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Secondary organic aerosol formation from toluene photooxidation under various NO_x conditions and particle acidity

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Abstract

Secondary organic aerosol (SOA) formation from photooxidation of toluene is studied using a 2 m³ indoor Teflon film chamber under three different NO_x conditions: low (≤ 3 ppb), intermediate (90–105 ppb) and high (280–315 ppb). SOA experiments are conducted in the presence of either neutral or acidic sulfate seed aerosols under two different humidity levels (%RH 15–22 or 38–49). NO_x concentrations in the chamber air affect not only SOA yields but also SOA growth described by the organic mass (OM) produced as a function of the toluene concentration consumed over the course of a single SOA experiment. The particle acidity effect on toluene SOA formation varies with NO_x concentrations. For the low and the intermediate NO_x experiments, SOA yields with acidic sulfate seed considerably increase by: 36%–115% at low %RH and 25–44% at high %RH compared to those with neutral seed. No significant particle acidity effect is observed for the high NO_x experiments. The humidity effect on SOA formation is also different at the three NO_x levels. For the low NO_x experiments, SOA yields are 29%–34% lower at high %RH than those at low %RH in the presence of either neutral or acidic sulfate seed. For the intermediate NO_x experiments, SOA yields at high %RH increase by 39% in the presence of neutral seed but slightly decrease by 7% in the presence of acidic sulfate seed compared to those at low %RH. For the high NO_x experiments with a high NO fraction, no significant humidity effect on SOA yields is found with both neutral and acidic sulfate seeds.

1 Introduction

As an important class of atmospheric particulate matter, secondary organic aerosol (SOA) refers to the aerosols formed by various atmospheric oxidation reactions of volatile organic compounds (VOCs) with atmospheric oxidants (e.g. ozone, hydroxyl radical, and nitrate radical). The last three decades of studies through a large number of chamber experiments suggest that the possible SOA formation pathways include

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self-nucleation, gas-particle partitioning and heterogeneous reactions.

In recent years, studies on contribution of heterogeneous reactions to SOA formation have drawn increasing attention.

It is believed that particle phase heterogeneous reactions of atmospheric organics such as carbonyls are important mechanisms for SOA formation (Jang et al., 2002, 2006; Johnson et al., 2004). The products of heterogeneous reactions-oligomeric species have been observed on diverse SOA generated from either biogenic or aromatic precursors (Gao et al., 2004a; Hamilton et al., 2008; Heaton et al., 2007; Iinuma et al., 2004, 2007; Kalberer et al., 2004; Tolocka et al., 2004). The contribution of heterogeneous reactions to SOA formation is influenced by reactivity of gas phase products from oxidation of organics. Jang et al. (2006) lumped major gas phase products of α -pinene ozonolysis into three groups of reactivity (slow, medium and fast) for the estimation of heterogeneous SOA formation. For example, heterogeneous reactions of compounds with fast reactivity, such as oxoaldehydes – the aldehydes that contain at least two C=O groups, can occur without the need of an acidic catalyst but can be accelerated by an acidic catalyst. Heterogeneous reactions of compounds with slow and medium reactivity such as oxo-carboxylic acids will be significant only when an acidic catalyst is present in the particle phase. Therefore, heterogeneous reactions of different types of gas phase oxygenated products will respond differently to particle acidity. In addition to acid-catalyzed chemistry, organic sulfate formation in aerosols appears to be an important pathway for heterogeneous SOA formation in the presence of acidic sulfate seed (Iinuma et al., 2007; Surratt et al., 2007). The relative importance of the proposed heterogeneous reactions to SOA production depends on the composition of gas phase products from a precursor VOC, NO_x concentrations, particle acidity, temperature, and humidity.

The recent studies (Czoschke and Jang, 2006; Gao et al., 2004b; Iinuma et al., 2004; Kleindienst et al., 2006; Liggio et al., 2007; Northcross and Jang, 2007) on SOA formation from the atmospheric oxidation of biogenic terpene and isoprene have shown that particle acidity considerably influence biogenic SOA formation. Only a few

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studies have addressed the influence of acidic sulfates on the aromatic SOA formation and shown the contradictory results. For example, Ng et al. (2007) reported negligible SOA yield difference between acidic and neutral aerosols for aromatic SOA under two different NO_x conditions at extremely low humidity (%RH~5%). However, Cao and Jang (2007) observed that SOA yields were significantly enhanced by the presence of acidic sulfate seed aerosols without NO_x at two humidity levels (%RH~26 and 47), no matter whether the SOA experiments were conducted in the dark or under UV-Visible irradiation. Therefore, further research efforts are needed to clarify the effects of particle acidity on aromatic SOA formation. Such studies will be essential for the estimation of aromatic SOA loadings particularly in the acidic atmosphere.

Previous studies on SOA formation from aromatic photooxidation (Hurley et al., 2001; Johnson et al., 2004; Ng et al., 2007; Song et al., 2005) have shown that NO_x significantly reduces the aromatic SOA formation, suggesting that NO_x influences the fate of gas phase organic peroxide radicals (RO₂). Under high NO_x conditions, RO₂ radicals react with NO_x and produce relatively volatile organic nitrates; while under low NO_x conditions, RO₂ radicals react with hydroperoxyl radicals (HO₂) forming organic hydroperoxides (ROOH) that may further react with aldehyde species in the particle phase to produce the low volatile peroxyhemiacetals (Johnson et al., 2004). However, most of these previous studies were conducted under the neutral condition. The effects of particle acidity at varied NO_x conditions are poorly understood. NO_x levels are expected to influence the particle acidity effect on SOA formation because different NO_x levels lead to different gas phase products with diverse physical and chemical properties. Hence, more comprehensive SOA studies at different NO_x levels coupled with various particle acidities and humidity levels are needed.

