric levels will be valuable in understanding the complex physical and chemical interactions facilitated by aerosol acidity and evaluating the acidity effect more accurately, and to ultimately incorporate such effects into regional air quality model for improved SOA prediction.

Acknowledgments

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Tables

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[a,b] molality (mole kg^{-1}) (NH$_4$/SO$_4$)	~~Molar ratio[b]~~ Aerosol pH[c]	Temp.[d] (°C)	RH[e] (%)	Seed ~~conc.~~ (µg m^{-3})	NO (~~ppbv~~ppb)	α-pinene (~~ppbv~~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)	~~2~~	~~24–31e~~31	~~47–29e~~29	4.4	66	15.9	84.2	3.~~4~~5	4.~~0~~2±0.1
2 / 1	H$^+$=~~5.~~3.2, NH$_4^+$=~~27.8~~15.3, HSO$_4^-$=~~22.7~~11.2, SO$_4^{2-}$=~~5.2~~3.7	~~−1.~~31	23–30	58–34	8.4	69	17.6	93.4	5.~~0~~2	5.~~4~~6±0.1
3 / 0.5	H$^+$=~~9.1~~5.0, NH$_4^+$=~~6.9~~7.0, HSO$_4^-$=~~11.8~~7.5, SO$_4^{2-}$=2.~~1~~3	~~0.5~~−1.50	24–30	61–38	6.3	68	13.6	71.8	4.~~6~~7	6.~~3~~6±0.~~2~~1
4 / 0.2	H$^+$=~~10.6~~7.2, NH$_4^+$=~~1.8~~2.7, HSO$_4^-$=~~8.7~~6.2, SO$_4^{2-}$=1.9	~~0.2~~−1.66	26–34	58–33	7.9	72	17.0	89.9	6.~~6~~8	7.~~3~~6±0.2
Low-NO$_x$ conditions										
5 / 2	(NH$_4$)$_2$SO$_4$ (no liquid phase)	~~2~~	25–32	67–43	12.6	<0.3	19.6	96.7	~~33.5~~34.1	~~34.6~~35.2±1.1
6 / 1	H$^+$=~~5.2~~1.9, NH$_4^+$=~~28.6~~14.8, HSO$_4^-$=~~23.1~~8.5, SO$_4^{2-}$=~~5.4~~1	~~1~~−0.93	25–32	64–37	12.6	<0.3	17.4	79.1	22.~~1~~6	~~27.9~~28.6±1.~~2~~5
7 / 0.5	H$^+$=~~9.1~~3.2, NH$_4^+$=~~7.0~~10.6, HSO$_4^-$=~~11.~~8.0, SO$_4^{2-}$=2.~~1~~9	~~0.5~~−1.22	26–33	64–38	11.9	<0.3	19.3	92.6	33.~~0~~7	~~35.6~~36.3±1.~~2~~5
8 / 0.2	H$^+$=~~10.5~~.3, NH$_4^+$=~~2~~4.1, HSO$_4^-$=~~8.9~~5.6, SO$_4^{2-}$=1.9	~~0.2~~−1.35	24–33	66–36	11.4	<0.3	19.5	88.6	~~27.6~~28.4	~~31.2~~32.0±1.9
Adding seeds after photooxidation										
9 / 2	(NH$_4$)$_2$SO$_4$ (no liquid phase)	~~2~~	23–31	57–34	9.7	82	20.4	~~109.3~~	~~1.4~~	~~1.5±0.1~~
10 / 0.5	H$^+$=~~5.9~~.1, NH$_4^+$=~~6.9~~7.0, HSO$_4^-$=~~11.~~8.4, SO$_4^{2-}$=2.~~1~~3	~~0.5~~−1.72	24–31	56–33	12.2	72	18.5	~~98.9~~	~~1.1~~	~~1.3±0.1~~
11 / 2	(NH$_4$)$_2$SO$_4$ (no liquid phase)	~~2~~	25–33	68–42	7.4	<0.3	16.1	~~34.9~~	~~3.4~~	~~10.8±0.5~~
12 / 0.5	H$^+$=~~4.9~~.2, NH$_4^+$=~~9.6~~.7, HSO$_4^-$=~~11.7~~9.3, SO$_4^{2-}$=2.~~1~~6	~~0.5~~−1.64	25–33	57–33	11.4	<0.3	17.3	~~40.4~~	~~3.6~~	~~10.0±0.3~~

