We sincerely thank the Referee for the valuable comments. Our manuscript has been revised according to the comments from the Referee and our responses to the comments are as follows. For clarity, the comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red.

Responses to Anonymous Referee #1

This smog chamber study investigated the effects of NH_3, SO_2, and NO_x on SOA formation under UV irradiation from 1,2,4-trimethylbenzene (TMB) over a period of 5-6 hours. The smog chamber was monitored in real time using a scanning mobility particle sizer; gas analyzers for SO_2, NO_x, NH_3, and O_3; and gas chromatography-flame ionization for TMB. Offline analysis used infrared spectrophotometry, ion chromatography, and liquid chromatography-mass spectrometry. The study found that the presence of NH_3 and SO_2 both individually and synergetically increase SOA yield, and that SO_2 speeds nucleation, possibly through uptake onto H_2SO_4 surfaces. New organosulfates were identified and reaction schemes and structures were proposed for some; some organosulfates had molecular weights consistent with TMB-derived aerosol components found in the atmosphere. NH_3 was found to react to form organic nitrogen compounds in the aerosol phase, but only in the presence of SO_2, attributed to formation of ammonium sulfate. Aerosol components had a wide range of volatility almost nine orders of magnitude, as predicted by elemental composition from mass spectrometry.

This study is a good match for the scope and aims of ACP, and it does an excellent job conveying its own novelty even if the reader is not well versed in aromatic aerosol chemistry. It represents a necessary contribution to the aerosol research community's understanding of SO_2 and NH_3 dynamics, and has implications for reactions of a large number of aromatic VOCs as well as human health in the findings regarding enhanced UFP fraction.

Major Comments

This article is solid, if not concise, and all sections contribute to the main point as a

cohesive whole. The introduction, methods section, and discussion of limitations are excellent, and while there is far more description of results than there is analysis of results I believe that both the analysis and discussion of atmospheric implications are sufficient. All of my suggestions for improvement are minor, relating to clarity and readability.

Minor Comments

line 13: Consider a brief explanation of the atmospheric relevance of TMB in the abstract.

Author Reply:

Aromatic hydrocarbons can dominate the VOC budget in certain urban areas with TMB being one of the most significant species (Ran et al., 2009). TMB is mostly emitted from anthropogenic sources such as solvent use (Mo et al., 2021). Recent studies have recognized TMB as an important species in SOA formation in the atmosphere (Wang et al., 2020; Zaytsev et al., 2019; Mehra et al., 2020). Hence, the following text has been added in the abstract to explain the relevance of TMB in the atmosphere.

Aromatic hydrocarbons can dominate the volatile organic compounds budget in the urban atmosphere. Among them, 1,2,4-trimethylbenzene (TMB), mainly emitted from solvent use, is one of the most important secondary organic aerosols (SOA) precursors.

line 69-70: "Equivocally not originated from biogenic VOCs" is a little unclear. Possibly change to "unidentified OSs with C2-C25 skeletons that may not have originated from biogenic VOCs" or similar.

Author Reply:

We have modified the sentence in the revised manuscript as: Recent field studies reported that some unidentified OSs with C_2–C_{25} skeletons may not be originated from biogenic VOCs.

line 254-55: Make it clear whether ammonium sulfate particles were introduced during

experiments or as an independent wall loss experiment.

Author Reply:

Ammonium sulfate (AS) particles were not introduced into the chamber over the course of particle formation experiments. We used inert AS particles only in independent wall loss experiments in order to characterize the wall loss rate of AS particles, which was adopted to correct aerosol particle concentrations. This particle wall-loss correction method has been commonly used in previous studies (Chen et al., 2019; Charan et al., 2020). For clarity, we have included the following sentences in the revised manuscript.

Page 5, lines 166–167

Seed particles were not introduced into the chamber over the course of particle formation experiments.

Page 10, line 273–274

In order to determine the particles wall loss rates, we carried out independent wall loss experiments using ammonium sulfate particles.

Is this dependent on humidity or hygroscopicity of the particles? Not VERY important, but may be a limitation worth discussing.

Author Reply:

We agree with the Referee that particle wall depositions are affected by the physicochemical properties of particles to some extent. It should be noted that the description of an important step of the wall loss experiments was missing in our original manuscript. Indeed, the AS solution was added to a TSI atomizer (Model 3076) to produce droplets, which passed simultaneously through a silica gel diffusion dryer to produce dry AS particles. Although the hygroscopicity of AS particles is not totally similar to aerosol particles generated, the wall-losses of particles are commonly evaluated by independent seed experiments where inert AS particles are used (Chen et al., 2019; Charan et al., 2020).

Aerosol particles can deposit onto the chamber walls due to gravitational settling, Brownian diffusion, convection, and electrostatic effects (Crump and Seinfeld, 1981).

The wall-loss rate of particles depends mainly on the smog chamber design parameters (Charan et al., 2019). Previous studies showed that elevating RH inside the chamber did not remarkably influence the particle wall loss rates (Yu et al., 2011; Ge et al., 2017). Ge et al. (2017) used a same wall loss constant for the particle wall-loss corrections in experiments with RH ranged from 11% to 90%. Although the changes in RH can also influence the hygroscopicity, density, size, and chemical composition of particles (Hinks et al., 2018; Yu et al., 2011), almost identical humidity ((25 ± 1) %) condition was achieved among each experiment in the current work. Therefore, we believe that the particle wall depositions are not basically influenced by humidity or hygroscopicity of the particles. The description about the wall loss experiments has been included in the revised manuscript as follow.

Page 10, lines 274–280

An aqueous solution of ammonium sulfate was fed to a constant output atomizer (Model 3706, TSI, USA) to produce droplets, which passed simultaneously through a silica gel diffusion dryer to introduce dry particles into the chamber. The size distributions of ammonium sulfate particles were measured by SMPS for 480 min. Almost identical humidity ((25 ± 1) %) condition was achieved among each experiment. The wall losses of particles are size-dependent and, thus, we used a size-dependent particle wall-loss correction approach, which is described in detail in the Supplement.

line 284: Were these from two single experiments? If so, include experiment numbers. Otherwise I want to know the standard deviations for these values.

Author Reply:

Yes, the reported particle number concentrations were obtained in independent SO_2-free experiments with different initial NO_x levels. We have highlighted the experiment numbers in the revised manuscript as:

After 300 min UV irradiation without SO_2 introduction, the total maximum number concentration of aerosol particles was only 2.7×10^4 cm^{-3} and 2.9×10^4 cm^{-3} under low-NO_x (Exp. 1) and high-NO_x (Exp. 5) experiments, respectively.

line 291-95: Before noting that UFP are more harmful to human health, you may want to make it explicit in the text analysis of figure 1 that increased SO_2 concentration increases the fraction of UFP in the aerosol size distribution.

Author Reply:

The SMPS instrument could measure particles larger than 4.50 nm in this work. In order to more clearly analyze the effects of SO_2 on the ultrafine particle formation, the number concentrations of ultrafine particles in the range of 4.50–100 nm were summed up and they are shown in Fig. R1, where it can be seen that the total number concentration of ultrafine particles is significantly enhanced with increasing SO_2 levels. Therefore, the following text was added in the revised manuscript and Fig. R1 was added as Fig. S2 in the revised supplement.

Page 11, lines 309–314

Interestingly, the particle maximum number concentration considerably increased with increasing SO_2 levels, regardless of low- or high-NO_x conditions (Table 1). As shown in Fig. 1, although the unimodal particle size distribution in the presence of SO_2 was similar to that in its absence, particles with mobility diameter ranging from 10 to 80 nm, especially, dominated particle number concentrations with SO_2 addition. The time series of total ultrafine particles (diameter < 100 nm) number concentration are shown in Fig. S2, where it is seen that SO_2 considerably enhanced ultrafine particle formation.

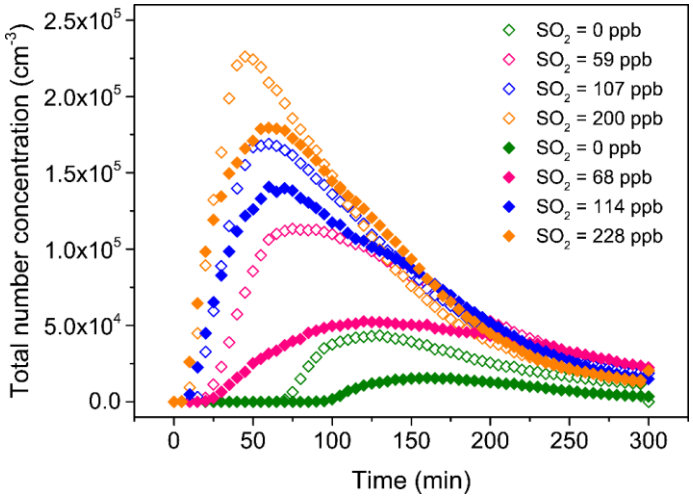

Figure R1. The total number concentrations of ultrafine particles (< 100 nm) as a function of reaction time (Exps. 1–8). The open symbols and solid symbols represent low- and high-NO*x* experiments, respectively.

line 323: I would be interested in more detail about the mechanics of H_2SO_4 as a "condensed surface for key compounds." I take this to mean reactive uptake or heterogeneous reactions of VOCs with H_2SO_4. However, you don't justify this assertion; I might recommend citing Wang et al. 2010 (doi.org/10.1021/es9036868) and/or Zhang et al. 2019 (doi.org/10.1021/acsearthspacechem.9b00209) for VOC heterogeneous reaction with sulfuric acid surfaces.

Author Reply:

The oxidation of SO_2 can contribute to the formation of H_2SO_4 in SO_2-involved experiments. The formed H_2SO_4 plays a key role in nucleation and can contribute to the increase in nucleation rate (Sipila et al., 2010; Lehtipalo et al., 2018; Yao et al., 2018), which are responsible for the short nucleation time observed in the TMB/NO_x/SO_2 regime (Wyche et al., 2009). Several H_2SO_4 nucleation mechanisms have been suggested, including binary nucleation, ternary nucleation, ion-induced nucleation, and so on (Sipila et al., 2010; Lehtipalo et al., 2018; Yao et al., 2018). SOA-forming compounds can be produced in the gas-phase via photooxidation of TMB, and the chamber walls and particle surfaces are competitive condensation sinks for these compounds (Charan et al., 2020). Seed particles were not introduced into the chamber during particle production experiments in this work. In the original sentence, we meant that the H_2SO_4-induced new particles are an attractive condensation sinks for SOA-forming compounds and can subsequently provide surfaces like seed particles onto which the compound can condense.

We have carefully read the two recommended papers. Wang et al. (2010) found that H_2SO_4 can effectively uptake gas-phase alkylamines, hence contributing to the growth of aerosol particles. Zhang et al. (2019) highlighted the significance of uptake of isoprene-derived epoxydiols onto sulfate aerosol particles. This process can influence the phase state, morphology, and acidity of aerosol particles. Reactive uptake or heterogeneous reactions of organic vapors with H_2SO_4 are important, which can promote the growth of particle and the increase in particle mass (Deng et al., 2017; Wang et al., 2010). However, it should be noted that we focused on analyzing SO_2

effects on the particle nucleation time in line 323 of the original text. The heterogenous reactions promote mainly the formation of the accumulation mode particles instead of the nucleation mode particles (Lu et al., 2019). The original sentence has been revised as: The formed H_2SO_4 could induce nucleation and increase the nucleation rate (Zhao et al., 2018; Blair et al., 2017), and these processes are responsible for the short nucleation time observed in the TMB/NO_x/SO_2 regime (Wyche et al., 2009).

We fully agree with the Referee that acidic surfaces on aerosol particles can promote the reactive uptake of organic vapors (Zhang et al., 2019; Wang et al., 2010). The acid-catalyzed heterogenous reactions were already discussed in Sect. 3.1.2 in the original manuscript as follows.

"The increase in aerosol acidity could be largely responsible for the observed enhancements in SOA formation in SO_2-invloved experiments. The OH oxidation of TMB can result in the formation of multifunctional carbonyl compounds (Liu et al., 2012; Zaytsev et al., 2019), which could promote SOA formation via acid-catalyzed heterogeneous reactions."

line 329-30: As neither this work nor that of Julin et al. attempts to explain the "nonlinear dynamics of aerosol populations," rather than attributing your results to these dynamics it might be more effective to say something like "The nonlinear response of the mean particle diameter to SO_2 initial concentration is similar to results found by Julin et al. (2018) in a modelling study."

Author Reply:

We have carefully read the study of Julin et al. (2018) again, who suggested nonlinear response of particle size distributions to ammonia emissions. In the revised manuscript, the sentence has been revised as follows:

The nonlinear response of the particle mean diameter to SO_2 initial level is similar to the findings of Julin et al. (2018), who found the response of particle size distribution to NH_3 emissions to be also nonlinear.

line 336: Is this the mean particle diameter after 30 minutes? Be explicit. You defined initial growth rate as average for 0-30 minutes, but did not define a timeframe for mean diameter.

Author reply:

Figure R2 shows the mean diameter of aerosol particles at different reaction times, which was measured with SMPS. The particle mean diameter can stabilize after about 300 min photooxidation. Therefore, the particle mean diameter measured at 300 min in each experiment are compared in Fig. 2 in the main manuscript. The related text and Fig. 2 have been updated in the revised manuscript as follows.

Page 11, lines 330–334

The particle size rapidly increased within 30 min after nucleation, and gradually reached a stable level within 300 min photooxidation (Fig. 1). Consequently, the initial growth rate (GR_{inital}), calculated based on the method of Kulmala et al. (2012), is defined as the particle growth rate within 30 min after nucleation (Li et al., 2018). The mean diameter reported in this work represents the particle mean diameter measured at 300 min in each experiment.

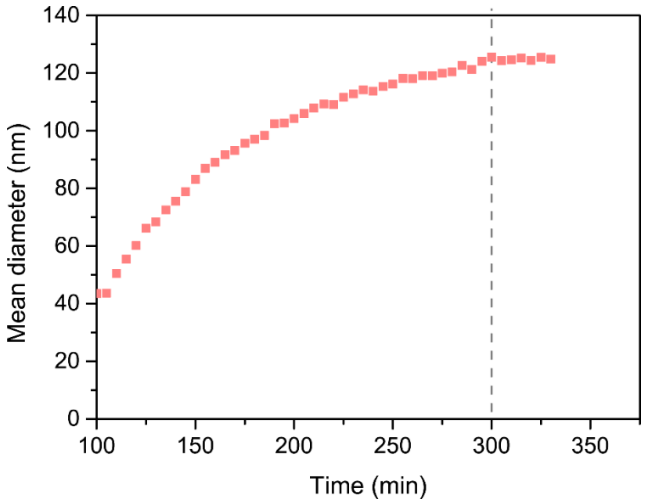

Figure R2. The mean diameter of aerosol particles generated as a function of reaction time.