Aromatic hydrocarbons constitute about 20–50% (in PPbC) of the total non methane VOCs in urban atmospheres of the United States and Europe (Calvert et al., 2002) and contribute a significant fraction of anthropogenic SOA loadings in urban area. In this paper, toluene is selected as an aromatic precursor for the study on SOA formation because toluene is the most abundant aromatic VOC in urban atmosphere comprising

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about 20–40% of the total aromatic compounds (Calvert et al., 2002) and produces high SOA yields compared to other aromatic VOCs (Dechapanya et al., 2003). The main focus of the present study is to investigate the effect of NO_x, particle acidity and humidity on the toluene SOA formation. The SOA yields and the aerosol growth patterns have been studied based on three levels of NO_x concentrations (low: ≤3 ppb, intermediate: 90–105 ppb and high: 280–315 ppb). Each level of the NO_x studies included four sub-level experiments under two different particle acidities (non acid vs. acid) and two different humidity levels (%RH: 15–22 or 38–49). The particle acidity and humidity effects on SOA formation have been evaluated within the uniform NO_x levels to exclude the possible confounding NO_x influences.

2 Experimental section

All experiments were conducted in a 2 m³ indoor Teflon film chamber under UV-visible light conditions. The detailed description for the chamber experiments has been provided elsewhere (Cao and Jang, 2007). The chamber is equipped with sixteen fluorescent lamps (Solarc Systems Inc., FS40T12/UVB) that have emission in the UV range between 300–400 nm with the maximum near 314 nm. Temperature increase due to the light sources is less than 2 K for the duration of the experiments. The particle size distribution was monitored with a Scanning Mobility Particle Sizer (SMPS, TSI Model 3080, Shoreview, MN) coupled with a condensation nuclei counter (CNC, TSI, Model 3025A). Particle data were corrected for the aerosol loss to the chamber wall (McMurtry and Grosjean, 1985) with a first order decay. The gas-phase toluene concentrations were measured with an HP 5890 GC-FID. Temperature (295–299 K) and %RH of the chamber were measured with an electronic thermo-hygrometer (Dwyer Instrument, INC, USA). Prior to each experiment, the chamber was flushed with clean air from clean air generators (Aadco Model 737, Rockville, MD; Whatman Model 75-52, Haverhill, MA). The inorganic seed aerosols were injected into the chamber by atomizing the inorganic aqueous solution (various combinations of ammonium sulfate,

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ammonium bisulfate and sulfuric acid) with a Constant Output Atomizer (TSI, Model 3076, Shoreview, MN).

For the low NO_x (≤3 ppb) experiments, toluene was oxidized by OH radicals from the photolysis of H₂O₂. When the seed aerosols stabilized, a known volume of toluene was injected into the chamber. The gas phase of H₂O₂ was then introduced into the chamber by gently purging the nitrogen at 1 L/min over a 50% H₂O₂ aqueous solution (Aldrich). The UV-Visible lights were turned on at the beginning of the H₂O₂ injection. The initial H₂O₂ concentrations in the chamber ranged from 3.48–3.71 ppm which were estimated by mass loss of the 50% H₂O₂ solution between before and after H₂O₂ injection and the mole fraction of H₂O₂ in vapor mixture (water+H₂O₂) (Manatt and Manatt, 2004).

For the intermediate (90–105 ppb) and the high NO_x (280–315 ppb) experiments, a known amount of NO and NO₂ was added in the chamber from a certificate NO tank (99.5% nitric oxide, Linde Gas). After the NO_x concentrations stabilized, a known volume of toluene was injected and the UV lights were turned on, which marked the starting point of the SOA experiment. During the experiments, ozone and NO_x concentrations were monitored with a photometric ozone analyzer (model 400E, Teledyne Instruments, San Diego, CA) and a chemiluminescence NO_x detector (model 200E, Teledyne Instruments, San Diego, CA).

The experimental conditions and the resulting SOA data are summarized in Table 1. The SOA yield (Y) defined as the ratio of the produced secondary organic mass (OM, $\mu\text{g}/\text{m}^3$) to the consumed toluene concentration (ΔROG , $\mu\text{g}/\text{m}^3$), was calculated with the OM density of 1.4 g/mL (Dommen et al., 2006; Gao et al., 2004a).

In Table 1, the particle acidity is described by proton concentrations ($[\text{H}^+]$, $\mu\text{g}/\text{m}^3$) that are calculated from the mass fraction of H⁺ estimated using an inorganic thermodynamic model (ISORROPIA) (Nenes, 2006) and the inorganic seed mass (M_{seed}) at a given humidity and a seed composition. M_{seed} is calculated from the density and the volume concentration of seed aerosols in the chamber air. The density of inorganic seed aerosols ranging from 1.332–1.634 g/mL is calculated with the method developed

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by Semmler et al. (2006) at a given composition of aqueous inorganic solution. The $[H^+]$ in the seed aerosols of this study ranged from 0.01 to $1.19 \mu\text{g}/\text{m}^3$ (Table 1).