[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 ~~extended inorganic aerosol thermodynamics model II (the~~ E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php). ~~[b] Ratios for ammonium sulfate/sulfuric acid aqueous solution.~~ [e] II. [c] Aerosol pH was calculated with the E-AIM output. [d] Initial and final temperature inside the chamber. [e] Initial and final RH ~~are reported~~inside the chamber.

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Table 2. Comparison of experimental parameters and SOA yields reported in literature for the photooxidation of α-pinene.

Reference	Temp. (°C)	RH (%)	Oxidant	Seed	NO_x (ppb)	α-pinene (ppb)	ΔHC (µg m^{-3})	ΔM_0 (µg m^{-3})	SOA Yield (%)
Chu et al. (2014)	28	12, 50	HONO	AS	n.a.	8.1, 11.7	n.a.	5.9, 9.3	15.1, 23.4
	28	12,50	HONO	$FeSO_4$	n.a.	9.7, 10.0	n.a.	5.0, 2.9	10.9, 5.7
Kim and Paulson (2013)	33–42 [a]	15–25 [a]	propene	no seed	47–230	143–153	n.a.	9–118	5.9–17
Eddingsaas et al. (2012)	20–25	<10	H_2O_2	AS	n.a.	45.0–48.5	247–265	63.5–76.6	25.7–28.9
	20–23	<10	HONO, CH_3ONO	AS	~800	44.9–52.4	249–258	37.2–60.3	14.4–24.2
Ng et al. (2007a)	23–25	5.3–6.4	H_2O_2	AS	0,1	n.a.	76.7, 264.1	29.3, 121.3	37.9–45.8
	25–26	3.3–3.7	H_2O_2+NO, HONO	AS	198–968	n.a.	69.8–259.1	4.5–40.8	6.6–21.2
Kleindienst et al. (2006)	26.3	29	NO_x	no seed	242, 543	2550	1190, 815	130, 67.3 [b]	10.9, 8.3 [c]
	26.3	29	NO_x	sulfate	242, 543	2550	1190, 815	87–172 [b]	10.7–14.5 [c]
Takekawa et al. (2003)	10	~60	propene	Na_2SO_4	30–53	55–100	260–540	36–89	20–23
	30	~60	propene	Na_2SO_4	54–102	93–196	500–1000	20–95	5.2–10
Odum et al. (1996)	35–40	~10	propene	AS	300	~19–143	104–769	1.3–96.0	1.25–12.5