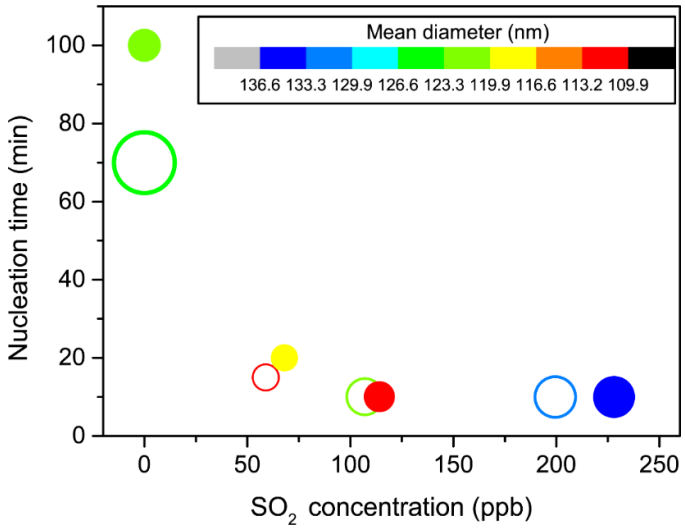

Figure 2. Particle nucleation time as a function of initial SO_2 concentration under low-NO_x (open circles) and high-NO_x (solid circles) conditions (Exps. 1–8). The symbol color indicates the particle mean diameter and symbol size represents the particle initial growth rate. Values of the particle parameters are listed in Table S1.

line 383-84: If you believe you have not sufficiently justified the necessity of chemical composition studies, I recommend you do so in the introduction instead.

Author Reply:

In the Introduction, we initially highlighted the necessity to analyze the chemical composition of particles as follows:

"To better understand TMB-SOA formation and growth, detailed laboratory characterization of TMB-SOA composition and TMB oxidation mechanisms with inorganic perturbation are required."

"The mechanisms leading to secondary aerosol formation in the urban environment remain highly elusive and controversial, particularly for the processes related to changes in secondary aerosol mass and chemical composition."

However, based on the Referee's suggestion, we moved the original sentence to the Introduction to further supplement the necessity of studying particle chemical composition.

Page 2, lines 55–62

High levels of SO_2, NH_3, and VOCs have been reported in certain regions such as

Guangzhou (Zou et al., 2015), Beijing (Meng et al., 2020), Handan (Li et al., 2017) in China. During haze pollution episodes, Li et al. (2017) observed that SO_2 levels can be up to 200 ppb in Handan, China. A recent study also showed significant increasing NH_3 levels in the atmosphere over the United States and the European Union (Warner et al., 2017). However, less focus has been placed on the SO_2 and NH_3 perturbations on SOA formation and chemical composition. Aerosol particles contain a multitude of compounds with different physicochemical properties.

line 589: Figure 9 may belong in the supplement, because it has only a brief mention in the text that is limited to the observation that positive mode MS spectra skew toward lower m/z's.

Author Reply:

Figure 9 has been moved to the supplement.

line 594, 600: The contents of Figure 10 are also not discussed in the text, so it could be moved to the supplement as well.

Author Reply:

Figure 10 presents the predicted saturation mass concentrations of detected products, which is an important part of our discussion. Therefore, we keep Fig. 10 (now labeled as Fig. 9) in the revised manuscript.

line 509-10: use comparable measures to compare the SO_2-involved and SO_2 free conditions. I would recommend including the multiplicative factor of the change for both.

Author Reply:

We have modified the original sentence following the Referee's suggestion as: Increasing the NH_3 level to 200 ppb enhanced the particle maximum number concentration by factors of 2.0 and 1.7 under SO_2-free and SO_2-involved conditions, respectively.

line 524-26: The sentence "Initial growth rate... as shown in Fig. S6" is redundant, and to the next sentence "In SO_2-free experiments... initial growth rate of aerosol particles" I would add something like "compared to the SO_2-involved condition."

Author Reply:

We have deleted the sentence "Initial growth rate... as shown in Fig. S6" in the revised manuscript. In addition, we already compared the initial growth rate of particles in SO_2-free and SO_2-involved experiments in the original manuscript as: "**In SO_2-free experiments**, the increase in NH_3 initial concentrations led to remarkable increase of the initial growth rate of aerosol particles. High initial growth rates were also found in the photooxidation of other aromatics such as toluene and o/m/p-xylene with NH_3 addition (Li et al., 2018). This result may be explained by the fact that under SO_2-free condition, NH_3 mainly reacts with acids to produce ammonium salts. Previous studies have reported that ammonium salts could partition into the initial growth process of new secondary aerosol particles and thus increase the particle initial growth rate (Li et al., 2018; Zhu et al., 2014). More interestingly, NH_3 level did not substantially affect the initial growth rate of particles **in the presence of SO_2** (Fig. S9)."

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We sincerely thank the Referee for the valuable comments. Our manuscript has been revised according to the comments from the Referee and our responses to the comments are as follows. For clarity, the comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red.

Responses to Anonymous Referee #2

General comments

The authors have studied SOA formation from photo-oxidation of 1,2,4-trimethylbenzene under different concentrations of NOx, SO2 and NH3 in an indoor smog chamber. The reactants and the particle generation and growth were monitored using a series of standard instrumentations. The chemical functional groups were characterized by ATR-FTIR in each experiment and inorganic constituents were analyzed using ion chromatography. The molecular level information is provided using UPLC-HRMS and dd-MS2 scans. Ten new organosulfates are identified in the presence of SO2, including 3 in which the origin was previously unknown and some previously reported to be originated from biogenic precursors. Formation mechanisms for 8 of the newly identified organosulfates are proposed based on previous literature. Their results indicate that SO2 is a key parameter for ultrafine particle formation. A synergistic effect of NH3 and SO2 in particle formation is also shown, indicating the importance of reducing both SO2 and NH3 emissions to improve lowering PM. Their results also suggest that ammonium sulfate form by the reaction of NH3 with H2SO4 facilitate aerosol formation and growth through condensation of organic vapors.

This article advances the current knowledge of aerosol formation from photo-oxidation of a typical aromatic hydrocarbon in the presence of NOx, SO2 and NH3, therefore is of interest to the scientific community of ACP. The manuscript is well written and organized. The experiments are well executed, methods are explained adequately, results are discussed thoroughly, and conclusions are well supported. I have some minor comments to improve the quality of this manuscript that are listed below. I recommend accepting this manuscript for publication in ACP with minor revisions.

Specific comments

Line 13 Indicate the major emission sources of TMB.

Author Reply:

Aromatic hydrocarbons can dominate the VOC budget in certain urban areas with TMB being one of the most significant species (Ran et al., 2009). TMB is mostly emitted from anthropogenic sources such as solvent use (Mo et al., 2021). Recent studies have recognized TMB as an important species in SOA formation in the atmosphere (Wang et al., 2020; Zaytsev et al., 2019; Mehra et al., 2020). Hence, the following text has been added in the abstract.

Aromatic hydrocarbons can dominate the volatile organic compounds budget in the urban atmosphere. Among them, 1,2,4-trimethylbenzene (TMB), mainly emitted from solvent use, is one of the most important secondary organic aerosols (SOA) precursors.

Line 45 Define 'certain regions.

Author Reply:

The original text has been supplemented as follows: High levels of SO_2, NH_3, and VOCs have been reported in certain regions such as Guangzhou (Zou et al., 2015), Beijing (Meng et al., 2020), Handan (Li et al., 2017) in China. During haze pollution episodes, Li et al. (2017) observed that SO_2 levels can be up to 200 ppb in Handan, China. A recent study also showed significant increasing NH_3 levels in the atmosphere over the United States and the European Union (Warner et al., 2017).

Line 54-56 Add reference/s.

Author Reply:

The following studies have been added to the references list.

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5. Zhang, Y., Chen, Y., Lei, Z., Olson, N. E., Riva, M., Koss, A. R., Zhang, Z., Gold, A., Jayne, J. T., Worsnop, D. R., Onasch, T. B., Kroll, J. H., Turpin, B. J., Ault, A. P., and Surratt, J. D.: Joint Impacts of Acidity and Viscosity on the Formation of Secondary Organic Aerosol from Isoprene Epoxydiols (IEPOX) in Phase Separated Particles, ACS Earth Space Chem., 3, 2646-2658, 10.1021/acsearthspacechem.9b00209, 2019.

They are cited in the revised manuscript as follows:

The presence of OSs could alter aerosol morphology (Riva et al., 2019), viscosity (Riva et al., 2019; Zhang et al., 2019), particle acidity (Riva et al., 2019), phase state (Zhang et al., 2019), hygroscopicity (Estillore et al., 2016; Hansen et al., 2015), and optical properties (Fleming et al., 2019), thereby resulting in large climate effects.

Line 98-99 Briefly indicate what MCM is and add a link to the version.

Author Reply:

The Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCMv3.2/, last access: 23 February 2021) is a near-explicit chemical mechanism that can describe, in detail, the tropospheric degradation of numerous VOCs. The oxidation processes of VOCs are highly complex. Explicit chemical mechanisms might cause missing oxidation pathways and products, thus leading to large gaps between the modeled and measured SOA mass. Wang et al. (2020) suggested that recently identified autoxidation pathways for OH oxidation of TMB are not included in the current MCM and the detected products are more diverse than the products shown in MCM. The updates for the OH-initiated oxidation mechanism of TMB can be achieved only when the rate, branching ratios and product distributions can be explicitly obtained. Therefore, more investigations are needed to further explore the detailed chemical processes for OH oxidation of TMB. According to the suggestion of the Referee, the following text was added in the revised manuscript.

Page 4, lines 122–131

In addition, the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCMv3.2/, last access: 23 February 2021) is a near-explicit chemical mechanism that can describe, in detail, the tropospheric degradation of TMB. A recent study reported that identified autoxidation pathways during OH oxidation of TMB are not included in the current MCM and the detected TMB products are more diverse than the products shown in MCM (Wang et al., 2020b). The updates for the OH-initiated oxidation mechanism of TMB can be achieved only when the rate constants, branching ratios and product distributions can be explicitly obtained. However, TMB photooxidation is highly complex and sensitive to environmental conditions. To better understand TMB SOA formation and growth, investigating chemical processes of TMB photooxidation with inorganic perturbation is required.

Line 210 Indicate how the mass calibration was performed.

Author Reply:

We used standard calibration solutions provided by the manufacturer to calibrate the MS instrument every five days. The following text was added in the revised manuscript.

Page 9, lines 257–258

The MS instrument was calibrated every five days with standard calibration solutions provided by the manufacturer.

Line 200 Indicate the mass resolution in full MS, top N in dd-MS2, isolation width (mass window) etc

Author Reply:

In the revised manuscript, detailed parameters are indicated as follows:

Page 9, lines 251–257

MS spectra were recorded in the range of *m/z* 50 to 750 in full MS scan with a mass resolving power of 70000 (FWHM at *m/z* 200). The full MS scan was followed by data-dependent MS/MS (dd-MS^2) scans using stepped collision energies of 20, 40, and 60 eV via high-energy collisional dissociation. The resolution was 17500 and an isolation width of 2 *m/z* units was applied for the dd-MS^2 scan. The other parameters for MS^2 experiments were as follow: AGC target, 2×10^5; maximum IT, 50 ms; loop count, 3; minimum AGC target, 1×10^5; apex trigger, 2–6 s; dynamic exclusion, 6 s.

Line 277 Add initial growth rates to Table 1 or SI.

Author Reply:

The aim of depicting Fig. 2 in the original manuscript was to clearly reflect the changes of the particle nucleation time, initial growth rate, and mean diameter with the initial SO_2 concentration. The specific particle parameters including the particle initial growth rate have been summarized in the table below.

Table R1. Particle parameters for experiments 1–8.

Exp.	Nucleation time (min)	Particle mean diameter (nm)	Initial particle growth rate (nm h^{-1})
1	70	125.5	46.53
2	15	109.9	20.09
3	10	121.2	27.42
4	10	130.6	31.09
5	100	123.1	23.51
6	20	118.5	19.30
7	10	112.4	22.14
8	10	136.5	29.82

Table R1 has been added in the revised supplement as Table S1 and the caption of Fig. 2 has been also updated as follows.

Figure 2. Particle nucleation time as a function of initial SO_2 concentration under low-NO_x (open circles) and high-NO_x (solid circles) conditions (Exps. 1–8). The symbol color indicates the particle mean diameter and symbol size represents the particle initial growth rate. Values of the particle parameters are listed in Table S1.

Line 277-280 Can the authors elaborate the reasons for the observed non-linear response of the particle diameter with initial SO_2 concentrations?

Author Reply:

OH-initiated oxidation of VOCs can yield a number of products with different degrees of volatility (Xu et al., 2014). The growth of aerosol particles is related to the coagulation, the condensation of non-volatility oxidation products, and gas-particle partitioning of semi-volatility organic compounds (SVOCs). For SVOCs, the evaporation is important after partitioning to the particle phase. Therefore, the rate at which SVOCs participate in the particle growth is lower than their condensation rate. Interestingly, recent studies showed that the particle-phase chemistry such as heterogeneous reactions of SVOCs are substantially pronounced for particle growth (Shiraiwa et al., 2013; Paasonen et al., 2018; Apsokardu and Johnston, 2018). Apsokardu and Johnston (2018) explored the influences of particle-phase chemistry on the growth rate of aerosol particles with a kinetic growth model and found that some

SVOCs can undergo accretion reactions in the particle-phase to further accelerate the particle growth. Paasonen et al. (2018) also showed that the increase in particle growth rate is related to particle-phase reactions. The study of Shiraiwa et al. (2013) highlighted the importance of particle-phase chemistry in the changes of SOA size distribution and suggested that particle-phase chemistry depends to some extent on particle acidity. Organosulfates can be produced by particle-phase reactions involving interactions between organics and inorganics. In this work, we measured organosulfates only in SO_2-involved photooxidation, indicating that additional particle-phase reactions can occur under SO_2-involved conditions. Increasing initial SO_2 levels could induce the formation of more sulfate (Fig. S4) and the enhancement in the particle acidity during photooxidation (Liu et al., 2016; Kroll et al., 2006). The elevated particle acidity can promote more SVOCs to transform into non-volatile products in the particle phase (Lin et al., 2014; Lal et al., 2012). Additional SVOCs could be moved from the gas phase to particle phase to increase the particle size and the evaporation of SVOCs can be inhibited, thereby promoting the particle growth.