3 Results and discussion

3.1 SOA yields

5 3.1.1 NO_x effect on SOA formation

Table 1 and Fig. 1 summarize the toluene SOA yields under three NO_x conditions and two humidity levels in the presence of non acidic/acidic sulfate seed aerosols. For each high NO_x experiment, the SOA formation was investigated for the two separate NO_x profiles: low NO and high NO, since the conversion of NO to NO₂ over the course 10 of the experiment turned the high NO conditions to the low NO conditions leading to the different SOA formation patterns (see Sect. 3.2). The SOA yields were 0.2–0.38 at low NO_x; 0.13–0.28 at intermediate NO_x; 0.17–0.21 at low NO fraction of high NO_x conditions and 0.027–0.031 at high NO fraction of high NO_x conditions. Overall, SOA formation was considerably influenced by NO_x concentrations showing the highest SOA 15 yield at low NO_x and the lowest SOA yield at high NO_x with high NO fraction of NO_x. This observation is consistent with the studies of other research groups (Hurley et al., 2001; Johnson et al., 2004; Ng et al., 2007; Song et al., 2005). Such tendency can be explained by the fact that different NO_x levels lead to different reaction pathways 20 of peroxy radicals (RO₂), which are produced from the gas phase reactions of toluene with OH radicals in the presence of oxygen. The possible subsequent reactions of RO₂ include the self-reaction of RO₂ (channel A in Fig. 2); the reaction with HO₂ (channel B in Fig. 2) to generate hydroperoxide (ROOH) and carbonyls; the reaction with NO to produce RO radicals and further carbonyls (channel C in Fig. 2); and the formation 25 of organic nitrates (channel D in Fig. 2). The relative importance of these reactions depends on the concentrations of NO and HO₂ in the system. Channels A and B are

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the dominant pathways under the low NO_x conditions, while channels C and D are significant under the intermediate and high NO_x conditions. The higher SOA yield with low NO_x concentrations indicates that the ROOH readily produces SOA mass through heterogeneous reactions with carbonyls in the particle phase (Johnson et al., 2004). For 5 the intermediate NO_x conditions, channel C is likely the dominant pathway to convert NO to NO₂ and generate carbonyls. The multifunctional carbonyls from toluene oxidation have been considered highly reactive compounds for heterogeneous reactions (either in the presence or the absence of acidic sulfate seed aerosols) and increase SOA mass.

10 The presence of high initial concentrations of NO_x with the high NO fraction of the total NO_x is likely to facilitate the generation of compounds with no or very small contribution to SOA formation resulting in the low SOA yields. Figure 3 demonstrates the simplified possible reaction pathways which produce organic nitrates (e.g. peroxybenzoyl nitrate, benzyl nitrate and peroxy acyl nitrates) or nitro compounds (e.g. nitrotoluene) in the presence of high NO_x concentrations. Peroxybenzoyl nitrate is formed 15 from reactions between peroxybenzoyl radicals and NO₂; Benzyl nitrate is produced from reactions of benzyl peroxy radicals with NO; Nitrotoluene is from OH-aromatic adducts reacting with NO₂; and peroxy acyl nitrates (PAN-like products) are likely to be formed at high NO₂ concentrations from the reactions of NO₂ with RC(O)OO_. radicals 20 which are produced from H-abstraction of aldehydes in the presence of oxygen. Laboratory studies (Hurley et al., 2001; Jang and Kamens, 2001) of aromatic oxidation at high NO_x observed nitro compounds and organic nitrates that are expected to be stable for particle phase heterogeneous reactions and contribute to SOA formation mainly through the gas-particle partitioning. However, organic nitrates (e.g. benzyl nitrate and 25 peroxy acyl nitrates) are volatile and thus the contribution of organic nitrates to SOA formation may be insignificant: e.g. the estimated vapor pressure for benzyl nitrate is 0.00155 atm using the group contribution methods by Schwarzenbach et al. (1993). Nitro compounds in the gas phase may partition to the preexisting aerosols increasing SOA. But under the high NO_x conditions with high NO fraction, the nitro compounds

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comprise only a small fraction of the gas phase oxygenated products compared to the organic nitrates, therefore SOA formation is greatly suppressed in the beginning of the experiments. It is believed that these channels may be significant in the laboratory studies under the high NO_x concentrations. The suppression of SOA formation with high NO_x (high NO fraction) in the laboratory chamber may not be observed in the atmosphere.

Table 2 summarizes the relative SOA yield increase under different NO_x concentrations at a given particle acidity and %RH level. The relative SOA yield increase between the low and the intermediate NO_x conditions was the smallest at high %RH in the presence of acidic seed, compared to those under other particle acidity and humidity levels. The detailed description for NO_x effect on SOA incorporated with impacts of acidity and humidity will be discussed in the Sect. 3.1.2.

3.1.2 Acidity and humidity effects on SOA formation

Relative SOA yield difference. Both acidity and humidity effects on the SOA yields were examined for each NO_x level. Two types of the relative SOA yield difference are defined: the SOA yield difference (ΔY_{A-NA}) between neutral and acidic sulfate seed experiments at the same humidity level, Eq. (1), and the SOA difference ($\Delta Y_{HRH-LRH}$) between low humidity and high humidity experiments with the same type of the seed aerosols, Eq. (2). The resulting ΔY_{A-NA} and $\Delta Y_{HRH-LRH}$ are summarized in Table 3 along with experimental conditions used for this study.

$$\Delta Y_{A-NA}(\%) = \frac{Y_{acid} - Y_{nonacid}}{Y_{nonacid}} \times 100\% \quad (\text{at the same \%RH level}) \quad (1)$$

$$\Delta Y_{HRH-LRH}(\%) = \frac{Y_{HRH} - Y_{LRH}}{Y_{LRH}} \times 100\% \quad (\text{for the same type of seed aerosols}) \quad (2)$$

The three major factors which operate the acidity effect and humidity effect on ΔY_{A-NA} and $\Delta Y_{HRH-LRH}$ are particle acidity, water vapor concentration (WV) and water content

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in the particle (WP) at a given temperature. The impacts of WV and WP on SOA formation depend on the types of gas phase products and thus vary under different NO_x conditions as shown in Fig. 2. The WV effect may be significant only for the low NO_x conditions by affecting the HO₂ chemistry in the gas phase (discussed in "low NO_x conditions" of this section). The effect of WP on SOA formation is considerable for aldehydes- the major products for the intermediate NO_x level (discussed in "intermediate NO_x conditions" of this section). WP may also influence the gas-particle partitioning of hydrophilic products. More water content in the particle at high %RH can facilitate partitioning of hydrophilic products resulting in more SOA production. The magnitude of such WP effect varies with the fraction of hydrophilic products of the total oxygenated products which depends upon NO_x levels.

