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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 particle acidity levels. 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%–7.3%) increased nearly linearly with the increase in particle acidity under high-NO_x conditions. In contrast, the SOA yield (27.9%–35.6%) 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 under high-NO_x conditions, which is likely due to the inaccessibility of the acidity over time with the coating of α-pinene SOA. 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. 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. 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. The results of this study suggest that inorganic acidity have a significant role to play in determining various organic aerosol chemical properties such as oxidation state, mass yields, and organic nitrate content. It 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

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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 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). 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 has not been considered in most atmospheric chemistry models thus far due to the large uncertainties associated with its quantification.

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, epoxides, alcohols, and organic nitrates (Yasmeen et al., 2012). 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. 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 SOA mass from photooxidation of α-pinene under high-NO_x conditions (Surratt et al., 2007a, 2008). A linear increase of 0.04% 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. 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.

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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). Most previous studies were conducted with different acidity levels, and therefore a quantitative comparison of the acidity effect among various studies is problematic. Laboratory studies were usually performed with relatively high loading 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 oxidation products by introducing relatively volatile nitrogen-containing organic species, 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, many previous studies have been performed at very low RH (e.g., less than 10%) or even dry 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 under conditions of relatively low α-pinene loadings and moderate RH, which are more representative of the ambient atmosphere. The dependence of α-pinene SOA yield on particle acidity is characterized under high- and low-NO_x conditions. The changes in the chemical composition of α-pinene SOA with particle acidity and NO_x level are also examined. Finally, the potential significance of aerosol acidity in the formation of organic nitrates under high-NO_x conditions is discussed.

2 Experimental methods

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_2O_2) vapor was introduced into the chamber to produce OH radicals during the first 6 hours of flushing. 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_2O_2 vapor, NO, seed particles, and α-pinene) were conducted after the RH reached approximately

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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_2O_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_2O_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. 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 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 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 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 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 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.

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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 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 contributed by self-nucleation was estimated to be less than 0.1 μg cm^{-3} in the studied system. 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. OH concentration in each experiment was estimated from a linear fitting of the first order decay of gaseous α-pinene by OH radicals, i.e., the difference between the total α-pinene decay and the α-pinene consumed by O_3, as described by Liu et al. (2015). The OH concentrations were calculated to be approximately 4.3–5.9 × 10^6 and 0.8–1.1 × 10^6 molecules cm^{-3} for experiments under high- and low-NO_x conditions, respectively.

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, 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-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 production of OH radicals from H_2O_2 photolysis under 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 deposited on the chamber wall. Approximately less than 47% of α-pinene was consumed by ozonolysis.

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The α-pinene SOA yield was 4.0% when using $(NH_4)_2SO_4$ seed particles under high-NO_x condition, which is a factor of 8.7 lower than that under low-NO_x condition (34.6%) (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., 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-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 relatively volatile species such as organic nitrates and reduce 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 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 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 among these studies most likely depend on different experimental conditions, suggesting that laboratory studies performed under conditions near atmosphere are important for an intercomparison among studies and 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

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%, and 7.3% 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, 1.6, and 1.8 times the SOA yield for neutral particles (i.e., 4.0%). Conversely, the final SOA yields for acidic particles varied from 27.9% to 35.6% under low-NO_x conditions, from which a systematic increase in SOA yield with particle acidity was not observed. 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

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facilitated by particle acidity (as discussed in Sect. 3.4). The dependence of α-pinene SOA yield on particle acidity under only high-NO_x 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 40–80% 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).

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 and neutral particles under high- and low-NO_x conditions is shown in Figure 3. Under high-NO_x conditions, the increase of SOA yield with particle acidity (black through green points) 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 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 were less accessible gradually with increased organic coating of acidic particles. This indicates that the acidity effect is important in particular in the initial stage 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 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 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 μg m^{-3} at the irradiation time of approximately 20 min compared to those for neutral particles (NH_4/SO_4 molar ratio = 2) (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. 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 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).

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However, we cannot identify organic sulfates clearly based upon the AMS measurement, since their fragmentation results mainly in inorganic sulfate fragments (Farmer et al., 2010).