It is somewhat interesting that the particle mean diameter in low-SO_2 ($[SO_2]_0 < 100$ ppb) experiments is smaller than that in SO_2-free experiments. Our result is in line with the study of Wyche et al. (2009), who attributed this phenomenon to the larger number of particles produced under SO_2-involved condition. In this work, the presence of 59 ppb SO_2 caused the maximum number concentration of particles to increase by 8.5×10^4 cm^{-3} under low-NO_x condition. When the SO_2 level increased from 0 to 68 ppb in high-NO_x experiments, the corresponding particle number concentration increased from 2.9×10^4 to 9.3×10^4 cm^{-3}. Therefore, the amounts of products that condensed onto each aerosol particles may significantly decrease in low-SO_2 experiments, which can result in the decrease in particle diameter (Liu et al., 2015). The promoting effect of particle-phase chemistry on the particle size growth may not offset the inhibiting effect of the emergence of large number of particles on the particle size growth, thereby leading to the low particle diameter in low-SO_2 experiments. We have added the following text to explain the reasons for the observed non-linear response of the particle diameter with initial SO_2 level.

Page 12, lines 356–381

Aerosol particles can grow in different ways such as gas-particle partitioning of semi-volatility organic compounds (SVOCs). Since the evaporation of SVOCs is important after partitioning to the particle phase, the rate at which SVOCs participate in the particle growth is lower than their condensation rate. However, recent advances give an insight that the particle-phase chemistry such as heterogeneous reactions of SVOCs are substantially pronounced for the particle growth (Shiraiwa et al., 2013; Paasonen et al., 2018; Apsokardu and Johnston, 2018). Organosulfates can be produced by particle-phase reactions involving interactions between organics and inorganics. In this work, organosulfates were only detected in SO_2-involved photooxidation, indicating that additional particle-phase reactions can occur under SO_2-involved conditions. Increasing the initial SO_2 level could induce the formation of more sulfate (Fig. S4) and the enhancement in the particle acidity during photooxidation (Liu et al., 2016; Kroll et al., 2006). The elevated particle acidity can promote more SVOCs to transform into low-volatile products such as organosulfates in the particle phase, thereby promoting the particle growth (Lin et al., 2014; Lal et al., 2012). Then, additional SVOCs could be further transferred from the gas phase to the particle phase to increase the particle size. However, the particle mean diameter in low-SO_2 ($[SO_2]_0 <$ 100 ppb) experiments is smaller than that in SO_2-free experiments. Our result is in line with the study of Wyche et al. (2009), who attributed this phenomenon to the larger number of particles produced under SO_2-involved condition. The presence of 59 ppb SO_2 caused the maximum number concentration of particles to increase by 8.5×10^4 cm^{-3} under low-NO_x condition. When the SO_2 level increased from 0 to 68 ppb in high-NO_x experiments, the corresponding particle number concentration increased from 2.9×10^4 to 9.3×10^4 cm^{-3}. Therefore, the amounts of products that condensed onto each aerosol particles significantly decreased in low-SO_2 experiments, which could result in the decrease in particle diameter (Liu et al., 2015). The promoting effect of particle-phase chemistry on the particle size growth may not offset the inhibiting effect of the emergence of large number of particles on the particle size growth, thereby leading to the low particle diameter in low-SO_2 experiments.

Figure 4 – Indicate what error bars represent.

Author Reply:

The error bars represent errors in the SOA yield results. The errors were calculated from error propagation using the sum of the uncertainties in TMB data and the systematic error of SMPS. The following note was included in the caption of Fig. 4.

The error bars represent errors in the SOA yield results and the errors were calculated from error propagation using the sum of the uncertainties in TMB data and the systematic error of SMPS.

Figure 5 – Indicate the experiment numbers relevant to a) to f)

Author Reply:

The experimental numbers have been added in the caption of Fig. 5 as:

Figure 5. ATR-FTIR spectra of aerosol particles generated from TMB/NO_x (a, Exp. 1; b, Exp. 5), TMB/NO_x/SO_2 (c, Exp. 4; d, Exp. 8), TMB/NO_x/NH_3/SO_2 (e, Exp. 12), and TMB/NO_x/NH_3 (f, Exp. 10) photooxidation.

Lines 346-348 – Add detailed information of the common products observed in SO2 free and SO2 involved experiments to the SI.

Author Reply:

The detailed information of representative products mentioned in the original manuscript were provided in Table S3 in the revised supplement.

Table S3 – Indicate clearly whether this table shows the compounds that are detected in both SO2 free and SO2 involved experiments with NH3 or the products only formed from the experiments involved both NH3 and SO2.

Author Reply:

The major products shown in Table S3 are the products detected in both SO_2-free and SO_2-involved experiments with NH_3 addition. The revised table in the supplement is now labeled as Table S4 and the caption was revised as: Observed products in both

SO_2-free and SO_2-involved experiments with NH_3 addition.

Tables S2 and S3 – Add UPLC retention times.

Author Reply:

The retention times have been added in the indicated tables, which are now labeled as Table S3 and S4.

Technical corrections

Line 105 – Add 'in the atmosphere' to the end of "Given the ubiquity of SO2, NH3, and TMB…

Author Reply:

According to the suggestion of the Referee, we have added "in the atmosphere" at the indicated place in the revised manuscript.

Line 200 – It is better to write it as data-dependent MS/MS (dd-MS2) scans

Author Reply:

We have modified it in the text.

Line 206 – Add B after 3%.

Author Reply:

We have added "B" in the revised manuscript.

Figure 6 – Label the red structures as OS-226, OS-228…etc. (Authors may replace the chemical formula with their abbreviated names as the structures are shown.)

Author Reply:

The red structures in Fig. 6 have been marked with OS-266, OS-228…etc.

Figure 10 – Match the color of the TMB on the figure with carbon number (should be light blue as it has 9 carbons)

Author Reply:

We have corrected it in the revised manuscript.

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We sincerely thank the Referee for the valuable comments. Our manuscript has been revised according to the comments from the Referee and our responses to the comments are as follows. For clarity, the comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red.

Responses to Anonymous Referee #3

Overview:

The manuscript by Yang et al. examined the effect of SO_2 and NH_3 on the formation of SOA from 1,2,4-trimethylbenzene photooxidation. After the injection of SO_2 and/or NH_3, the apparent yield of the SOA increased after wall loss correction, which demonstrated the synergistic effect of SO_2 and NH_3 in facilitating SOA formation. The authors also used ATR-FTIR, IC, and UPLC-MS to systematically analyze the particle phase composition and identified various inorganic and organo-sulfates compounds. My main comments are about the control experiment setup in this manuscript, which are discussed below. Other than the main comments, the manuscript is written clearly and comprehensive.

Major Comments:

The authors demonstrate that the addition of SO_2 and/or NH_3 during the photo-oxidation experiments can enhance the SOA formation and yield. However, part of the aerosol growth can arise from the formation of H_2SO_4 or $(NH_4)_2SO_4$ particles even without the presence of any SOA, which should be deducted from the enhancement effect of SO_2 and/or NH_3. I suggest the authors add in three control experiments (pure SO_2, pure NH_3, and SO_2+NH_3 mixtures but with similar levels of OH radicals and UV intensity using H_2O_2 or other OH generators) without any VOCs to rule out the formation of inorganic species contributing to the SOA.

Author Reply:

In the SO_2-added experiments, H_2SO_4 can be produced by OH oxidation of SO_2

upon photooxidation. With the coexistence of SO_2 and NH_3, the formed H_2SO_4 can be neutralized by NH_3 to form $(NH)_4SO_4$ particles. Therefore, the addition of SO_2 and/or NH_3 to the TMB/NO_x mixtures can lead to the increase in the volume concentration of aerosol particles by the formation of inorganic species and/or the enhanced organic products (Ye et al., 2018; Jaoui et al., 2008; Liu et al., 2019). In the present study, we discussed the SO_2 dependence of the SOA yield as shown in Fig. 4, and we showed the role of NH_3 in the total particle number and volume concentrations (as discussed in Sect. 3.2.1). We believe that the introduction of SO_2 can enhance SOA yield based on our careful analysis as following:

(1) Some studies on the effects of SO_2 and/or NH_3 on SOA formation employed aerosol mass spectrometer to measure in-situ the inorganic and organic components in aerosol particles (Liu et al., 2016; Chen et al., 2019). For our online measurement of aerosol particles, we solely used SMPS, whose data are insufficient to quantitatively explain the contribution of organic aerosols to the increase in aerosol mass. Offline measurement methods are also commonly adopted in chamber studies. Ion chromatography (IC) is one of the most widely used instruments providing inorganic aerosol information. Kleindienst et al. (2006) investigated the SO_2 effects on SOA yields from the isoprene/NO_x/SO_2 photooxidation and used IC to determine the mass concentrations of inorganic components. Jiang et al. (2020) revealed the influences of SO_2 and NH_3 on furan SOA yield based on SMPS and IC measurements. In this work, the concentrations of inorganic ions were measured through IC. To determine the net SOA yield, the mass of inorganic components was subtracted from the total particle mass based on IC and SMPS data as mentioned in Sect. 3.1.2 in the original manuscript (Jiang et al., 2020). When SO_2 initial levels increased from 0 to 200 ppb, the net SOA yield increased from 3.8% to 17.6% in the low-NO_x regime. Similarly, elevating SO_2 initial concentration to 228 ppb under high-NO_x condition enhanced the net SOA yield by a factor of 3.49. The promoting effects of SO_2 on SOA yields were in line with previous studies (Chen et al., 2019; Liu et al., 2019).

(2) We used an estimation method to explore the contribution of the generated

H_2SO_4 to the particle formation enhancement in TMB/NO_x/SO_2 photooxidation, where we assumed the full conversion of the consumed SO_2 into H_2SO_4 aerosol particles (Ye et al., 2018; Wyche et al., 2009). As shown in Fig. R1, the contribution of the formed H_2SO_4 to the increase in particle volume concentration was less than 100%. Furthermore, a previous study showed that half of the reacted SO_2 could transform into sulfur-containing organic species during the photooxidation of 1,3,5-trimethylbenzene/o-xylene/octane/toluene (Vivanco et al., 2011). HRMS measurements reveal the OSs production in this work, which may result in the decrease in the amount of H_2SO_4 in particle phase. Therefore, the enhanced SOA formation is also responsible for the increased particle volume concentration in the presence of SO_2.

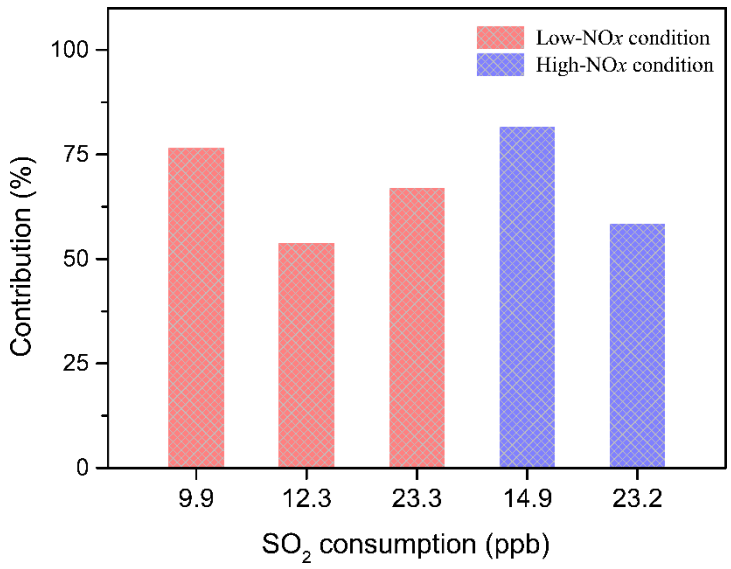

Figure R1. Contribution (%) of the formed H_2SO_4 to the increase in particle volume concentration during low-NO_x and high-NO_x experiments.

(3) We also performed different experiments without introducing TMB, which could provide significant information about secondary inorganic aerosol formation as suggested by the Referee. In TMB/NO_x/SO_2 photooxidation, the consumption of 9.9 and 23.3 ppb SO_2 can cause the particle volume concentration to increase by 32.9 and 89.2 μm^3 cm^{-3}, respectively. In pure SO_2 photooxidation, the volume concentrations of the formed particles were only 25.3 and 43.2 μm^3 cm^{-3} when the consumptions of SO_2

were 9.5 and 24.2 ppb, respectively. Comparison of the results of TMB/NO_x/SO_2 and pure SO_2 oxidation experiments demonstrates that the enhancement in aerosol particles by SO_2 introduction cannot be solely attributed to inorganic aerosol formation.

The yields shown in Table 1, obtained after ruling out the influences of inorganic species, were net SOA yields. Now, the following note was included in Table 1 in the revised manuscript. For SOA mass calculation, the inorganic mass concentration has been subtracted from the particle mass concentration.

Besides, we have added the following text in the revised manuscript and supplement to provide more evidence about SO_2 effects on the net SOA yield.

Manuscript, page 14, lines 400–404

We assumed full conversion of the consumed SO_2 into H_2SO_4 aerosol particles and found that the contribution of the formed H_2SO_4 to the increase in particle volume concentration was less than 100% (See Sect. S2). In addition, pure SO_2 oxidation experiments without TMB addition also indicated that the enhancement in aerosol particles by SO_2 introduction cannot be solely attributed to inorganic aerosol formation (See Sect. S2).

Supplement

S2. The formed H_2SO_4 estimation and inorganic mixture experiments

In order to evaluate the SO_2 effects on SOA formation, we used the method of Ye et al. (2018) to calculate the contribution of the generated H_2SO_4 to the particle formation enhancement in TMB/NO_x/SO_2 photooxidation (Ye et al., 2018; Wyche et al., 2009), where we assumed full conversion of the consumed SO_2 into H_2SO_4 aerosol particles. The contribution of the formed H_2SO_4 to the increase in particle volume concentration was less than 100% (Fig. S6), demonstrating that the enhanced SOA formation is also responsible for the increased particle volume concentration. Additionally, a previous study has shown that half of the reacted SO_2 can transform into sulfur-containing organic species during the photooxidation of 1,3,5-trimethylbenzene/o-xylene/octane/toluene (Vivanco et al., 2011). HRMS

measurements revealed the OSs production in this work, which may result in the decrease in the amount of H_2SO_4 in the particle phase. Therefore, the enhancement in aerosol particles by SO_2 introduction cannot be solely attributed to inorganic aerosol formation. Pure SO_2 oxidation experiments without introducing TMB were also carried out. In the TMB/NO_x/SO_2 regime, the consumption of 9.9 and 23.3 ppb SO_2 could cause the particle volume concentration to increase by 32.9 and 89.2 μm^3 cm^{-3}, respectively. However, in pure SO_2 oxidation experiments, the volume concentrations of the formed particles were only 25.3 and 43.2 μm^3 cm^{-3} when the consumptions of SO_2 were 9.5 and 24.2 ppb, respectively. Comparison of the results of TMB/NO_x/SO_2 and pure SO_2 oxidation experiments also demonstrates that the enhancement in aerosol particles by SO_2 introduction cannot be solely attributed to inorganic aerosol formation.