Low NO_x conditions

Shown in Table 3, ΔY_{A-NA} values are 36% at low %RH and 25% at high %RH. At the same %RH level, ΔY_{A-NA} refers to the additional SOA formation by the presence of acidic sulfate seed through heterogeneous acid-catalyzed reactions or organic sulfate formation. The particle acidity effect described by ΔY_{A-NA} is 11% higher at low %RH than at high %RH because the proton concentrations in the acidic seed aerosols are higher at low %RH ($\Delta[H^+] = 0.11 \mu\text{g}/\text{m}^3$).

$\Delta Y_{HRH-LRH}$ values are -29% with non acidic seed and -34% with acidic sulfate seed as shown in Table 3. $\Delta Y_{HRH-LRH}$ is influenced by WV, particle acidity and WP, corresponding to the reactions in the gas and the particle phase and the partitioning process of oxygenated gas products. Firstly, the formation of peroxyhemiacetals (Fig. 2) in the particle phase reactions between a hydroperoxide (ROOH) and an aldehyde (Johnson et al., 2004) may be relatively not sensitive to the particle acidity but to WV in the system. Organic hydroperoxides are produced through the reactions of RO₂ with HO₂ radicals. Kanno et al. (2005) found that the HO₂ self-reactions were considerably enhanced by the presence of water vapor. Therefore, at high %RH, the available amounts of HO₂ radicals for the formation of hydroperoxide decrease, leading

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to less SOA formation. Secondarily, heterogeneous reactions of carbonyls (e.g. heterogeneous acid-catalyzed reactions or organic sulfate formation) are responsible for the higher SOA yields in the presence of acidic sulfate seed aerosols compared to those in neutral seed aerosols. SOA yield reduction ($\Delta Y_{\text{HRH-LRH}}$) is larger for the SOA with acidic sulfate seed than with neutral seed. This is probably due to the acidity decrease by water dilution of proton concentration in the acidic particle. Thirdly, the partitioning processes may be influenced by *WP* particularly for hydrophilic products.

Intermediate NO_x conditions

The *WP* effect on $\Delta Y_{\text{HRH-LRH}}$ is significant in the presence of neutral seed aerosols with the SOA yield 39% higher at high %RH than at low %RH. This is likely due to the reactions of gas phase toluene oxidation products such as aldehydes with particle phase water on the seed aerosols- the mechanisms for SOA formation proposed by Koehler et al. (2004). Such carbonyls are dominantly produced by Channel C in Fig. 2 under the intermediate NO_x conditions. In addition, Hastings et al. (2005) suggested that the surface water layer of solid aerosols can trigger polymerization of glyoxal dihydride monomer to form an organic layer. In the presence of acidic sulfate seed, SOA yields are not apparently changed by %RH ($\Delta Y_{\text{HRH-LRH}} = -7\%$) due to the combination of two opposite effects: increase of SOA yields ($\uparrow\uparrow$) via heterogeneous reactions of carbonyls triggered by water and decreases of SOA yields (\downarrow) by the reduced particle acidity associated with dilution of proton concentration at higher humidity (Table 3). The results for $\Delta Y_{\text{HRH-LRH}}$ suggest that these two effects are equally important under our experimental conditions.

The apparent particle acidity effect ($\Delta Y_{\text{A-NA}}$) on SOA formation at intermediate NO_x levels is much stronger compared to those under low and high NO_x levels. $\Delta Y_{\text{A-NA}}$ is 115% at low %RH and 44% at high %RH (Table 3). The high $\Delta Y_{\text{A-NA}}$ value (115%) at the low %RH is due to not only the particle acidity but also the *WP*. The non acidic seed aerosols made of ammonium sulfate are solid below the efflorescence point (30–35%RH) (Martin et al., 2003), while the acidic sulfate seed particles are

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aqueous regardless of %RH. Therefore, the difference in *WP* between neutral and acidic sulfate seeds is significant in the SOA experiments at low %RH. Compared to non acidic aerosols, more *WP* is available in acidic sulfate seed aerosols, increasing SOA formation via heterogeneous reactions of the gas phase oxygenated products with *WP*.

High NO_x conditions

For the SOA experiments at high NO fraction of the high NO_x conditions, both $\Delta Y_{\text{A-NA}}$ and $\Delta Y_{\text{HRH-LRH}}$ are within the uncertainty range for all particle acidities and humidity levels. This observation is in agreement with the previous studies by Cocker et al. (2001) and Edney et al. (2000) showing no humidity effect on the aromatic SOA formation at high NO_x levels. The main pathway for SOA formation under the high NO_x conditions is likely the gas-particle partitioning of organic nitrates and nitro compounds (see Sect. 3.1.1) that are relatively volatile with the estimated vapor pressure ranging from 10^{-3} to 10^{-6} atm (Schwarzenbach et al., 1993) and inert for heterogeneous reactions. Therefore, insignificant particle acidity effect on SOA yields is observed in the high NO fraction of the high NO_x conditions.

NO_x conditions change from high NO to low NO fraction as the SOA formation progresses. For the low NO fraction of high NO_x experiments, no SOA yield difference ($\Delta Y_{\text{HRH-LRH}} = 0$) is observed with the neutral seed indicating that the *WP* effect is not significant in this condition. The inorganic seed aerosol is coated with organic matter as the NO fraction converts from high to low conditions. Although heterogeneous reactions of gas phase oxygenated products with *WP* could be enhanced by the water on the inorganic seed aerosols (Koehler et al., 2004), *WP* effect may be reduced when this organic mass is present in the particle phase.