3.2.3 Acidity effect on later-generation SOA

Due to organics coating on acidic particles, the effect of particle acidity on SOA formation in the later experimental stage may be underestimated when introducing seed particles before α-pinene photooxidation, in particular under low-NO_x conditions with higher SOA yield. The SOA yield growth curves from 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 $\Delta M_0/\Delta HC$. Aerosol particles from the nucleation of gas molecules were not 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 aerosol mass increased immediately after adding seed particles for all experiments. A slightly higher SOA yield 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 acidic particles even under low-NO_x conditions, where this 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 early-generation products of α-pinene photooxidation, which makes the acidic particles accessible to further acid-catalyzed chemistry. 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. Considering there is no discernable acidity effect observed for the low-NO_x cases previously, it is expected that the actual yield in Figure 5 could be even higher. 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. Therefore, acidity effect could be different for α-pinene SOA products from multiple oxidation steps. Detailed analysis of those products in molecular level is essential to fully understand the acidity effect.

3.3 Chemical composition of SOA

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 6a). In contrast, $C_xH_yO_1^+$ (39–40%) was the most dominant organic fragment, followed by $C_xH_y^+$ (33–36%) and $C_xH_yO_2^+$

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(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 high-NO_x conditions. Also, lower O/C ratios of α-pinene SOA were observed under high-NO_x conditions (0.49–0.54, averaged at the irradiation time of 1–6 hours) compared to those under low-NO_x conditions (0.60–0.62, 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 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). 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 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 0.49 to 0.54 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 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 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

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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 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.

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. It has been reported that particle acidity may enhance the partitioning of gaseous organic nitrates into the particle phase due to the acid-catalyzed hydrolysis of particle-phase organic nitrates, especially under high RH and aqueous conditions (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 would lead to decrease in both their gas and particle phase amounts (Rindelaub et al., 2015). 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.

The time-dependent mass concentrations of NO^+ and NO_2^+ fragments for varied 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 apparent 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 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; Farmer et al., 2010; Fry et al., 2009). The average NO^+/NO_2^+ ratio was 9.13, 9.28, 9.31, and 10.44 for particles with initial NH_4/SO_4 molar ratio of 2, 1, 0.5, and 0.2, respectively. These values are significantly higher than 2.6 ± 0.2 from the current AMS measurement of pure ammonium nitrate, but very similar to that of 11 ± 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 NO^+/NO_2^+ ratio again suggests that organic nitrates were enhanced with the increase in particle acidity under high-NO_x conditions.

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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 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 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/rates of gas phase NO_x via its conversion to particle nitrates with differing atmospheric lifetimes.

Finally, further studies on SOA formation from various other hydrocarbons under conditions near ambient atmospheric levels will be valuable in evaluating the acidity effect more accurately, and to ultimately incorporate such effects into regional air quality model for improved SOA prediction.

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Tables

Table 1. Experimental conditions and SOA yields from OH-initiated photooxidation of α-pinene under high- and low-NOx conditions.