[a] Final temperature and RH were presented. [b] OC mass was reported. [c] SOC yield was reported.
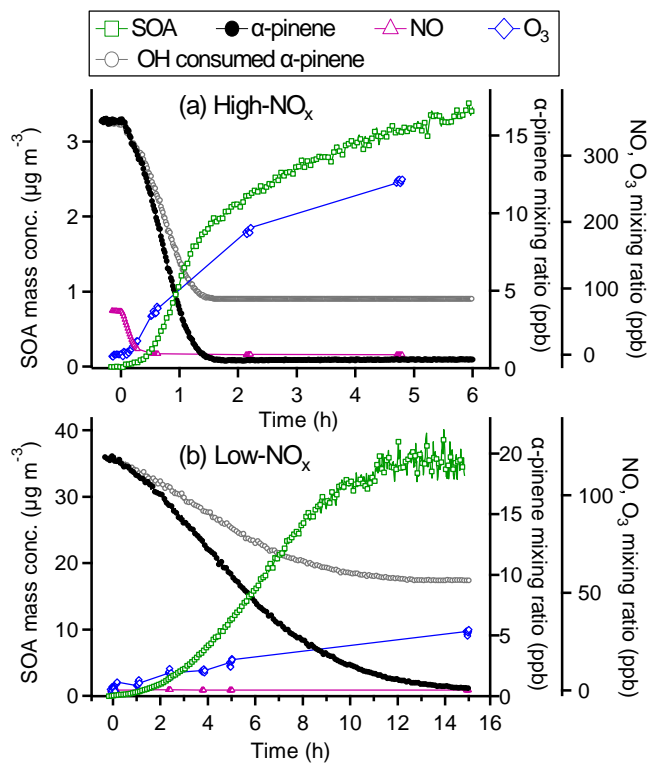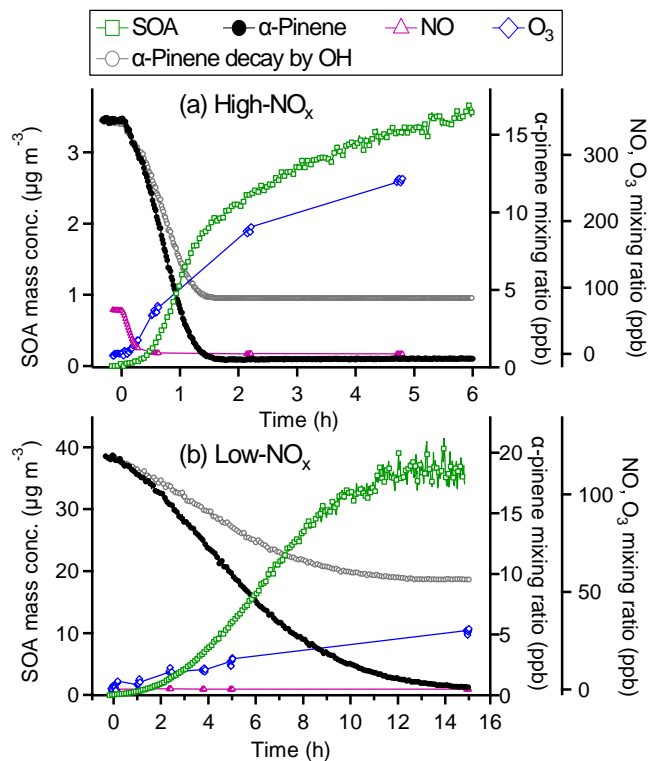
Figures