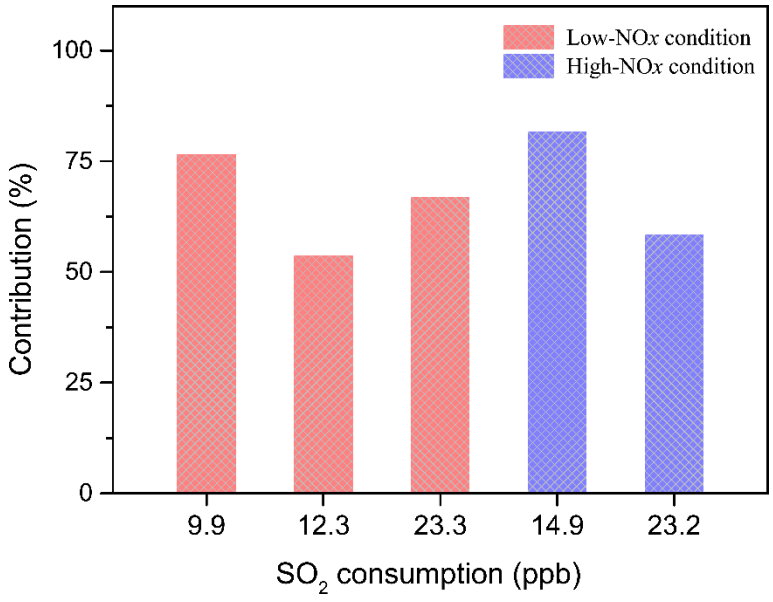

Figure S6. Contribution (%) of the formed H_2SO_4 to the increased particle volume concentration during low-NO_x and high-NO_x experiments.

Figure S7 shows the mass spectra with and without SO_2 and/or NH_3 are similar, suggesting that maybe inorganic species formed with OH are the likely source of enhancement. It would be important to understand that after ruling out this part of the inorganic aerosol formation, how much enhancement the SO_2 and/or NH_3 would add to

the yield of the SOA.

Author Reply:

It should be noted that Fig. S7 (now labeled as Fig. S10 in the revised supplement) compared the mass spectra of aerosol particles from NH_3-free and NH_3-added experiments. First, we carried out pure NH_3 oxidation experiments and found that aerosol particles were not formed within 480 min of UV irradiation. In addition, the promoting effect of NH_3 on SOA formation was not as strong as that of SO_2 with similar level. Under SO_2-free condition, the net SOA yield increased slightly from 3.5% to 5.1% as NH_3 initial level increased from 0 to 200 ppb. Our result is consistent with the finding of Chen et al. (2020a), who showed that NH_3 did not significantly affect SOA formation from toluene/NO_x photooxidation under dry condition. Therefore, the NH_3-induced changes in the absolute concentrations of organic components might be small in SO_2-free experiments, leading to similar mass spectra for Fig. S10(a) and Fig. S10(b). Under SO_2-involved conditions, the introduction of NH_3 resulted in MS differences in the range of *m/z* 200–400 as presented in Fig. S10(d). The sum of the ion signals in the ranges of 50–199, 200−299, 300−399, and 400−750 were compared in Fig. S11, where it can be seen that the abundance of organic compounds with *m/z* > 200 were enhanced with the addition of NH_3 in TMB/NO_x/SO_2 photooxidation.

We have revised the text to explain why the mass spectra of aerosol particles from NH_3-free and NH_3-added experiments are similar.

Page 22, lines 640–643

NH_3 could slightly enhance SOA formation in SO_2-free experiment as mentioned in Sect. 3.2.1. Therefore, the NH_3-induced changes in the absolute concentrations of organic components might be small in SO_2-free experiments, leading to similar mass spectra for Fig. S10(a) and Fig. S10(b). In addition, the major products (Table S4) are likely generated by similar chemical mechanisms (Fig. 8), which are not sensitive to the change in initial NH_3 levels under current experimental conditions.

It is also necessary to show how much enhancement NH_3 would add to the net SOA yield according to the Referee's suggestion. Hence, the discussions were revised in the

revised manuscript as following:

Page 20, lines 564–573

However, the effect of NH_3 on particle formation was not as pronounced as that of SO_2 with similar concentration (Fig. 7). In TMB/NO_x/NH_3 photooxidation, the net SOA yield increased slightly from 3.5% to 5.1% as NH_3 initial level increased from 0 to 200 ppb (Table 1). Our result is consistent with the finding of Chen et al. (2020a), who showed that NH_3 did not significantly affect SOA formation from toluene/NO_x photooxidation under dry condition. Interestingly, SMPS measurements demonstrated that the coexistence of SO_2 and NH_3 can considerably promote secondary aerosol formation (Fig. 7). After subtracting the inorganic components, it was seen that the net SOA yield could increase to 13.7% with the introduction of 200 ppb NH_3 and 234 ppb SO_2, indicating the synergetic effects of NH_3 and SO_2 (Chu et al., 2016).

Another comment I have is that the enhancement of the SOA from the addition of SO_2 and/or NH_3 can also be attributed to the increase of the surface area from the formation of inorganic species, which shifts the gas-particle equilibrium more to the particle side. Can the authors discuss more about the effect of this shift of equilibrium? It seems Figure 4 shows that the first three experiments after adding SO_2 seem to follow this rule.

Author Reply:

An important mechanism of SOA formation and growth is gas-particle partitioning of semi-volatile compounds (SVOCs) generated from the atmospheric oxidation of VOCs. The gas-particle partitioning of SVOCs have a great sensitivity to particle surface areas in the batch-mode chamber experiments (Zhang et al., 2015; Han et al., 2019). Increasing particle surface area can limit the gas-wall interactions of organic vapors and is favorable for moving more SVOCs from the gas phase to the particle side (Han et al., 2019). These additional SVOCs may undergo further particle chemistry to strongly enhance aerosol particle formation (Apsokardu and Johnston, 2018).

Recently, the effects of the particle surface area concentration on organic aerosol formation have been explored by Han et al. (2019), who found that increasing the

particle surface area concentrations can significantly increase organic aerosol mass yield due to greater partitioning of semi-volatility organic products to the particle-phase. In addition, some studies have confirmed that the SOA yields depend on the surface areas of inorganic aerosols when condensation of organic vapors onto particles is kinetically limited (McVay et al., 2014; Nah et al., 2016; Zhang et al., 2014). In the present work, the surface area concentrations of aerosol particles increased with increasing mixing ratios of SO_2 and/or NH_3 inside the chamber (Table 1), which may facilitate the gas-particle equilibrium shifting to the particle phase. The particle surface area concentrations have been included in Table 1. Based on the suggestion of the Referee, we have enriched the discussion in the revised manuscript as following:

3.1.2 SOA yield in SO_2-added photooxidation

Page 14, lines 421–437

In addition, the particle surface area concentrations significantly increased with increasing SO_2 initial concentrations in both low-NO_x and high-NO_x conditions (Table 1), which might also result in the enhancement in the SOA yield. Besides gas-particle partitioning of SVOCs, the fates of SVOCs in the chamber also include chemical reactions and chamber wall losses. Therefore, in the batch-mode chamber experiments, the gas-particle partitioning of SVOCs have a great sensitivity to particle surface areas (Zhang et al., 2015; Han et al., 2019). Recently, Zhao et al. (2018) examined the SO_2 effects on the SOA formation and suggested that providing additional particle surfaces by SO_2-induced new particle formation leads to the increase in SOA yield. The effects of the particle surface area concentration on organic aerosol formation were explored by Han et al. (2019), who also found that increasing the particle surface area concentrations can significantly increase the organic aerosol mass yield due to greater partitioning of semi-volatility organic products to the particle-phase. Increasing the particle surface area can limit the gas-wall interactions of organic vapors and is favorable for the movement of more SVOCs from the gas phase to the particle side (Han et al., 2019). These additional SVOCs can also undergo further particle chemistry such as acid-catalyzed heterogenous reactions to strongly enhance aerosol particle

formation in TMB/NO_x/SO_2 photooxidation (Apsokardu and Johnston, 2018).

3.2.1 Particle formation and growth in NH_3-involved photooxidation

Page 20, lines 573–577

The flux of the gas-phase products diffusing to a particle partly depends on the surface area of the particle. The coexistence of SO_2 and NH_3 promoted the increase in particle surface area concentrations (Table 1). The ability of particle formation originating from gas-to-particle conversion may be significantly stronger with SO_2 and NH_3 introduction, leading to the enhancement in particle formation.

3.2.2 Particle chemical composition in NH_3-involved photooxidation

Page 23, lines 662–665

The introduction of SO_2 and NH_3 lead to the formation of ammonium sulfate (Fig. S12), which is an attractive condensation sink for organic vapors. High particle surface area concentration in TMB/NO_x/SO_2/NH_3 experiments may increase the abundance of organic compounds in the bulk phase.

Minor Comment:

L217: Can the author make an additional plot in the SI or show how the size dependent wall loss factor is generated?

Author Reply:

The wall-loss of particles are commonly evaluated by seed-only experiments where inert ammonium sulfate (AS) particles are used (Chen et al., 2019; Charan et al., 2020). In the current work, the AS solution was added to a TSI atomizer (Model 3076) to produce droplets, which passed simultaneously through a silica gel diffusion dryer to inject dry AS particles into the chamber. AS particles were lost to the chamber walls due to diffusion, gravitational settling, and electrostatic forces during experiment and the mass size distributions of AS particles were measured by SMPS for 480 min.

The size-dependent particle wall-loss rate constants were determined based on the SMPS-measured particle size distribution. First-order loss rate constants (k_i) of particles in each size bin i across all measured sizes were firstly calculated as the slope of the

corresponding ln-linear fit line:

$$\ln[M_i(t)] = -k_i t + C \quad \text{(R1)}$$

where M_i (μg m^{-3}) is the mass concentration of particles in the size bin i at time t (min) and C is an arbitrary constant. Then, the relationship between the k_i and the particle diameter ($d_{p,i}$) can be described as follows:

$$k_i(d_{p,i}) = a d_{p,i}^{b} + c d_{p,i}^{-d} \quad \text{(R2)}$$

The optimized fitted line shown in Fig. R2 can express well our independent seed experimental results.

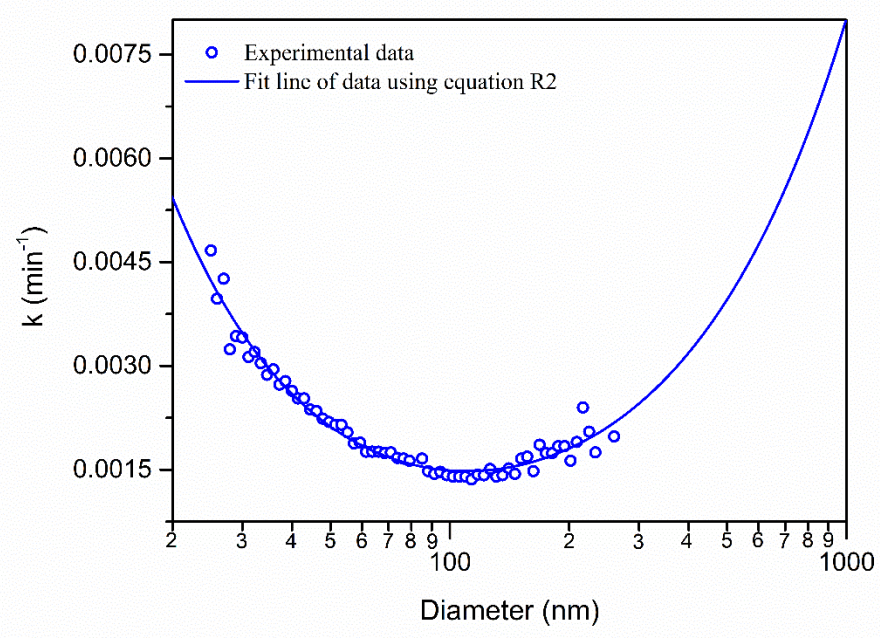

Figure R2. Wall loss rate constant of particles as a function of particle diameter.

The description about the wall loss experiments has been updated in the revised manuscript as follows:

In order to determine the particles wall loss rates, we carried out independent wall loss experiments using ammonium sulfate particles. An aqueous solution of ammonium sulfate was fed to a constant output atomizer (Model 3706, TSI, USA) to produce droplets, which passed simultaneously through a silica gel diffusion dryer to introduce dry particles into the chamber. The size distributions of ammonium sulfate particles were measured by SMPS for 480 min. Almost identical humidity ((25 ± 1) %) condition

was achieved among each experiment. The wall losses of particles are size-dependent and, thus, we used a size-dependent particle wall-loss correction approach, which is described in detail in the Supplement.

Besides, the following text and Fig. R2 were added in the revised supplement to explain how the size dependent wall loss constant was obtained.

S1. Size-dependent wall loss correction method

In the present work, the size-dependent particle wall-loss rate constants were determined based on the SMPS-measured particle size distribution. The first-order loss rate constants (k_i) of particles in each size bin i across all measured sizes were firstly calculated as the slope of the corresponding ln-linear fit line:

$$\ln[M_i(t)] = -k_i t + C \quad \text{(S1)}$$

where M_i (μg m^{-3}) is the mass concentration of particles in size bin i at time t (min) and C is an arbitrary constant. Then, the relationship between the k_i and the particle diameter ($d_{p,i}$) can be described as follows:

$$k_i(d_{p,i}) = a d_{p,i}^{b} + c d_{p,i}^{-d} \quad \text{(S2)}$$

The optimized fitted line shown in Fig. S1 can express well our independent seed experimental results. Parameters a, b, c, and d in Eq. (S2) were determined to be 5.5×10^{-6}, 1.05, 0.18, 1.19, respectively. Therefore, the size-dependent loss rate (k) of ammonium sulfate particles can be expressed as $k = 5.5\times10^{-6}\times d_p^{1.05} + 0.18\times d_p^{-1.19}$.

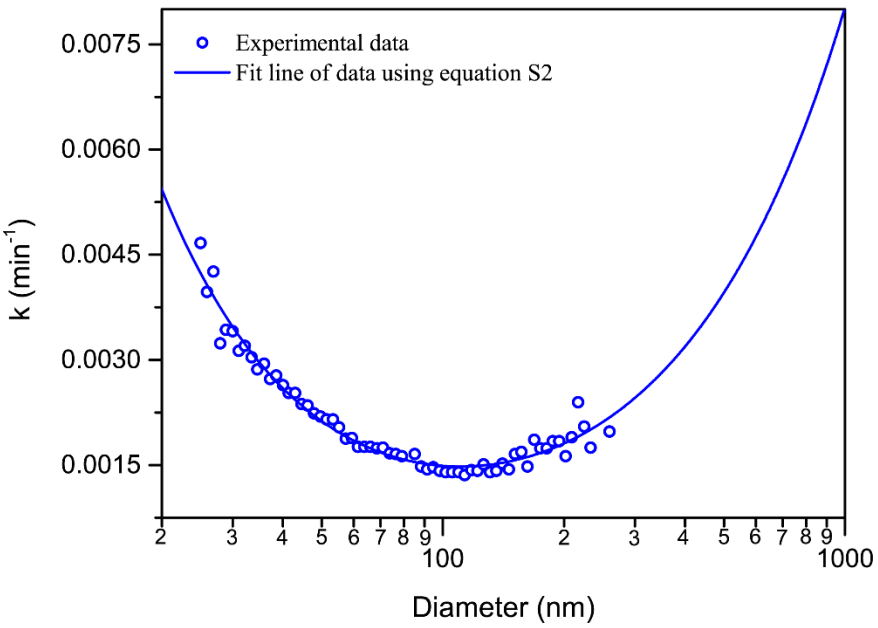

Figure S1. Wall loss rate constant of particles as a function of particle diameter.