Unlike the observations under the neutral conditions, humidity effect in the presence of acidic aerosols is noticeable for the low NO fraction of the high NO_x conditions, leading to lower SOA yields at the high %RH ($\Delta Y_{\text{HRH-LRH}} = -19\%$). The gas phase chemistry for SOA formation in the low NO fraction of the high NO_x conditions is similar

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to that under the intermediate NO_x conditions. Channel C in Fig. 2 becomes dominant and produces carbonyls as the major oxidation products. Therefore, the SOA yield reduction by high %RH is likely due to the decrease in heterogeneous reactions of carbonyls by the reduction of particle acidity.

The particle acidity effect in the low NO fraction is only found at the low %RH ($\Delta Y_{\text{A-NA}}=17\%$) and is not as strong as that observed in the intermediate NO_x conditions. The NO concentrations of the intermediate NO_x in the beginning of toluene oxidation are similar to those in the low NO fraction, which occurs at about 90 min after the high NO_x experiments begin, but particle acidities are different between these two systems. The aerosol acidity decreases as the acidic seed aerosol is coated with SOA through organic sulfate formation in the aerosol. In our study, the change of aerosol acidity was monitored over the course of the experiments using the colorimetric method integrated with a UV-Visible spectrometer (Jang et al., 2008) (Fig. 4). Although both the intermediate NO_x and the high NO_x experiments were initiated at the similar particle acidity, the particle acidity was lower in the low NO region of the high NO_x experiments (e.g. after 90 min, Fig. 4) than it was at the intermediate NO_x experiments, due to the fact that the acidity decayed over the course of the experiments.

3.2 Time-dependent growth curve

A time-dependent growth curve, expressed by a plot of the produced OM vs. the concentrations of the organic precursor consumed over the course of an experiment, has been recently used in a few studies (Chan et al., 2007; Ng et al., 2007) to understand SOA formation mechanisms. Figure 5 illustrates the time-dependent growth curves for our experiments at three different NO_x levels. For the low (Fig. 5A) and the intermediate NO_x experiments (Fig. 5B), the time-dependent growth curves appear to be linear over the course of the experiments. This tendency is also observed in other chamber studies for the aromatic SOA formation under no NO_x conditions (Song et al., 2007) and the low NO_x conditions (Ng et al., 2007).

However, the shape of the dynamic SOA yield curve (the figure on the top of each

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Fig. 5A, 5B, 5C), presented by plots of yield vs. OM for a single experiment, clearly shows that SOA formation varies with particle acidity particularly in the beginning of the experiments. In the presence of acidic sulfate seed, SOA yields are the highest in the beginning followed by a plateau; while in the presence of neutral seed, SOA yields increase for a short period and reach a plateau. These observations infer that different mechanisms would contribute to SOA formation to different degrees between neutral and acidic sulfate seed aerosols. With the acidic sulfate seed available, heterogeneous acid-catalyzed reactions and organic sulfate formation would be major pathways for SOA formation and occur rapidly in the beginning when the inorganic acid is abundant. The reduction in acidic SOA yields after the maximum SOA yield possibly results from the decrease in the amount of acid available to catalyze the reactions in the SOA through the conversion of acidic sulfates to organic sulfates over time. In addition, as heterogeneous reactions proceed in aerosols, the gas-particle partitioning of oxygenated products that are inert to heterogeneous reactions may become less favorable due to increases in both the average molecular weight of OM and the activity coefficients of SOA products (Jang et. al., 2006).

The high NO_x experiments began with high NO concentrations (~ 222–242 ppb) and changed to low NO concentrations (~59–91 ppb) due to the conversion of NO to NO_2 over the course of the experiment. Correspondingly, two different SOA formation patterns are observed in the high NO_x experiments as illustrated in Fig. 5C. The criterion between high and low NO conditions was set at the point where the instantaneous NO concentration fell into the range of the initial NO concentration of the intermediate NO_x experiments. The fact that the two SOA growth patterns were distinguished by the NO criterion indicates that SOA formation is related to the NO concentrations.

The SOA slowly formed in the high NO fraction indicating that the oxygenated products of toluene irradiation in the presence of abundant NO are either relatively volatile or inert for heterogeneous reactions (also see Sect. 3.1.1). However, when the system turned into the low NO fraction with high concentrations of NO_2 , the aerosol growth pattern changed dramatically, showing a rapid increase of SOA formation. This is likely

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because large amounts of nitro products existed in the system at high NO_x concentrations (Fig. 3) and the gas-particle partitioning of nitro products act as the dominant pathways for SOA formation.

3.3 Chamber experiments under conditions relevant to the atmosphere

- 5 To gain insights into the atmospheric implication of the chamber experiments, SOA experiments (shown in Table 4) were conducted with low initial toluene concentrations (~40 ppb) in the presence of small amounts of inorganic seed aerosols (~10 µg/m³). The acidic seed solution for the seed aerosols was made of 70% ammonium bisulfate and 30% sulfuric acid. As shown in Table 4, such weak particle acidity still increases
10 SOA yields by 12.5% compared to neutral SOA under our NO_x conditions (initial NO is about 100–115 ppb). This result can be applied to SOA formation under the similar ambient NO_x conditions. For example, on a weekday morning near freeways in California (Fujita et al., 2003), the average 1-h NO_x concentrations were about 100–200 ppb.