(a) High-NO$_x$

(b) Low-NO$_x$

Legend: SOA, α-pinene, NO, O$_3$, OH consumed α-pinene

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Figure 1. Time series of the mass concentrations of generated SOA and the mixing ratios of NO, O$_3$, total α-pinene decay, and OH consumed α-pinene in (a) high- and (b) low-NO$_x$ experiments using ammonium sulfate as seed particles. Time = 0 hour is defined as α-pinene photooxidation initiated when ~~the~~ lamps were turned on.
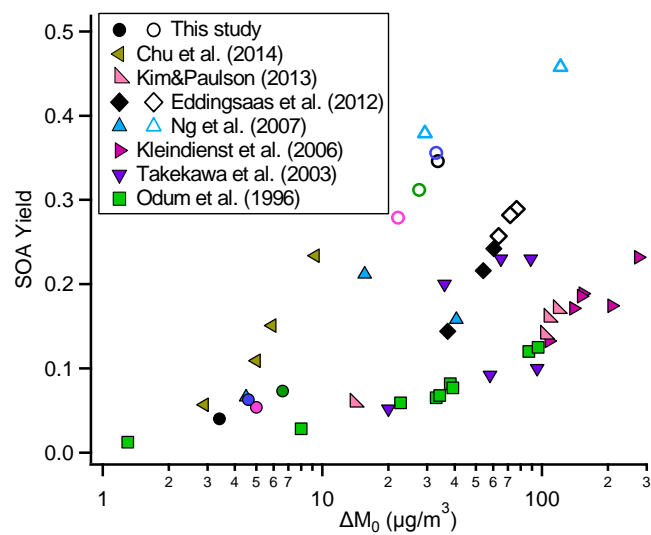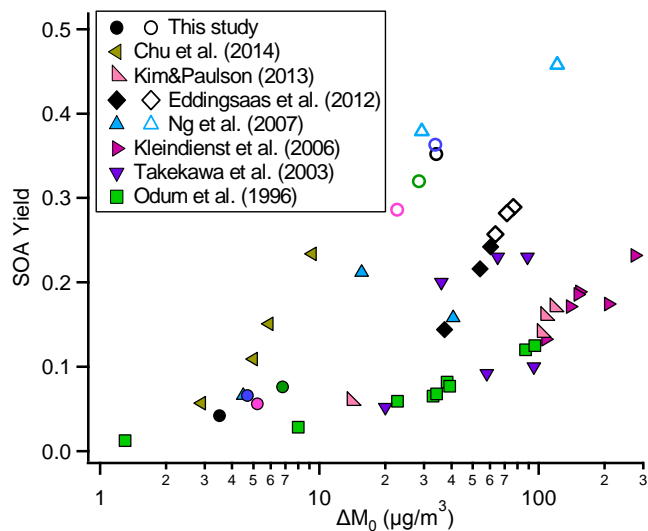