Figure 1: It would be better to change the plots all in the same scale for easy comparison of different conditions.

Author Reply:

Figure 1 has been revised according to the comment of the Referee as follows:

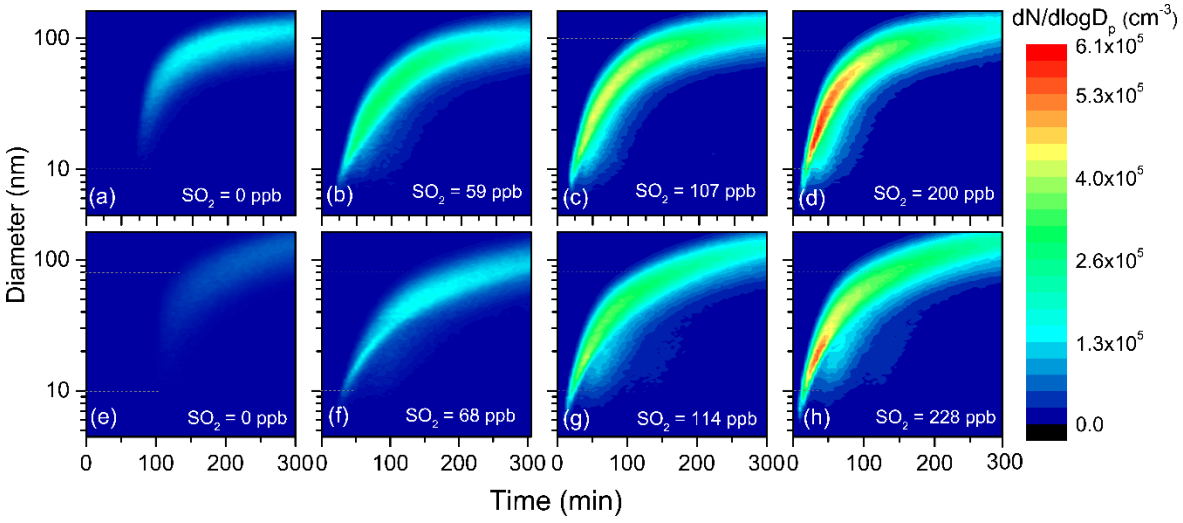

Figure 1. Evolutions of the number distributions of aerosol particles generated from TMB photooxidation in low-NO_x (Panels a–d) and high-NO_x (Panels e–h) experiments.

L305: an extra space before “to”

Author Reply:

The extra space has been deleted in the revised manuscript.

L367: Please add the recent paper by Chen et al. 2020 also demonstrate that OS-228 could be from isoprene-derived SOA.

Author Reply:

We have cited the study of Chen et al. (2020b) and added the related description. Please, refer to the last comment.

L389: The author should also consider adding Zhang et al. 2019 here, which discussed the effects of inorganic sulfates to organosulfates conversion in affecting aerosol growth, multiphase chemistry, and pH.

Author Reply:

The paper by Zhang et al. (2019) has now been cited and the original sentence was modified as follow:

The conversion of inorganic sulfates to organosulfates could cause changes in aerosol growth, multiphase chemistry, and acidity (Zhang et al., 2019; Riva et al., 2019).

L525: As mentioned, OS-228 was observed by Chen et al. 2020 from the aging of isoprene-SOA. Even though the source might be different from the OS-228 here, the author should mention it in the conclusion instead of defining OS-228 as from unknown source.

Author Reply:

We have carefully read the literature suggested by the Referee. Chen et al. (2020b) investigated the heterogeneous OH oxidation of 2-methyltetrol sulfate diastereomers and identified OS at *m/z* 227 as the oxidation product of 2-methyltetrol sulfate diastereomers. Methyltetrol sulfates are significant tracers for isoprene-derived SOA. Therefore, the OH aging of isoprene SOA is also a potential source of OS-228 in the

atmosphere. The inappropriate conclusion has been removed in the revised manuscript. We have added the following text in Sect. 3.1.3 to describe the findings in the study by Chen et al. (2020b).

Page 18, lines 504–509

More recently, Chen et al. (2020b) suggested that heterogeneous OH oxidation of isoprene-derived SOA can contribute to the formation of an organosulfate with molecular weight at 228. Our results show the detection of OS-226, OS-228, OS-240, and OS-268 organosulfates, which are isomers of organosulfates derived from isoprene (Cai et al., 2020), isoprene (Chen et al., 2020b), limonene (Cai et al., 2020), and limonene (Boris et al., 2016), respectively.

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SO_2 and NH_3 emissions enhance organosulfur compounds and fine particles formation from the photooxidation of a typical aromatic hydrocarbon

Zhaomin Yang[1], Li Xu[1], Narcisse T. Tsona[1], Jianlong Li[1], Xin Luo[2], Lin Du[1]

[1]Environment Research Institute, Shandong University, Qingdao, 266237, China
[2]Technology Center of Qingdao Customs, Qingdao, 266003, China

Correspondence to: Lin Du (lindu@sdu.edu.cn)

Abstract. Aromatic hydrocarbons can dominate the volatile organic compounds budget in the urban atmosphere. Among them, 1,2,4-trimethylbenzene (TMB), mainly emitted from solvent use, is one of the most important secondary organic aerosols (SOA) precursors. Although atmospheric SO_2 and NH_3 levels can affect secondary aerosol formation, the influenced extent of their impact and their detailed driving mechanisms are not well understood. The focus of the present study is to examine the chemical compositions and formation mechanisms of SOA from TMB photooxidation influenced by SO_2 and/or NH_3. Here, we showed that SO_2 emission could considerably enhance aerosol particle formation due to SO_2-induced sulfate generation and acid-catalyzed heterogeneous reaction. Orbitrap mass spectrometry (MS) measurements revealed the generation of not only typical TMB products but also hitherto unidentified organosulfates (OSs) in SO_2-added experiments. The OSs designated as unknown origin in earlier field measurements were also detected in TMB SOA, indicating that atmospheric OSs might be also originated from TMB photooxidation. For NH_3-involved experiments, results demonstrated a positive correlation between NH_3 levels and particle volume as well as number concentrations. The effects of NH_3 on SOA composition was slight under SO_2-free conditions but stronger in the presence of SO_2. A series of multifunctional products with carbonyl, alcohols, and nitrate functional groups were tentatively characterized in NH_3-involved experiments based on infrared spectra and MS analysis. Plausible formation pathways were proposed for detected products in the particle-phase. The volatility distributions of products, estimated using parameterization methods, suggested that the detected products gradually condense onto the nucleation particles to contribute to aerosol formation and growth. Our results suggest that strict control of SO_2 and NH_3 emissions might remarkably reduce organosulfates and secondary aerosol burden in the atmosphere. Updating the aromatic oxidation mechanism in models could result in more accurate treatment of particles formation for urban regions with considerable SO_2, NH_3, and aromatics emissions.

1 Introduction

Secondary organic and inorganic aerosols have been observed to account for a considerable fraction of fine particulate matter (aerosol particles ≤ 2.5 μm in aerodynamic diameter, $PM_{2.5}$) during $PM_{2.5}$ pollution events, which had frequently occurred and lasted for days or even weeks in China during the last decade (Huang et al., 2014; Guo et al., 2014). These particles can directly and indirectly impact regional and global climate (Kanakidou et al., 2005), air quality (Zhang et al., 2015), and human health (Lelieveld et al., 2015).

Secondary organic aerosols (SOA) arise predominantly from the oxidation of volatile organic compounds (VOCs) in the atmosphere. Early atmospheric models underestimated the measured SOA mass concentrations in field studies by 1–2 orders of magnitude (Volkamer et al., 2006; Heald et al., 2010). Although recent efforts such as updating missing SOA precursors, accounting unknown processes of gas-to-particle conversion, and improving emission inventories have narrowed the observed gap between the modeled and measured SOA mass, uncertainties still exist in organic aerosol estimates (Shrivastava et al., 2011; Cheng et al., 2021). Inorganic perturbations on SOA formation (Shrivastava et al., 2017) are partly responsible for these uncertainties, and they include the addition of mineral particles (Yu and Jang, 2019), nitrogen oxide (NO_x) (Zhao et al., 2018), ammonia (NH_3) (Hao et al., 2020), and sulfur dioxide (SO_2) (Yang et al., 2020), which can engage in the gas- or particle-phase chemistry and subsequently influence SOA formation and growth (Friedman et al., 2016; Ng et al., 2007; Na et al., 2006). NO_x effects on particle formation are generally known to be pronounced. High levels of SO_2, NH_3, and VOCs have been reported in certain regions such as Guangzhou (Zou et al., 2015), Beijing (Meng et al., 2020), Handan (Li et al., 2017) in China. During haze pollution episodes, Li et al. (2017) observed that SO_2 levels can be up to 200 ppb in Handan, China. A recent study also showed significant increasing NH_3 levels in the atmosphere over the United States and the European Union (Warner et al., 2017). However, less focus has been placed on the SO_2 and NH_3 perturbations on SOA formation and chemical composition. Aerosol particles contain a multitude of compounds with different physicochemical properties. Previous laboratory studies examined the photooxidation of cyclohexene, fuel, and 1,3,5-trimethylbenzene in the presence of SO_2 and reported organosulfates (OSs) formation (Yang et al., 2020; Liu et al., 2017; Blair et al., 2017). The atmospheric oxidation of SO_2 can generate sulfuric acid that is critical for the increase of particle acidity. SO_2-induced acidic sulfate plays an active role in the production of OSs, which have been recognized as significant SOA tracers describing the enhancement in SOA by SO_2 emission (Xu et al., 2015).

OSs are ubiquitous in ambient aerosol particles and they are estimated to account for 3–30% of the organic mass in fine aerosol particles (Surratt et al., 2008; Tolocka and Turpin, 2012). The presence of OSs could alter aerosol morphology (Riva et al., 2019), viscosity (Riva et al., 2019; Zhang et al.,

2019), particle acidity (Riva et al., 2019), phase state (Zhang et al., 2019), hygroscopicity (Estillore et al., 2016; Hansen et al., 2015), and optical properties (Fleming et al., 2019), thereby resulting in large climate effects. A large number of OSs have previously been observed in field measurements but only a few biogenic VOCs can be clearly designated as OSs precursors (Wang et al., 2019b; Shalamzari et al., 2014). Recent field studies reported that some unidentified OSs with C_2–C_{25} skeletons may not be originated from biogenic VOCs and suggested that anthropogenic VOCs may contribute to these OSs formation (Wang et al., 2016; Blair et al., 2017). In addition, Ma et al. (2014) demonstrated that OSs derived from aromatic hydrocarbons contribute to up to 67% of the total OSs mass in Shanghai, China, highlighting the potentially significant role of anthropogenic aromatics in organosulfate formation. While several studies have shown that SO_2 emissions have implications for the SOA burden and OSs formation, detailed characterizations of OSs formation from anthropogenic monocyclic aromatic photooxidation are poorly performed.

NH_3 is the most abundant form of reduced nitrogen and it is ubiquitous in the ambient environment. NH_3 levels increased substantially in recent years and are estimated to continue to increase in the future (Warner et al., 2017). It is established that the increased NH_3 emissions could reduce the effectiveness of $PM_{2.5}$ control by controlling SO_2 and NO_x (Wu et al., 2016; Fu et al., 2017). However, the effects of NH_3 on the formation of aerosol particles have not been well understood. NH_3 has a promoting effect on the formation of new particles (Wang et al., 2020a) where low volatile organic compounds could condense to form SOA in the atmosphere. A previous chamber study reported that the addition of NH_3 could lead to the enhancement in the volume and number concentrations of SOA from α-pinene ozone system (Na et al., 2007). Another study by Babar et al. (2017) utilized newly developed flow reactor and confirmed that the presence of NH_3 can enhance SOA formation from both ozonolysis and photooxidation of α-pinene. Besides α-pinene, the promoting effects of NH_3 on particle formation were also discovered in the photooxidation of aromatics (Chu et al., 2016) and vehicle exhaust (Chen et al., 2019). In contrast, addition of NH_3 decreased aerosol particle formation from the reaction of styrene with ozone owing to the decomposition of products by NH_3 nucleophilic attack (Na et al., 2006). Laboratory evidence suggests that NH_3 can influence SOA composition via the neutralization of organic acids (Hao et al., 2020) and via the NH_3 uptake by carbonyl-containing compounds (Flores et al., 2014). The reaction of organic compounds in particle-phase with NH_3 can decrease gaseous NH_3 concentrations and can enhance the formation of nitrogen-containing organic compounds (Liu et al., 2015b), which are a class of brown carbon and could modify SOA optical properties. The neglect of NH_3 effects on SOA formation might increase the model-measurement disagreement in SOA mass and can lead to an overprediction of NH_3 concentration in the gas-phase, especially in a complex urban environment. Consequently, it is necessary to explicitly explore the influence of NH_3 on aerosol particles formation.

The complex mixture of ozone and fine particles is an emerging environmental problem affecting regional and urban air quality in China (Song et al., 2017), and investigating the chemistry of aromatic hydrocarbons has become greatly important for ozone and $PM_{2.5}$ control because aromatics have high ozone- and SOA-forming potential (Chu et al., 2020). Aromatic hydrocarbons comprise a substantial fraction of the total VOCs at urban locations and even in rural areas (Guo et al., 2006; Ran et al., 2009), and evidence shows that global SOA formation from aromatic hydrocarbons lies in the range of 2 to 12 Tg yr^{-1} (Henze et al., 2008). 1,2,4-Trimethylbenene (TMB) is a small monocyclic aromatic emitted primarily from industrial solvent evaporation (Mo et al., 2021). In the troposphere, TMB is mainly oxidized via hydroxyl radical (OH), producing multigenerational oxidized compounds that can contribute to SOA formation and growth (Zaytsev et al., 2019; Mehra et al., 2020). The OH oxidation of TMB can also generate small dicarbonyls glyoxal and methylglyoxal (Zaytsev et al., 2019), which are significant precursors for light-absorbing SOA formation. In addition, the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCMv3.2/, last access: 23 February 2021) is a near-explicit chemical mechanism that can describe, in detail, the tropospheric degradation of TMB. A recent study reported that identified autoxidation pathways during OH oxidation of TMB are not included in the current MCM and the detected TMB products are more diverse than the products shown in MCM (Wang et al., 2020b). The updates for the OH-initiated oxidation mechanism of TMB can be achieved only when the rate constants, branching ratios and product distributions can be explicitly obtained. However, TMB photooxidation is highly complex and sensitive to environmental conditions. To better understand TMB SOA formation and growth, investigating chemical processes of TMB photooxidation with inorganic perturbation is required.