4 Conclusions

- 15 The present study demonstrates that SOA formation from photooxidation of toluene is influenced by NO_x concentrations, particle acidity and humidity using controlled chamber experiments. NO_x concentrations affect the types of gas phase products from toluene photooxidation and thus influence the contribution of possible mechanisms to SOA formation as well as the effects of particle acidity and humidity. At low NO_x conditions, reactions of the major gas phase oxygenated products-ROOH with carbonyls are dominant pathways for SOA formation. Such reactions occur rapidly even in the absence of acidic sulfate seed, thus the particle acidity effect is not as significant as that at intermediate NO_x conditions. At low NO_x, high %RH decreases SOA yields, because water vapor decreases the availability of HO₂ for the production of ROOH,
20 which reduces the contribution of heterogeneous reactions of ROOH and carbonyls to
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SOA formation. At intermediate NO_x conditions, heterogeneous acid-catalyzed reactions and organic sulfate formation play an important role for SOA formation. Therefore, particle acidity effect on SOA formation is strongest at intermediate NO_x compared to those at low and high NO_x. Unlike the humidity effect at low NO_x, high %RH increases
5 SOA yields at intermediate NO_x. This is probably due to heterogeneous reactions of gas phase oxygenated products with particle phase water enhancing SOA formation. At high NO_x, the high initial NO and NO₂ concentrations facilitate formation of volatile organic nitrates and nitro compounds that are not reactive for heterogeneous reactions and undergo the gas particle partitioning processes for SOA formation. Hence,
10 insignificant effects of particle acidity and humidity are observed at high NO_x.

The fact that the physical process and chemistry of oxygenated products in the gas and the particle phase for SOA formation depend on NO_x concentrations, particle acidity and humidity, emphasizes the need for comprehensive chamber studies under diverse environmental conditions. Such studies will be very useful to mimic the SOA
15 formation under the ambient conditions of a certain area. Our SOA yield studies and time-dependent growth curves provide the insight into the possible gas phase product distributions and corresponding dominant pathways for SOA formation under different conditions. Further studies on characterization of the gas and the particle products are required to identify effects of NO_x concentrations, particle acidity and humidity on SOA
20 formation.

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Table 1. Experimental conditions and resulting SOA data from photooxidation of toluene^a.

Exp# ^b	%RH	[H ⁺] ($\mu\text{g}/\text{m}^3$)	NO ^c (ppb)	NO ₂ ^c (ppb)	ΔTOL (ppm)	V _{seed} (nL/m ³)	V _{mix} (nL/m ³)	OM ($\mu\text{g}/\text{m}^3$)	Yield ^d
LNO _x -NA-LRH	18.4	0.01	≤ 1.5	≤ 1.5	0.10	169	245	106.3	0.28 \pm 0.020
LNO _x -NA-HRH	48.2	0.01	≤ 1.5	≤ 1.5	0.09	179	229	70.5	0.20 \pm 0.015
LNO _x -A-LRH	17.0	0.80	≤ 1.5	≤ 1.5	0.13	153	285	183.2	0.38 \pm 0.028
LNO _x -A-HRH	48.2	0.69	≤ 1.5	≤ 1.5	0.10	185	249	89.4	0.25 \pm 0.020
MNO _x -NA-LRH	15.8	0.01	66.2	28.6	0.13	218	263	66.5	0.13 \pm 0.010
MNO _x -NA-HRH	41.0	0.02	78.1	14.8	0.10	215	262	65.3	0.18 \pm 0.013
MNO _x -A-LRH	21.1	1.05	69.2	30.0	0.12	203	292	124.4	0.28 \pm 0.020
MNO _x -A-HRH	38.5	0.87	82.7	22.0	0.12	212	295	116.5	0.26 \pm 0.019
HNO _x (LNO)-NA-LRH	14.6	N/A ^e	90.5	180.2	0.17	256	340	117.6	0.18 \pm 0.013
HNO _x (LNO)-NA-HRH	42.7	N/A ^e	72.3	214.9	0.18	219	309	126.0	0.18 \pm 0.013
HNO _x (LNO)-A-LRH	19.9	N/A ^e	58.6	192.8	0.16	236	328	128.8	0.21 \pm 0.015
HNO _x (LNO)-A-HRH	40.9	N/A ^e	64.7	186.9	0.20	244	336	128.8	0.17 \pm 0.013
HNO _x (HNO)-NA-LRH	14.6	0.01	241.4	70.4	0.13	246	256	13.3	0.027 \pm 0.003
HNO _x (HNO)-NA-HRH	42.7	0.02	229.4	85.1	0.11	210	219	12.0	0.029 \pm 0.004
HNO _x (HNO)-A-LRH	19.9	1.19	226.1	62.0	0.12	227	236	12.6	0.027 \pm 0.003
HNO _x (HNO)-A-HRH	40.9	0.94	222.2	81.6	0.11	235	244	13.2	0.031 \pm 0.004

^a Temperature: 295–299 K.^b LNO_x: low NO_x level (OH radical source: photolysis of H₂O₂); MNO_x: intermediate NO_x level ([NO_x]~90–105 ppb); HNO_x: high NO_x level ([NO_x]~280–315 ppb); HNO: high NO fraction; LNO: low NO fraction; NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH level; HRH: high %RH level.^c Initial concentrations.^d SOA yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ΔROG through the propagation of uncertainty for divisions (Levie, 1997).^e N/A: not available.

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Table 2. Relative SOA yield increase under different NO_x concentrations at a given particle acidity and humidity^{a,b}.

Exp. conditions	$(Y_{\text{LNO}_x} - Y_{\text{MNO}_x}) / Y_{\text{MNO}_x}$ (%)	$(Y_{\text{LNO}_x} - Y_{\text{HNO}_x(\text{LNO})}) / Y_{\text{HNO}_x(\text{LNO})}$ (%)	$(Y_{\text{LNO}_x} - Y_{\text{HNO}_x(\text{HNO})}) / Y_{\text{HNO}_x(\text{HNO})}$ (%)
NA-LRH	115	56	937
NA-HRH	11	11	590
A-LRH	36	81	1307
A-HRH	-4	47	706

^a NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; LRH: low %RH level; HRH: high %RH level.^b LNO_x: low NO_x level (OH radical source: photolysis of H₂O₂); MNO_x: intermediate NO_x level ([NO_x]~90–105 ppb); HNO_x: high NO_x level ([NO_x]~280–315 ppb); LNO: low NO fraction; HNO: high NO fraction.