Figure 2. Comparison of final α-pinene SOA yields as a function of organic mass concentration (ΔM_0) under high- and low-NO$_x$ conditions in this study with those reported previously. The solid and open symbols represent the SOA yields under high- and low-NO$_x$ conditions, respectively. The black, pink, blue, and green cycles represent the SOA yield for experiments in this study with NH$_4$/SO$_4$ molar ratios of 2.0, 1.0, 0.5, and 0.2, respectively. A factor of 1.6 was used to convert SOC yield and OC mass concentration to SOA yield and OA mass concentration in Kleindienst et al. (2006).

(a) High-NO$_x$
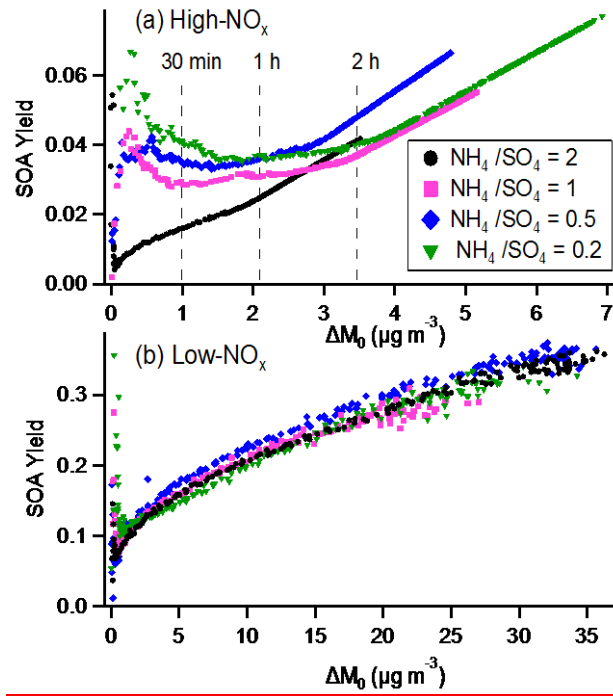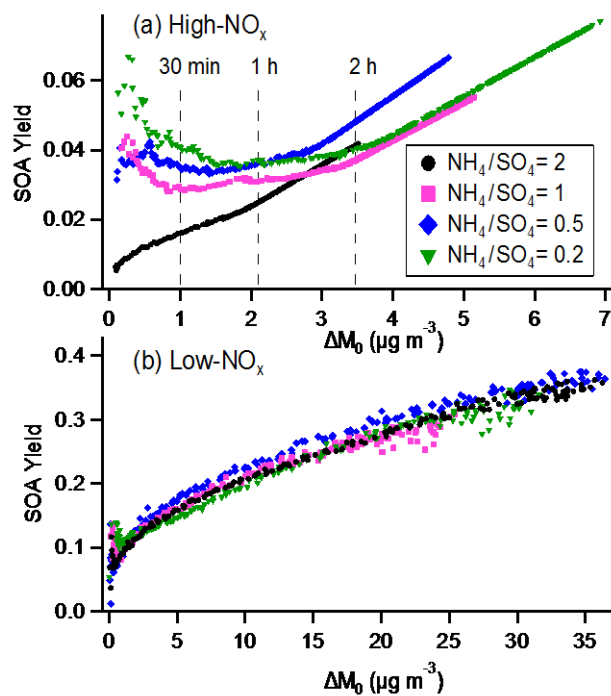
(b) Low-NO$_x$