The mechanisms leading to secondary aerosol formation in the urban environment remain highly elusive and controversial, particularly for the processes related to changes in secondary aerosol mass and chemical composition. Recent studies have suggested that inorganic pollution emissions could perturb SOA formation, yet very little is known about the SO_2 and NH_3 effects on SOA formation. Given the ubiquity of SO_2, NH_3, and TMB in the atmosphere, a key goal of this work is to determine the detailed chemical compositions and formation mechanisms of secondary aerosol from TMB photooxidation with SO_2 and/or NH_3. We investigated the effects of SO_2 and NH_3 on the growth of particles from TMB photooxidation for the first time and discussed the role of inorganic species in TMB chemistry. The chemical composition of TMB SOA was rigorously characterized based on laboratory measurements. We also revealed some hitherto unidentified organosulfates and tentatively proposed relevant formation pathways of products.

2 Experimental methods

2.1 Particle generation

Aerosol particles were produced from TMB photooxidation in the presence of NO_x in a new indoor smog chamber, which consists of a 1.1 m^3 Teflon reactor (0.6 mm Teflon film) housed in a temperature-controlled room. For photooxidation, a panel of black light lamps (F40BLB, GE) were used to provide ultraviolet (UV) irradiation centered at 365 nm. Before each run, the chamber was continually purged with dry and purified air prepared by zero air supply (Model 111, Thermo Scientific, USA) and simultaneously irradiated with UV lights until the concentrations of background contaminants (i.e., NO, NO_2, SO_2, and O_3) were lower than 1 ppb and the particle number concentration was below 5 cm^{-3}.

The TMB photooxidation experiments were carried out by the following steps. First, a known volume of TMB liquid (98%, Aladdin) was transported into the chamber through a heated (80 °C) Teflon tube carried by a flow of zero air. Second, according to experimental design, different quantities of NO (504 ppm in N_2, Qingdao Yuyan Gas Company, China), SO_2 (1013 ppm in N_2, Qingdao Yuyan Gas Company, China), and NH_3 (497 ppm in N_2, Qingdao Yuyan Gas Company, China) were introduced into the chamber from corresponding high-pressure cylinders using calibrated mass flow controllers (D07-7, Beijing Sevenstar Electronics Co., Ltd, China). Note that before the injection of NH_3, the inlet tubes were flushed with NH_3 flow for 30 min to minimize the adsorption losses of NH_3 in the tubes. After all species in the chamber were well mixed (initial concentrations of TMB, NO, and/or SO_2 were constant), black light lamps were turned on, marking the beginning of photooxidation experiments. The chamber was operated in batch mode with a reaction time of approximately 300–360 min. Seed particles were not introduced into the chamber over the course of particle formation experiments. Temperature and relative humidity (RH) inside the chamber were (299 ± 4) K and (25 ± 1) %, respectively. Detailed experimental conditions and results for each experiment are provided in Table 1. Twelve experiments were conducted under four different scenarios. In the first set of experiments (Exps. 1–4, Table1), SO_2 levels in the chamber varied from 0 to 200 ppb while the initial ratio of [TMB] to [NO_x] was kept higher than 10 ppbC ppb^{-1} (low-NO_x condition). The second set of experiments (Exps. 5–8, Table1) were performed under high-NO_x condition ($[TMB]_0/[NO_x]_0$ < 10 ppbC ppb^{-1}) with SO_2 concentration being the only variable (ranged from 0 to 228 ppb). The third part of experiments (Exps. 9–10, Table1) consisted of an irradiation of TMB, NO_x, and NH_3, while the subsequent part of experiments (Exps. 11–12, Table1) consisted of an irradiation of TMB, NO_x, SO_2, and NH_3.

Different physicochemical parameters were measured over the course of photooxidation experiments. A digital thermo-hydrometer (Model 645, Testo AG, Lenzkirch, Germany) was used to measure temperature and RH inside the chamber. The concentrations of NO and NO_x were

measured with a NO-NO_2-NO_x analyzer (model 42i, Thermo scientific, USA), while a Thermo scientific model 43i-TLE pulsed fluorescence SO_2 analyzer was used to measure SO_2 levels throughout the experiments. The O_3 level was monitored with a Thermo scientific model 49i O_3 analyzer. The initial concentration of NH_3 was calculated based on the introduced amount of NH_3 and the reactor volume. The decay of TMB was measured by a gas chromatography (GC, 7890B, Agilent Technologies, USA) equipped with a DB-624 column (30 m × 0.32 mm, 1.8 μm film thickness, Agilent Technologies, USA) and a flame ionization detector (FID). The GC temperature was programmed to increase from 80 to 200 °C at 20 °C min^{-1} rate. Particle size distributions and volume concentrations in all experiments were recorded in situ using a scanning mobility particle sizer (SMPS), which consists of a long differential mobility analyzer (long-DMA, Model 3082, TSI, USA) and a condensation particle counter (CPC, Model 3776, TSI, USA). The long-DMA was available for measuring the particle size distribution in the range of 13.8–723.4 nm while smaller particles between 4.5–162.5 nm were measured with a nano differential mobility analyzer (nano-DMA, Model 3085, TSI, USA). The measured volume concentration in each experiment was converted into particle mass concentration with an estimated particle density of 1.4 g cm^{-3}.

Table 1. Experimental conditions and results for the TMB photooxidation experiments.

Exp.	$[TMB]_0$ (ppb)	[TMB] consumed ($\mu g\ m^{-3}$)	$[TMB]_0/[NO_x]_0$ (ppbC ppb^{-1})	$[NO_x]_0$ (ppb)	$[SO_2]_0$ (ppb)	$[NH_3]_0$ (ppb)	[OH] × 10^{-6} (molecules cm^{-3}) [a]	RH (%)	T (K)	Surface area concentration × 10^{-3} ($\mu m^2\ cm^{-3}$) [b]	N_{max}× 10^{-5} (cm^{-3}) [c]	SOA mass ($\mu g\ m^{-3}$) [d]	SOA yield (%) [e]
1	374	1404	18.9	178	-	-	2.52	25	295	1.08	0.27	52.6	3.8 ± 0.4
2	350	1385	17.3	182	59	-	2.33	24	296	2.33	1.12	97.8	8.2 ± 0.7
3	368	1303	17.3	191	107	-	2.29	25	296	2.82	1.13	164.8	12.6 ± 1.3
4	220	766	10.0	199	200	-	3.00	25	295	3.45	1.40	175.6	17.6 ± 2.0
5	393	1693	7.6	465	-	-	3.62	26	298	1.21	0.29	59.4	3.5 ± 0.4
6	346	1599	6.8	457	68	-	3.44	24	295	2.65	0.93	120.7	7.9 ± 0.7
7	260	1069	5.1	457	114	-	3.12	26	298	2.06	0.98	78.7	8.0 ± 0.7
8	379	1534	7.4	464	228	-	3.06	24	297	3.76	1.10	186.9	12.2 ± 1.2
9	454	1880	8.6	475	-	100	3.42	26	303	1.58	0.45	70.6	3.8 ± 0.4
10	464	1946	9.1	457	-	200	3.37	25	299	2.13	0.60	99.3	5.1 ± 0.5
11	425	1972	8.6	447	227	100	3.51	24	299	4.45	1.57	209.6	12.9 ± 1.3
12	450	1974	8.9	455	234	200	3.32	26	303	4.80	2.00	244.9	13.7 ± 1.4

[a] The average OH concentration was determined from the measured TMB decay. [b] The particle surface area concentration measured by SMPS at 300 min of each experiment. [c] Aerosol particle maximum number concentration. [d] SOA mass concentrations have been wall-loss corrected. For SOA mass calculation, the inorganic mass concentration has been subtracted from the particle mass concentration. [e] Errors in SOA yield were calculated from error propagation using the sum of the uncertainties in TMB data and the systematic error of SMPS.

2.2 Particle collection and analysis

2.2.1 Attenuated total reflectance-Fourier transform infrared spectroscopy analysis

Following 300–360 min of reaction, aerosol samples were collected onto aluminum foils (25 mm, Jowin Technology Co. Ltd.) by a low-pressure impactor (DLPI+, DeKati Ltd, Finland) and were stored at -20 ℃ thereafter until analysis to reduce evaporative losses of aerosol. The chemical functional groups of aerosols were characterized by an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (Vertex 70, Bruker, Germany) with mercury cadmium telluride detector. The ATR-FTIR spectra of aerosol particles in each run were recorded by averaging 64 scans from 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. Prior to each measurement with ATR-FTIR, the surface of the diamond crystal was thoroughly cleaned with ethanol and ultrapure water to rule out interferences of other sources of contamination. The ATR-FTIR spectra of blank aluminum foils were also acquired to confirm the absence of IR absorption by the aluminum foil on which aerosols are collected.

2.2.2 Ion chromatography analysis

Following the ATR-FTIR measurements, aerosol samples were extracted in 3 mL of ultrapure water (Milli-Q water, 18.2 MΩ) under sonication in an ice bath for 30 min. The extracted samples were filtered through polyethersulfone syringe filters (0.22 μm pore size) and subsequently analyzed for their ionic concentrations using an ion chromatography (Dionex ICS-600, Thermo Fisher Scientific, USA) with electrical conductivity detection. A Dionex IonPac^{TM} AS19 column (4 × 250 mm) connected with AG19 guard column (4 × 50 mm, Dionex Ionpac) was used to separate anions. An aqueous solution of 20 mM potassium hydroxide (KOH) prepared by reagent-free controller (Dionex, Thermo Scientific, USA) was used as anion eluent. Cation analysis was carried out with the pair of CG12A guard column (4 × 50 mm, Dionex Ionpac) and analytical column (4 × 250 mm, CS12A, Dionex IonPac^{TM}) and an isocratic 20 mM methanesulfonic acid (CH_4O_3S). The same volume of extract was injected into the ion chromatograph by a six-way valve mounted with a loop of 250 μL. The elution flow rates of KOH and CH_4O_3S were both set to 1 L min^{-1}.

2.2.3 Ultra-high-performance liquid chromatography high resolution mass spectrometry analysis

Laboratory-generated aerosols were also collected on 47 mm polytetrafluoroethylene (PTFE) filters (0.22 μm pore size, Tianjin Jinteng Experimental Equipment, China) using a stainless steel inline filter holder (Sartorius 16254, Sartorius Stedim Biotech GmbH, Germany) with a flow rate of 10 L min^{-1}. The collected samples were wrapped in foil and stored in the freezer (-20 ℃) until mass spectrometry analysis. Filter samples were extracted twice with 5 mL of high-purity methanol

(Optima® LC-MS grade, Fisher Scientific) under sonication in ice for 30 min. The extracts were mixed, filtered with a 0.2 μm pore size PTFE syringe filter (Millipore), and concentrated to near dryness under a gentle stream of high-purity nitrogen. The concentrated samples were reconstituted with ultrapure water (Milli-Q water, 18.2 MΩ) and methanol (Optima® LC-MS grade, Fisher Scientific) with a volume ratio of 50:50. Control mass spectrometry measurements of solvent and extracts from blank PTFE filters were preformed to remove the interferences of solvent and handling protocols. The chemical compositions of aerosols were characterized using an ultra-high-performance liquid chromatography (UPLC, Ultimate 3000, Thermo scientific, USA) coupled to a Q-Exactive Focus Hybrid Quadrupole-Orbitrap mass spectrometry (MS, Thermo Scientific, USA) with electrospray ionization (ESI). The ESI source was operated in both positive (+) and negative (-) ionization mode. Product molecules could be detected as $[M + H]^+$ in the positive ion mode while products could be ionized via deprotonation and were detected as $[M - H]^-$ in the negative ion mode. The following parameters were set for the optimal operation of LC/ESI-MS: spray voltage (+), 3.5 kV; spray voltage (-), -3.0 kV; S-lens RF level (+), 50 V; S-lens RF level (-), 50 V; capillary temperature, 320 °C; sheath gas (nitrogen) pressure, 2.76×10^5 Pa; auxiliary gas (nitrogen) flow, 3.33 L min^{-1}. MS spectra were recorded in the range of *m/z* 50 to 750 in full MS scan with a mass resolving power of 70000 (FWHM at *m/z* 200). The full MS scan was followed by data-dependent MS/MS (dd-MS^2) scans using stepped collision energies of 20, 40, and 60 eV via high-energy collisional dissociation. The resolution was 17500 and an isolation width of 2 *m/z* units was applied for the dd-MS^2 scan. The other parameters for MS^2 experiments were as follow: AGC target, 2×10^5; maximum IT, 50 ms; loop count, 3; minimum AGC target, 1×10^5; apex trigger, 2–6 s; dynamic exclusion, 6 s. The MS instrument was calibrated every five days with standard calibration solutions provided by the manufacturer. The separation of analytes was carried out on an Atlantis T3 C18 column (100 Å, 3 mm particle size, 2.1 mm × 150 mm, Waters, USA) at 35 ℃. The mobile phases consisted of (A) 0.1% formic acid (Optima® LC-MS grade, Fisher Scientific) in ultra-pure water (Milli-Q water, 18.2 MΩ) and (B) 0.1% formic acid in methanol (Optima® LC-MS grade, Fisher Scientific). The injected volume of samples was 2 μL in this study. Samplers were eluted using a 60-min gradient elution program with a flow rate of 200 μL min^{-1}: initially set to 3% B over the first 3 min, the concentration of eluent B was increased linearly to 50% in 22 min, from 50% to 90% from 25 min to 43 min, then it was decreased from 90% to 3% from 43 to 48 min, and finally kept at 3% for 12 min. The chemical formulas of observed ions were proposed based on reaction pathways, chemical consideration, and measured *m/z* value with a mass tolerance of ± 5 ppm. All data were recorded and processed using Xcalibur V4.2.47 software package.