Exp.	Initial seed composition [a] mole kg^{-1}	Molar ratio [b] (NH_4/SO_4)	Temp. (°C)	RH (%)	Seed conc. (μg cm^{-3})	NO (ppbv)	α-pinene (ppbv)	ΔHC (μg m^{-3})	ΔM_0 (μg m^{-3})	Yield (%)
	High-NO_x									
1	$(NH_4)_2SO_4$ (no liquid phase)	2	24–31[c]	47–29[c]	4.4	66	15.9	84.2	3.4	4.0±0.1
2	H^+=5.3, NH_4^+=27.8, HSO_4^-=22.7, SO_4^{2-}=5.2	1	23–30	58–34	8.4	69	17.6	93.4	5.0	5.4±0.1
3	H^+=9.1, NH_4^+=6.9, HSO_4^-=11.8, SO_4^{2-}=2.1	0.5	24–30	61–38	6.3	68	13.6	71.8	4.6	6.3±0.2
4	H^+=10.6, NH_4^+=1.8, HSO_4^-=8.7, SO_4^{2-}=1.9	0.2	26–34	58–33	7.9	72	17.0	89.9	6.6	7.3±0.2
	Low-NO_x									
5	$(NH_4)_2SO_4$ (no liquid phase)	2	25–32	67–43	12.6	<0.3	19.6	96.7	33.5	34.6±1.1
6	H^+=5.2, NH_4^+=28.6, HSO_4^-=23.1, SO_4^{2-}=5.4	1	25–32	64–37	12.6	<0.3	17.4	79.1	22.1	27.9±1.2
7	H^+=9.1, NH_4^+=7.0, HSO_4^-=11.8, SO_4^{2-}=2.1	0.5	26–33	64–38	11.9	<0.3	19.3	92.6	33.0	35.6±1.2
8	H^+=10.5, NH_4^+=2.1, HSO_4^-=8.9, SO_4^{2-}=1.9	0.2	24–33	66–36	11.4	<0.3	19.5	88.6	27.6	31.2±1.9
	Adding seeds after photooxidation									
9	$(NH_4)_2SO_4$ (no liquid phase)	2	23–31	57–34	9.7	82	20.4	109.3	1.4	1.5±0.1
10	H^+=9.1, NH_4^+=6.9, HSO_4^-=11.8, SO_4^{2-}=2.1	0.5	24–31	56–33	12.2	72	18.5	98.9	1.1	1.3±0.1
11	$(NH_4)_2SO_4$ (no liquid phase)	2	25–33	68–42	7.4	<0.3	16.1	34.9	3.4	10.8±0.5
12	H^+=9.2, NH_4^+=6.7, HSO_4^-=11.7, SO_4^{2-}=2.1	0.5	25–33	57–33	11.4	<0.3	17.3	40.4	3.6	10.0±0.3

[a] Initial seed composition was estimated using extended inorganic aerosol thermodynamics model II (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php). [b] Ratios for ammonium sulfate/sulfuric acid aqueous solution. [c] Initial and final temperature and RH are reported.

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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.

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Figures

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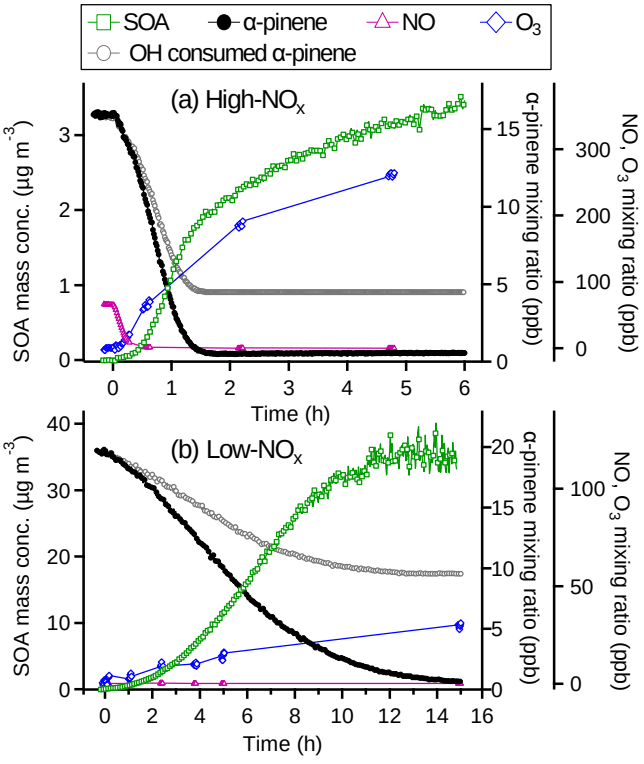

Figure 1. Time series of the mass concentrations of generated SOA and the mixing ratios of NO, O_3, total α-pinene decay, and OH consumed α-pinene in (a) high- and (b) low-NO_x experiments using ammonium sulfate as seed particles. Time = 0 hour is defined as α-pinene photooxidation initiated when the lamps were turned on.