Figure 3. SOA yields as a function of organic mass concentrations for experiments using seed particles with varied acidity levels under (a) high- and (b) low-NO$_x$ conditions. The dashed lines in (a) represent the irradiation time at approximately 30 min, 1 hour, and 2 hours, respectively.

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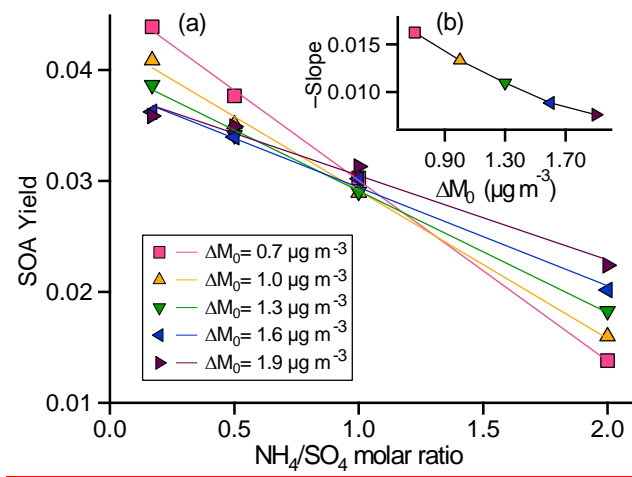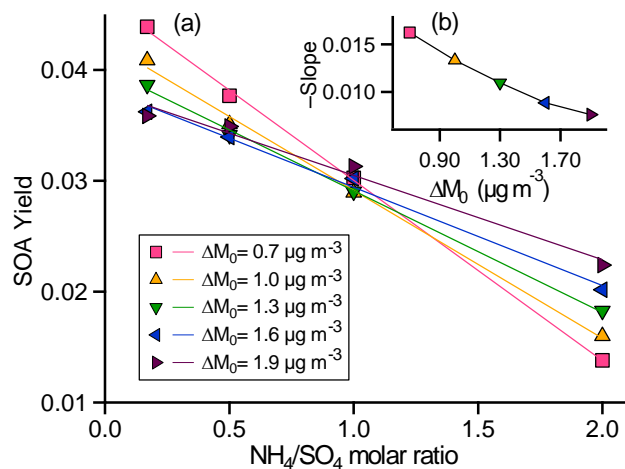
715   **Figure 4. (a) SOA yield versus NH_4/SO_4 molar ratio in the initial period of photooxidation (approximately 0–1 hours) under high-NO_x conditions. The colored lines represent the linear fitting of the markers. The SOA yields at specific ΔM_0 values were retrieved from the plotting of SOA yields versus ΔM_0 in Figure 3a. (b) The ~~negative~~ slope derived from the fitting of SOA yields with NH_4/SO_4 molar ratios in (a) ~~increased~~decreased with ΔM_0.**
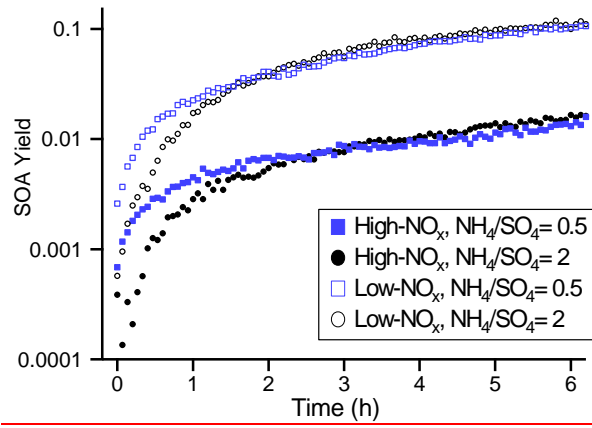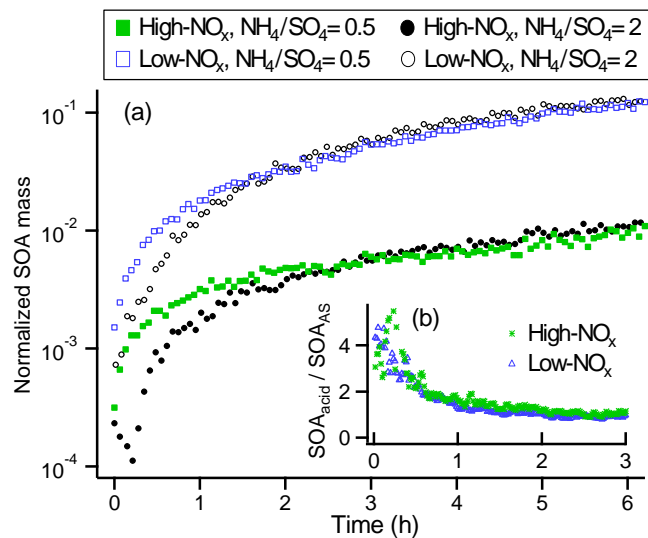
720