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Table 3. Summary of particle acidity effect (ΔY_{A-NA}) and humidity effect ($\Delta Y_{HRH-LRH}$) on SOA formation under various experimental conditions^a.

	NO _x conditions	Net %	WV	WP	Acid
ΔY_{A-NA} at LRH	LNO _x	36	N/A	↑↑	↑↑
ΔY_{A-NA} at HRH	LNO _x	25	N/A	↑	↑
ΔY_{A-NA} at LRH	MNO _x	115	N/A	↑↑↑	↑↑↑
ΔY_{A-NA} at HRH	MNO _x	44	N/A	↑↑	↑↑
ΔY_{A-NA} at LRH	HNO _x (HNO)	0	N/A	—	—
ΔY_{A-NA} at HRH	HNO _x (HNO)	7	N/A	—	—
ΔY_{A-NA} at LRH	HNO _x (LNO)	17	N/A	↑	↑
ΔY_{A-NA} at HRH	HNO _x (LNO)	6	N/A	—	—
$\Delta Y_{HRH-LRH}$ with NA	LNO _x	-29	↓	↑↑	—
$\Delta Y_{HRH-LRH}$ with A	LNO _x	-34	↓	↑	↓
$\Delta Y_{HRH-LRH}$ with NA	MNO _x	39	—	↑↑↑	—
$\Delta Y_{HRH-LRH}$ with A	MNO _x	-7	—	↑↑	↓
$\Delta Y_{HRH-LRH}$ with NA	HNO _x (HNO)	7	—	—	—
$\Delta Y_{HRH-LRH}$ with A	HNO _x (HNO)	15	—	—	—
$\Delta Y_{HRH-LRH}$ with NA	HNO _x (LNO)	0	—	—	—
$\Delta Y_{HRH-LRH}$ with A	HNO _x (LNO)	-19	—	↑	↓

^a ↑ represents SOA yield increase due to the specific effect; ↓ represents SOA yield decrease by the specific effect. The number of arrows represents the magnitude of the effects: ↑↑↑ (strong), ↑↑ (medium), and ↑ (weak). “—” sign denotes insignificant effects. N/A: not applicable.

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Table 4. SOA experiments conducted under the atmospheric relevant conditions at intermediate NO_x level^a ([NO_x]=100–115 ppb).

Exp ^b	%RH	[H ⁺] ($\mu\text{g}/\text{m}^3$)	NO ^c (ppb)	NO ₂ ^c (ppb)	ΔTOL (ppm)	V _{seed} (nL/m ³)	V _{mix} (nL/m ³)	OM ($\mu\text{g}/\text{m}^3$)	Yield ^d
LT-MNO _x -NA-HRH	42.7	0.001	83.8	29.9	0.012	9.78	20.1	14.5	0.32±0.026
LT-MNO _x -A-HRH	41.9	0.03	85.3	15.4	0.012	9.38	21.0	16.3	0.36±0.028

^a Temperature=299 K.

^b LT: Low initial toluene concentration; MNO_x: intermediate NO_x level; NA: in the presence of non acidic seed; A: in the presence of acidic sulfate seed; HRH: high %RH level.

^c Initial concentrations.

^d Yield was calculated with the density of organic matter of 1.4 g/mL. The uncertainties of the resulting SOA yields were calculated using the uncertainties of OM and ΔROG through the propagation of uncertainty for divisions (Levie, 1997).

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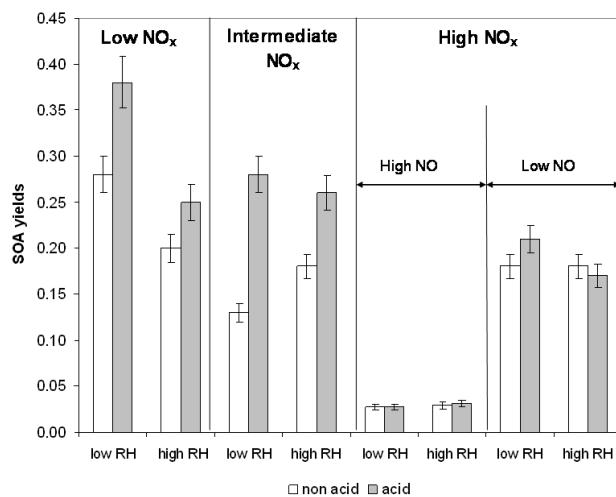


Fig. 1. SOA yields in the presence of neutral seed and acidic sulfate seed at two different %RH levels under three NO_x conditions. The data used are shown in Table 1.