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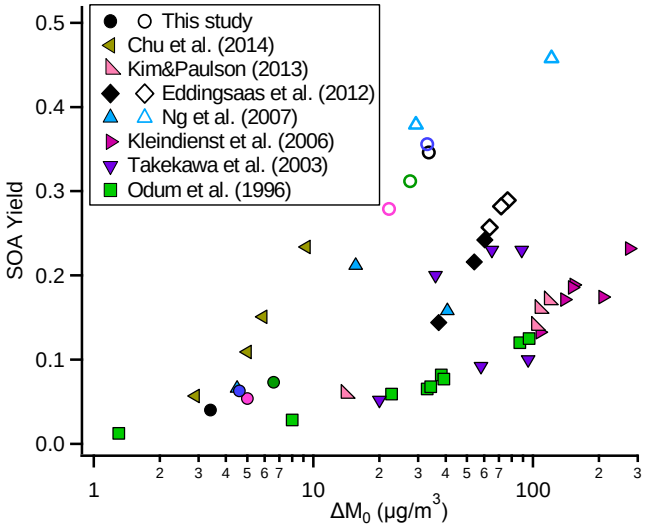

Figure 2. Comparison of final α-pinene SOA yields as a function of organic mass concentration (ΔM_0) under high- and low-NO_x conditions in this study with those reported previously. The solid and open symbols represent the SOA yields under high- and low-NO_x conditions, respectively. The black, pink, blue, and green cycles represent the SOA yield for experiments in this study with NH_4/SO_4 molar ratios of 2, 1, 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).

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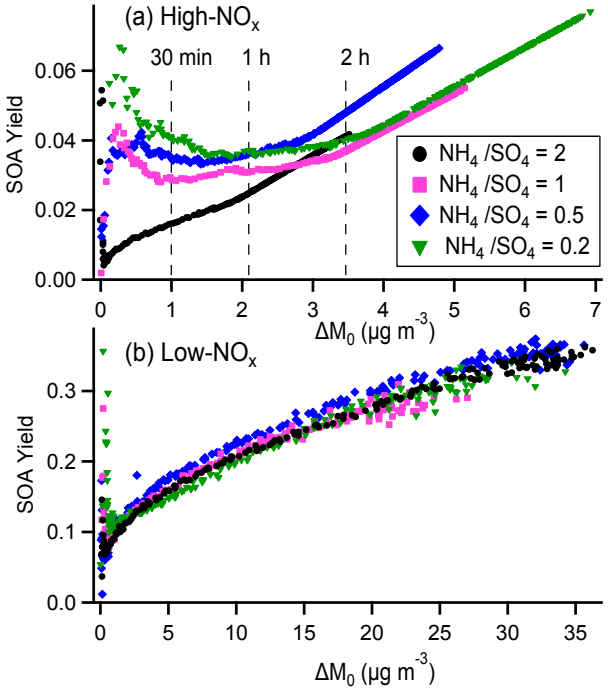

Figure 3. SOA yields as a function of organic mass concentrations for experiments using seed particles with varied acidity levels under (a) high- and (b) low-NO_x conditions. The dashed lines in (a) represent the irradiation time at approximately 30 min, 1 hour, and 2 hours, respectively.

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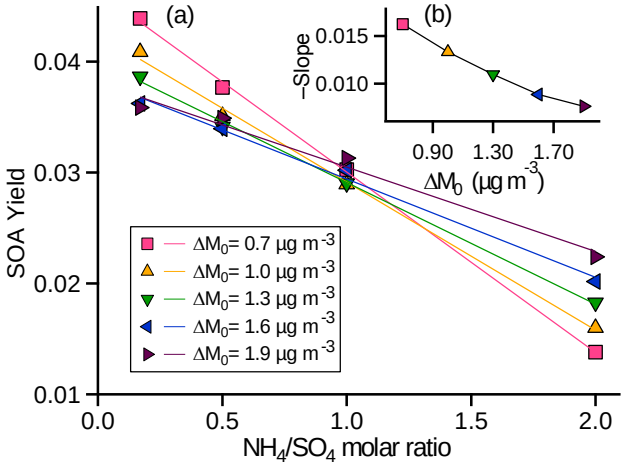

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Figure 4. (a) SOA yield versus NH_4/SO_4 molar ratio in the initial period of photooxidation (approximately 0–1 hours) under high-NO_x conditions. The colored lines represent the linear fitting of the markers. The SOA yields at specific ΔM_0 values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