Figure 5. **(a)** The increase of SOA ~~yields~~mass with time for experiments ~~with~~ injecting ~~neutral~~ammonium sulfate and acidic seed particles after α-pinene photooxidation for 2 and 4 hours under high- and low-NO$_x$ conditions, respectively (Exp. 9–12 in Table 1). Time ~~—~~ = 0 hour represents the beginning of reactive uptake of oxidation products after seed particles ~~added.~~

were added. The SOA mass was normalized by the reacted α-pinene concentration before adding seed particles. (b) The ratio of SOA mass for acidic particles to that of ammonium sulfate particles.
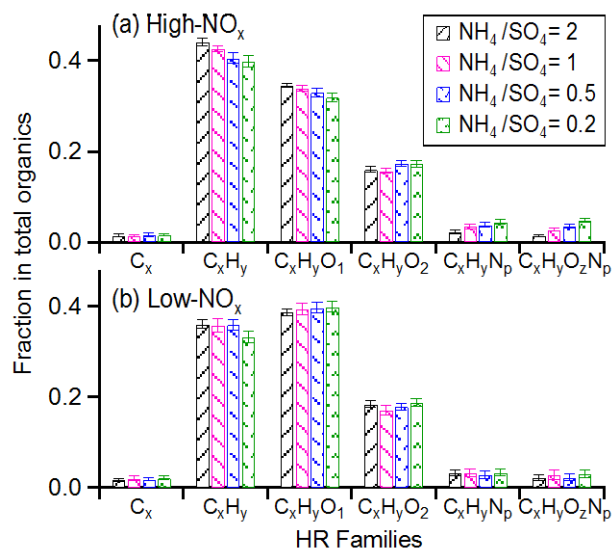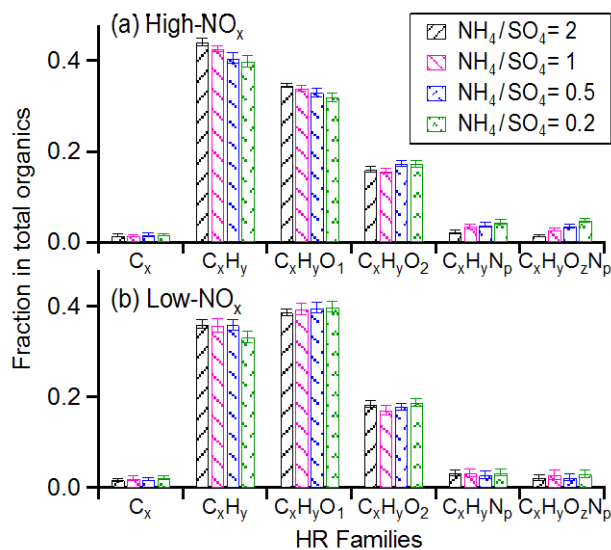
Figure 6. The mass fractions of organic fragment groups in total organic aerosols under (a) high- and (b) low-NO_x conditions. The organic mass spectra were averaged for the irradiation times of 1–6 and 2–12 hours under high- and low-NO_x conditions, respectively. The bars represent the standard deviations ($\pm 1\sigma$) of the mean values for individual fragment groups.
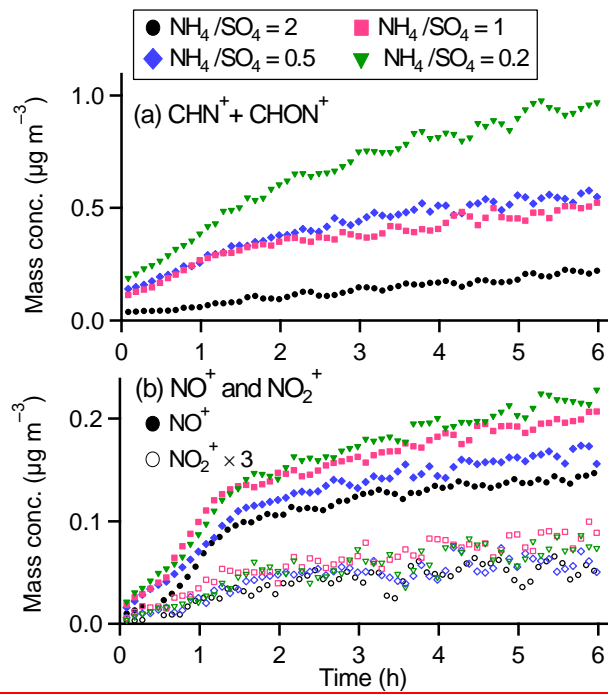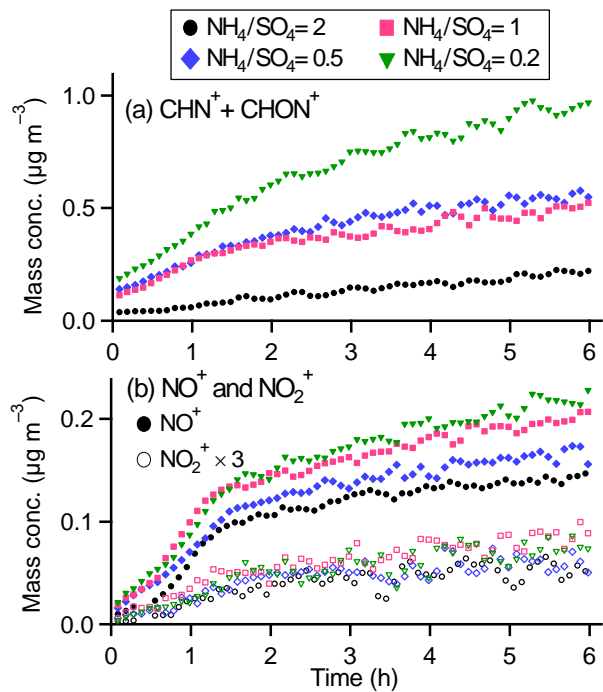
Figure 7. The temporal variations of (a) total N-containing organic fragments (the sum of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$) and (b) NO^+ and NO_2^+ fragments for experiments using ~~neutral~~**ammonium sulfate** and acidic particles under high-NO_x conditions.

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