2.3 Wall losses of vapors and particles

The SOA yield, usually used to quantify the propensity of a parent hydrocarbon to form SOA, could be determined as the ratio of the generated particle mass to the amount of consumed parent hydrocarbon. The particle and vapor wall depositions in chambers can lead to the underestimation

of the SOA yield. In order to determine the particles wall loss rates, we carried out independent wall loss experiments using ammonium sulfate particles. An aqueous solution of ammonium sulfate was fed to a constant output atomizer (Model 3706, TSI, USA) to produce droplets, which passed simultaneously through a silica gel diffusion dryer to introduce dry particles into the chamber. The size distributions of ammonium sulfate particles were measured by SMPS for 480 min. Almost identical humidity ((25 ± 1) %) condition was achieved among each experiment. The wall losses of particles are size-dependent and, thus, we used a size-dependent particle wall-loss correction approach, which is described in detail in the Supplement. The size-dependent loss rate (k) of ammonium sulfate particles could be expressed as $k = 5.5\times10^{-6}\times d_p^{1.05} + 0.18\times d_p^{-1.19}$ and was applied to correct the aerosol particle concentrations. The wall loss rates of NO, NO_2, SO_2, and TMB were determined to be 2.0×10^{-6}, 3.9×10^{-6}, 4.0×10^{-7}, and 2.3×10^{-6} s^{-1}, respectively, indicating that the wall losses of these species were negligible over the course of the experiment. However, gas-phase species that could deposit to the chamber walls include not just the parent hydrocarbon, in this case TMB, but also the oxidation products, which in general are not all totally monitored and characterized. It is difficult to correct directly and accurately for the impact of vapor wall losses on the SOA yield. Therefore, the SOA yield in this work is only the lower limit. Here, the underestimation of SOA yields due to vapor wall losses was determined by the method in the study of Zhang et al. (2014). In brief, the effect of vapor wall losses on SOA yield significantly arose from the competition between vapors condensation onto aerosol particles versus vapor depositions to chamber walls. The extent to which vapor wall depositions influence the SOA yield could be estimated by the ratio of the average timescale of gas-particle partitioning during the photooxidation experiments to the timescale of vapor wall deposition. The evaluated results suggested that the SOA yield could be underestimated by a factor of 1.8 to 8.4 without accounting for vapor losses.

3 Results and discussion

3.1 Effects of SO_2

3.1.1 Particle formation and growth in SO_2-added photooxidation

To evaluate the impacts of SO_2 on aerosol formation and growth from TMB photooxidation, a series of experiments were conducted with various initial SO_2 levels under both low- and high-NO_x conditions. Evolutions of the number distributions of secondary aerosols with particle size within 4.5–162.5 nm are provided in Fig. 1. There was no new secondary aerosol formation in the beginning of photooxidation. After a period of time, particles were burst produced and the number concentration of particle increased rapidly. At the same time, the particles continuously grew via condensation and coagulation mechanisms, consistent with a previous study (Jorga et al., 2020). After 300 min UV irradiation without SO_2 introduction, the total maximum number concentration of aerosol particles was only 2.7×10^4 cm^{-3} and 2.9×10^4 cm^{-3} under low-NO_x (Exp. 1) and high-

NO_x (Exp. 5) experiments, respectively. Interestingly, the particle maximum number concentration considerably increased with increasing SO_2 levels, regardless of low- or high-NO_x conditions (Table 1). As shown in Fig. 1, although the unimodal particle size distribution in the presence of SO_2 was similar to that in its absence, particles with mobility diameter ranging from 10 to 80 nm, especially, dominated particle number concentrations with SO_2 addition. The time series of total ultrafine particles (diameter < 100 nm) number concentration are shown in Fig. S2, where it is seen that SO_2 considerably enhanced ultrafine particle formation. Ultrafine particles are more harmful to human than larger particles because they can more easily penetrate deep into the lungs and blood circulation (Terzano et al., 2010). Our results indicate that SO_2 concentration is a key parameter for ultrafine particle formation. It has been suggested that reducing the number concentration of ultrafine particles can decrease mortality, highlighting again the need to continue to implement strict SO_2 emission standards (Fuzzi et al., 2015).

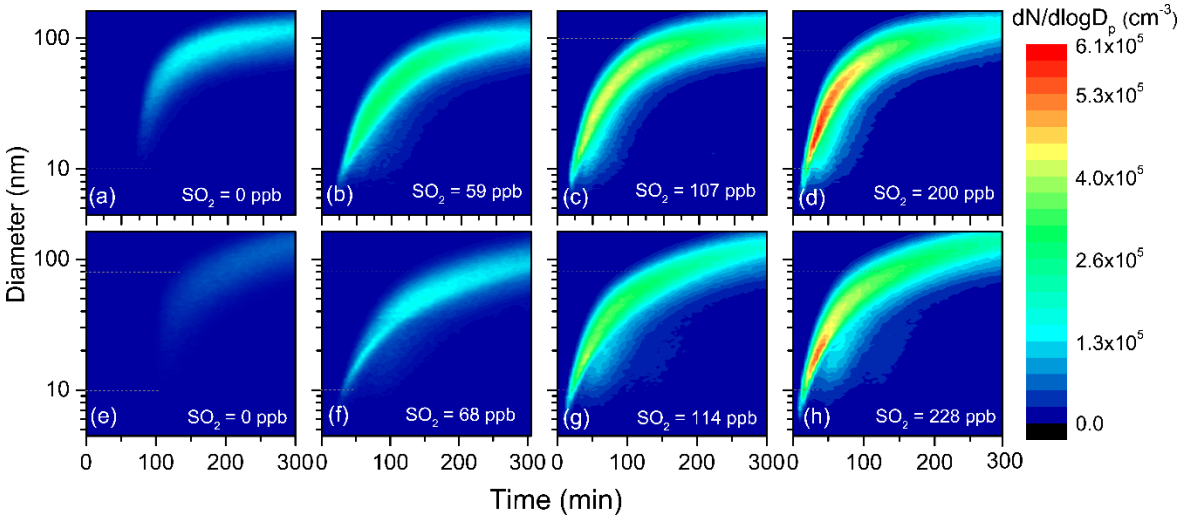

Figure 1. Evolutions of the number distributions of aerosol particles generated from TMB photooxidation in low-NO_x (Panels a–d) and high-NO_x (Panels e–h) experiments.

To fully give account for effects of changes in SO_2 emissions on aerosol formation, the key particle phase parameters (i.e., nucleation time, initial growth rate, and particle mean diameter) as a function of SO_2 levels are further compared in Fig. 2. In the present study, the SMPS instrument can measure particle larger than 4.5 nm and, therefore, the nucleation time here is defined as the time required for new secondary aerosols to grow to 4.5 nm after the lights have been turned on (Wyche et al., 2009). The particle size rapidly increased within 30 min after nucleation, and gradually reached a stable level within 300 min photooxidation (Fig. 1). Consequently, the initial growth rate (GR_{inital}), calculated based on the method of Kulmala et al. (2012), is defined as the particle growth rate within 30 min after nucleation (Li et al., 2018). The mean diameter reported in this work represents the particle mean diameter measured at 300 min in each experiment. From Fig. 2, a significant negative correlation was found between nucleation time and initial SO_2 level. Furthermore, when similar

amounts of SO_2 were introduced to the reaction mixture, the gap between the nucleation time of low-NO_x and high-NO_x would be reduced, which is in agreement with a previous study (Zhao et al., 2018). Under SO_2-free condition, new secondary aerosol could be generated by homogeneous nucleation involving key intermediate products of TMB oxidation. The delay time for particle formation largely corresponds to the time required for intermediate products to build to sufficient concentrations in such a way that their saturation vapor pressure relative to the particle phase is exceeded. New secondary aerosol consists of later stage oxidation products, which might be also responsible for the delayed occurrence. It was demonstrated that higher OH concentration in the chamber could result in faster particle formation (Sarrafzadeh et al., 2016). However, the average OH concentration in SO_2-free experiments is comparable with that in SO_2-added experiments (Table 1). There has been a gradual fall in the mixing ratio of SO_2 (Fig. S3) that could be oxidized to sulfuric acid (H_2SO_4) during TMB photooxidation. The formed H_2SO_4 could induce nucleation and increase the nucleation rate (Zhao et al., 2018; Blair et al., 2017), and these processes are responsible for the short nucleation time observed in the TMB/NO_x/SO_2 regime (Wyche et al., 2009). The mean diameter of secondary aerosol decreased by 4–10 nm when 60–70 ppb of SO_2 was included in the matrix (Fig. 2). In contrast, at high-SO_2 levels ($[SO_2]_0$ > 100 ppb), increase in the initial SO_2 concentration led to an increase in particle mean diameter, regardless of low- or high-NO_x. The initial growth rate also showed a similar dependence on the SO_2 level as presented in Fig. 2. The nonlinear response of the particle mean diameter to SO_2 initial level is similar to the findings of Julin et al. (2018), who found the response of particle size distribution to NH_3 emissions to be also nonlinear. Aerosol particles can grow in different ways such as gas-particle partitioning of semi-volatility organic compounds (SVOCs). Since the evaporation of SVOCs is important after partitioning to the particle phase, the rate at which SVOCs participate in the particle growth is lower than their condensation rate. However, recent advances give an insight that the particle-phase chemistry such as heterogeneous reactions of SVOCs are substantially pronounced for the particle growth (Shiraiwa et al., 2013; Paasonen et al., 2018; Apsokardu and Johnston, 2018). Organosulfates can be produced by particle-phase reactions involving interactions between organics and inorganics. In this work, organosulfates were only detected in SO_2-involved photooxidation, indicating that additional particle-phase reactions can occur under SO_2-involved conditions. Increasing the initial SO_2 level could induce the formation of more sulfate (Fig. S4) and the enhancement in the particle acidity during photooxidation (Liu et al., 2016; Kroll et al., 2006). The elevated particle acidity can promote more SVOCs to transform into low-volatile products such as organosulfates in the particle phase, thereby promoting the particle growth (Lin et al., 2014; Lal et al., 2012). Then, additional SVOCs could be further transferred from the gas phase to the particle phase to increase the particle size. However, the particle mean diameter in low-SO_2 ($[SO_2]_0$ < 100 ppb) experiments is smaller than that in SO_2-free experiments. Our result is in line with the study of Wyche et al. (2009), who attributed this phenomenon to the larger number of particles produced under SO_2-involved condition. The presence of 59 ppb SO_2 caused the maximum number

concentration of particles to increase by 8.5 × 10^4 cm^{-3} under low-NO_x condition. When the SO_2 level increased from 0 to 68 ppb in high-NO_x experiments, the corresponding particle number concentration increased from 2.9 × 10^4 to 9.3 × 10^4 cm^{-3}. Therefore, the amounts of products that condensed onto each aerosol particles significantly decreased in low-SO_2 experiments, which could result in the decrease in particle diameter (Liu et al., 2015a). The promoting effect of particle-phase chemistry on the particle size growth may not offset the inhibiting effect of the emergence of large number of particles on the particle size growth, thereby leading to the low particle diameter in low-SO_2 experiments.

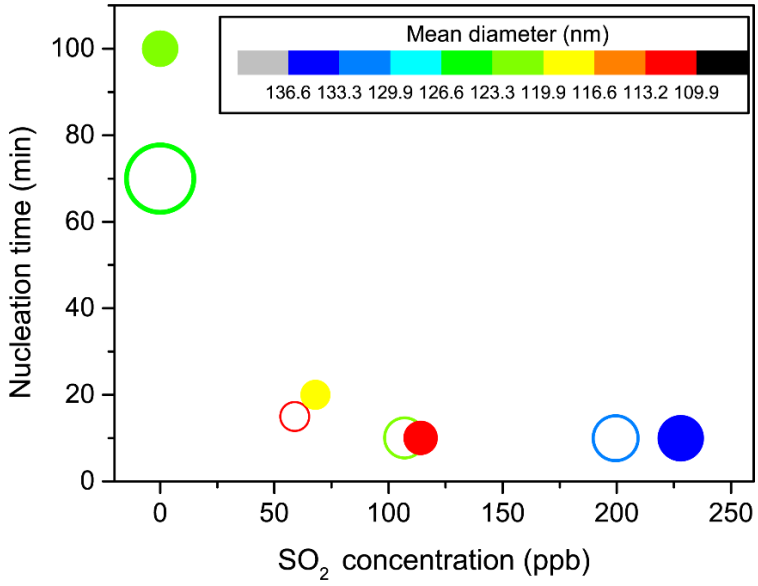

Figure 2. Particle nucleation time as a function of initial SO_2 concentration under low-NO_x (open circles) and high-NO_x (solid circles) conditions (Exps. 1–8). The symbol color indicates the particle mean diameter and symbol size represents the particle initial growth rate. Values of the particle parameters are listed in Table S1.

3.1.2 SOA yield in SO_2-added photooxidation

The particle volume concentration as a function of TMB consumption is presented in Fig. 3, where it can be observed that the particle formation increased with increasing initial SO_2 levels regardless of low- or high-NO_x conditions. The present result is consistent with a previous research, which found that limonene SOA formation is significantly promoted with SO_2 addition (Ye et al., 2018). SO_2 was found to perturb particle formation by inducing chemical reactions in the gas- and particle-phase (Wang et al., 2019a; Friedman et al., 2016). We are unable to fully rule out the SO_2 impacts on gas-phase chemistry. However, the decay of TMB was essentially unchanged when SO_2 was introduced into the chamber (Fig. S5), which suggests the unlikeliness of SO_2 addition to affect the gas-phase chemistry of TMB photooxidation (Kleindienst et al., 2006). Instead, it is more likely

attributed to the formation and condensation of H_2SO_4 and/or the enhancement of organic aerosols formation. We assumed full conversion of the consumed SO_2 into H_2SO_4 aerosol particles and found that the contribution of the formed H_2SO_4 to the increase in particle volume concentration was less than 100% (See Sect. S2). In addition, pure SO_2 oxidation experiments without TMB addition also indicated that the enhancement in aerosol particles by SO_2 introduction cannot be solely attributed to inorganic aerosol formation (See Sect. S2). To calculate the net SOA yield, the inorganic mass concentration was subtracted from the particle mass concentration based on IC measurements of generated particles. The influence of SO_2 initial level on SOA yield can be seen in Table 1 as high SO_2 levels contribute to produce somewhat high SOA yields. Figure 4 compares the SOA yields obtained from the present work with those found in previous studies with similar experimental conditions. The SOA yields from the two SO_2-free experiments are comparable to that reported from the study of Liu et al. (2012) and fit quite well with the yield curve of Odum et al. (1996). The SOA yields in our TMB/NO_x photooxidation experiments were 3.8% and 3.5%, which were closed to 3.9% and 4.2% derived from yield curve of Odum et al. (1996) under same mass concentration. In contrast, with similar mass concentration, the SOA yields in SO_2-added regimes were higher than those in previous studies (Odum et al., 1996; Liu et al., 2012). Here the neutralization degree of particle, which was calculated as the molar ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- (Lin et al., 2013), was used as a tool to roughly estimate the aerosol acidity of collected particle samples. The value of neutralization degree were lower than 1 in this work, indicating acidic aerosols (Lin et al., 2013). The increase in aerosol acidity could be largely responsible for the observed enhancements in SOA formation in SO_2-invloved experiments. The OH oxidation of TMB can result in the formation of multifunctional carbonyl compounds (Liu et al., 2012; Zaytsev et al., 2019), which could promote SOA formation via acid-catalyzed heterogeneous reactions. In addition, the particle surface area concentrations significantly increased with increasing SO_2 initial concentrations in both low-NO_x and high-NO_x conditions (Table 1), which might also result in the enhancement in the SOA yield. Besides gas-particle partitioning of SVOCs, the fates of SVOCs in the chamber also include chemical reactions and chamber wall losses. Therefore, in the batch-mode chamber experiments, the gas-particle partitioning of SVOCs have a great sensitivity to particle surface areas (Zhang et al., 2015; Han et al., 2019). Recently, Zhao et al. (2018) examined the SO_2 effects on the SOA formation and suggested that providing additional particle surfaces by SO_2-induced new particle formation leads to the increase in SOA yield. The effects of the particle surface area concentration on organic aerosol formation were explored by Han et al. (2019), who also found that increasing the particle surface area concentrations can significantly increase the organic aerosol mass yield due to greater partitioning of semi-volatility organic products to the particle-phase. Increasing the particle surface area can limit the gas-wall interactions of organic vapors and is favorable for the movement of more SVOCs from the gas phase to the particle side (Han et al., 2019). These additional SVOCs can also undergo further particle chemistry such as acid-catalyzed heterogenous reactions to strongly enhance aerosol particle formation in TMB/NO_x/SO_2 photooxidation (Apsokardu and

Johnston, 2018).