14491

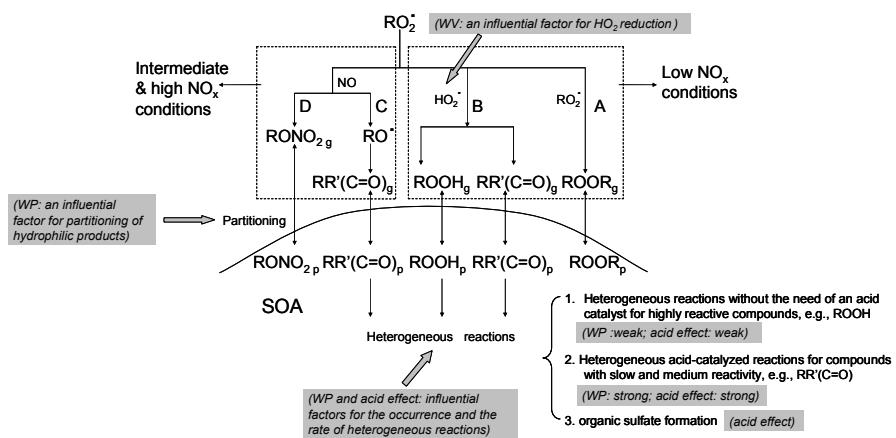


Fig. 2. The fates of RO_2 produced from toluene photooxidation under different NO_x conditions. Peroxides (ROOR) are produced from self-reactions of RO_2 radicals (channel A); Hydroperoxide (ROOH) and carbonyls ($\text{RR}'(\text{C}=\text{O})$) are produced from reactions of RO_2 and HO_2 radicals (channel B); Carbonyls, $\text{RR}'(\text{C}=\text{O})$, are produced from reaction of RO_2 with NO (channel C); Organic nitrates (RONO_2) are formed from reactions of RO_2 with NO (channel D). Gray boxes show the major influential factors on reaction channels in the gas and particle phase: the acidity and humidity effects discussed in Sect. 3.1.2 and Table 3.

14492

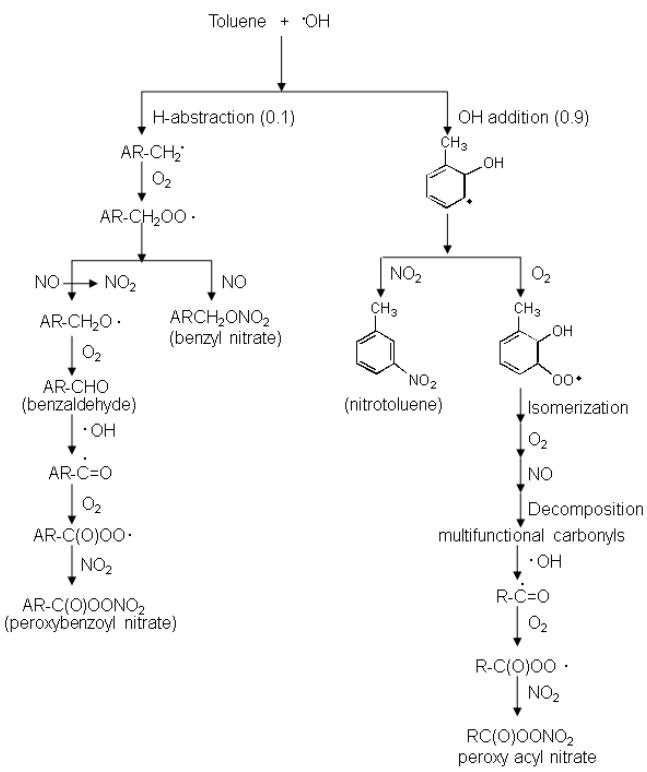


Fig. 3. The possible reaction channels for gas phase oxygenated products at high NO_x level. The numbers in the brackets are the branch ratios of the reaction channels. AR represents the benzene ring. R represents ring-opening structures.

14493

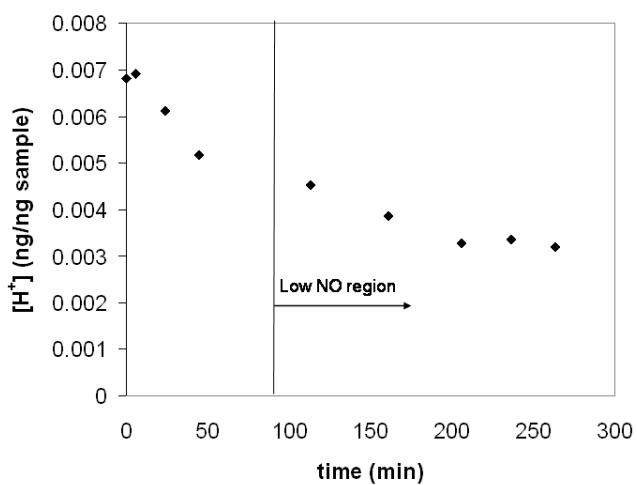


Fig. 4. A time profile of proton concentration $[\text{H}^+]$ over the course of an SOA experiment at high NO_x level in the presence of acidic sulfate seed.

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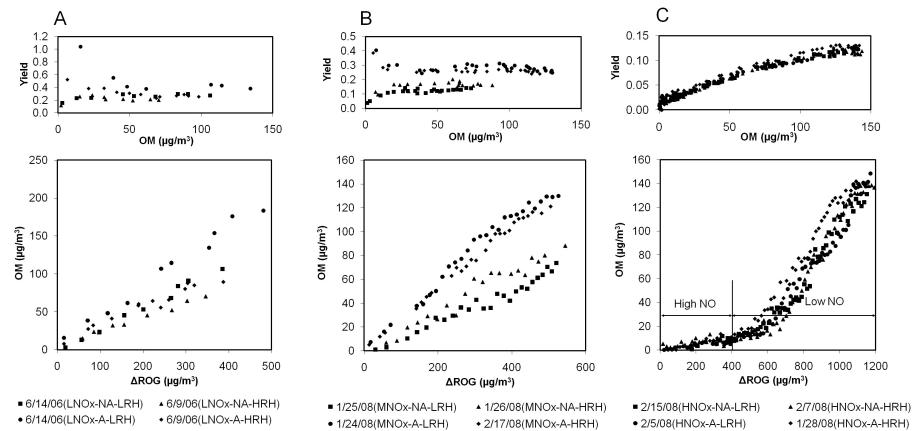


Fig. 5. Time-dependent growth curves and SOA yield curves over the course of an SOA experiment in Table 1 at low NO_x (**A**), intermediate NO_x (**B**) and high NO_x (**C**).