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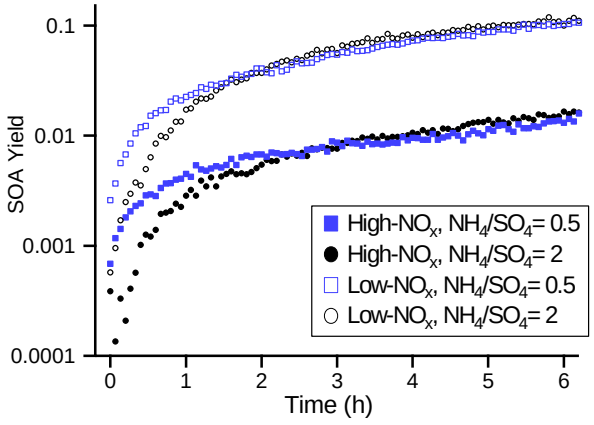

Figure 5. The increase of SOA yields with time for experiments with injecting neutral and acidic seed particles after α-pinene photooxidation for 2 and 4 hours under high- and low-NO_x conditions, respectively (Exp. 9–12 in Table 1). Time = 0 hour represents the beginning of reactive uptake of oxidation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

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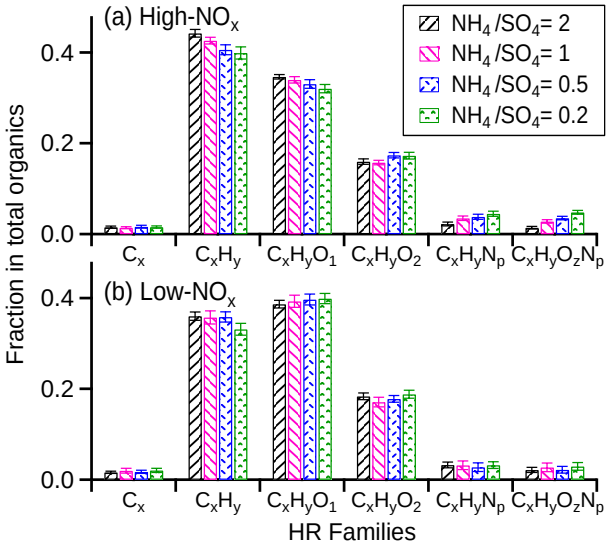

580 **Figure 6. The mass fractions of organic fragment groups in total organic aerosols under (a) high- and (b) low-NO_x conditions. The organic mass spectra were averaged for the irradiation times of 1–6 and 2–12 hours under high- and low-NO_x conditions, respectively. The bars represent the standard deviations (± 1σ) of the mean values for individual fragment groups.**

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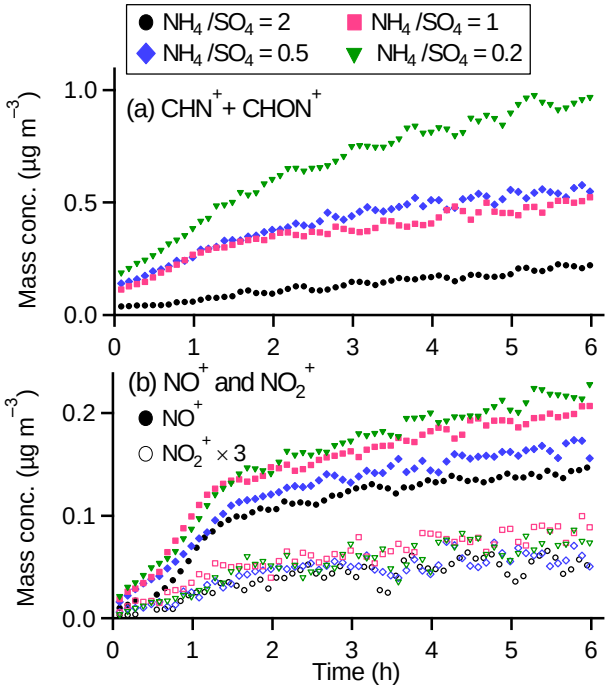

585 **Figure 7. The temporal variations of (a) total N-containing organic fragments (the sum of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$) and (b) NO^+ and NO_2^+ fragments for experiments using neutral and acidic particles under high-NO_x conditions.**