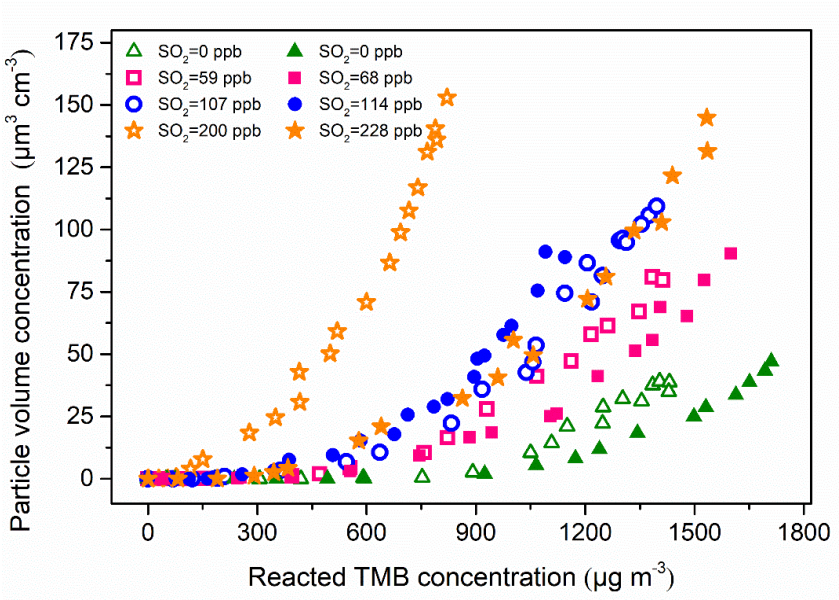

Figure 3. Growth of particle volume concentrations from TMB photooxidation as a function of TMB consumption for eight experiments with different initial SO_2 concentrations (Exps. 1–8). The open symbols and solid symbols represent low- and high-NO_x experiments, respectively.

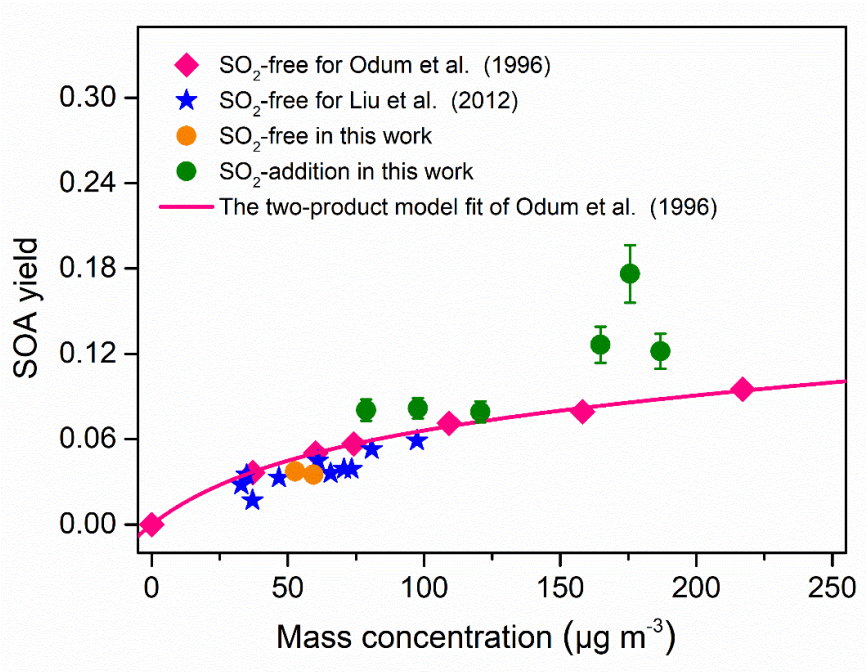

Figure 4. Comparison of SOA yields from TMB photooxidation as a function of SOA mass concentration with data reported from literature. The SOA density in the whole study was assumed to be 1.4 g cm^{-3}. The error bars represent errors in the SOA yield results and the errors were calculated from error propagation using the sum of the uncertainties in TMB data and the systematic error of SMPS. The SOA yields for Liu et al. (2012) were extracted from Table 1 in the study. The pink line is the best fit two-product model for the SOA yields and was extracted from Figure 2 in the work of Odum et al. (1996).

3.1.3 Particle chemical composition in SO_2-added photooxidation

In order to investigate the effects of SO_2 on the chemical composition of aerosol particles, the particles were first characterized by ATR-FTIR. Figure 5 compares the characteristic ATR-FTIR spectra of particles formed from the photooxidation of TMB under different conditions and the detailed information on the assignment of absorption peaks are given in Table S2. For the samples collected from TMB/NO_x photooxidation, the particles exhibited an O-H stretch at 3600–3000 cm^{-1} as shown in Fig. 5(a) and (b). The C=O stretch of carbonyl at 1720 cm^{-1} suggests that aldehydes, ketones, and carboxylic acids are significant particle components, while the absorptions at 844 cm^{-1} (NO symmetric stretch), 1284 cm^{-1} (NO_2 symmetric stretch), and 1647 cm^{-1} (NO_2 asymmetric stretch) are the characteristic peaks of organic nitrates. The slight absorbance at 941 cm^{-1} indicates the presence of peroxides containing O-O groups. Interestingly, compared with the particles from TMB/NO_x experiments, there was a new peak at 615 cm^{-1} for the particles generated from TMB/NO_x/SO_2 experiments, regardless of low- or high-NO_x conditions. The 615 cm^{-1} peak is characteristic of inorganic sulfates, and further highlights that the presence of SO_2 promotes the formation of inorganic sulfates as pointed out in previous studies (Chen et al., 2019; Liu et al., 2016). The strong absorption at 1081 cm^{-1} arises from the S=O bands in the particle components. Field and laboratory studies have reported that inorganic sulfate could convert into organosulfur compounds in the atmosphere (Riva et al., 2019; Nestorowicz et al., 2018). Therefore, the peak at 1081 cm^{-1} may be mainly from the absorption of both inorganic sulfates and organosulfur compounds.

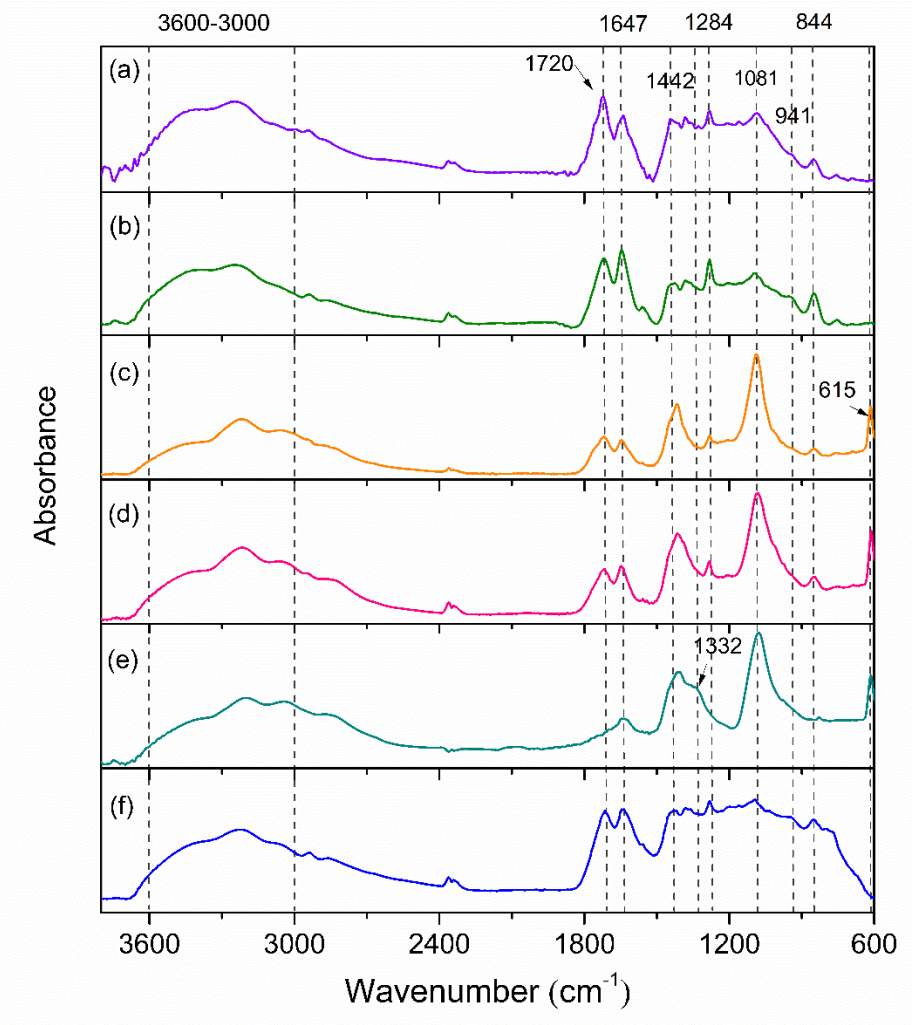

Figure 5. ATR-FTIR spectra of aerosol particles generated from TMB/NO_x (a, Exp. 1; b, Exp. 5), TMB/NO_x/SO_2 (c, Exp. 4; d, Exp. 8), TMB/NO_x/NH_3/SO_2 (e, Exp. 12), and TMB/NO_x/NH_3 (f, Exp. 10) photooxidation.

The chemical compositions of particles generated in TMB/NO_x and TMB/NO_x/SO_2 photooxidations were further measured with high-resolution mass spectrometry (HRMS), to determine whether organosulfur compounds were formed in SO_2-added experiments. The formation of organosulfur compounds was recognized by the oxidation mechanism and the loss of characteristic fragment ions at *m*/*z* 79.95 (SO_3^-), 80.96 (HSO_3^-), and 96.96 (HSO_4^-) in MS/MS spectra (Figs. S7-S8). The list of compounds observed in this work along with molecular weights (MW), measured masses and proposed structures are presented in Table S3. In SO_2-free experiments, the major aerosol components were multifunctional alcohols, peroxides, organic nitrates, ketoaldehydes, and ketocarboxylic acids. With the same analytical methods, the same products were also observed in SO_2-added photooxidation. The most striking result to emerge from Table S3 is that ten organosulfates (OS-214, OS-226, OS-228, OS-240, OS-242, OS-244, OS-268, OS-300, OS-316, and OS-345) and two organic sulfonates were only detected in filter samples collected from the

TMB/NO_x/SO_2 photooxidation experiment, indicating that SO_2 emissions in the atmosphere can alter the aerosol formation chemistry and thus influence the aerosol chemical composition. To the best of our knowledge, this is the first time the ten organosulfates are identified in TMB/NO_x/SO_2 photooxidation experiments. Recently, some sulfur-containing compounds from field measurements were designated as compounds of unknown origin. For example, the MW 214 organosulfate has been detected in $PM_{2.5}$ collected from the highly polluted megacity Shanghai (Cai et al., 2020). However, the VOC precursor for this organosulfate formation was not reported. The MW 242 organosulfate found in Baengnyeong Island was also classified as organosulfur of unknown origin (Boris et al., 2016). O'Brien et al. (2014) found the formation of MW 228 organosulfate in ambient aerosol particles but its specific source was not pointed out. Evidence from this study suggests that TMB photooxidation in the presence of SO_2 might contribute to the formation of these organosulfates (MW = 214, 228, and 242) in the ambient air. Importantly, an organosulfur compound with a formula of $C_7H_{12}O_7S$ (MW = 240) was observed in ambient fine aerosols and was tentatively assigned to an oxidation product of anthropogenic 1,3,5-trimethylbenzene (Boris et al., 2016). The finding of the current study suggests that the organosulfur compound (MW = 240) may also be produced from the photooxidation of 1,2,4-trimethylbenzene in the presence of SO_2. In addition, the MW 226, 240, and 268 organosulfur compounds were designated as biogenic-derived organosulfates in previous field studies (Cai et al., 2020; Boris et al., 2016). More recently, Chen et al. (2020b) suggested that heterogeneous OH oxidation of isoprene-derived SOA can contribute to the formation of an organosulfate with molecular weight at 228. Our results show the detection of OS-226, OS-228, OS-240, and OS-268 organosulfates, which are isomers of organosulfates derived from isoprene (Cai et al., 2020), isoprene (Chen et al., 2020b), limonene (Cai et al., 2020), and limonene (Boris et al., 2016), respectively. More studies need to be undertaken to differentiate various sources of organosulfates in the ambient aerosols through chemical synthesis of authentic organosulfates standards.

The mechanisms describing the formation of OS-226, OS-228, OS-240, OS-242, OS-244, OS-300, OS-316, and OS-345 are proposed in Fig. 6. Following analogous mechanisms for toluene photooxidation, the oxidation of TMB is dominantly initiated by OH addition to the benzene ring to form TMB-OH adduct, which can react with O_2 through recombination to produce bicyclic peroxy radical. It has been established that a series of ring-retaining (product A in Fig. 6) and ring-opening products (products B, C, and D in Fig. 6) can be generated by the further reaction of bicyclic peroxy radical in the presence of NO (Zaytsev et al., 2019; Li and Wang, 2014). Both ring-opening and ring-retaining compounds are expected to contribute significantly to organosulfate production. Here, we take unsaturated ketoaldehyde (product C in Fig. 6) as an example to describe the possible formation mechanism of organosulfate observed in the present study. The reaction of OH with compound C involves OH addition to unsaturated C=C bonds to form an alkyl radical, which can react subsequently with O_2 to yield organic peroxy radical. Further reactions of organic peroxy

radical can follow two different pathways. One pathway is that the organic peroxy radical undergoes a 1,5-H-shift isomerization to form a new acyl radical. Insight from a previous review suggested that acyl radical react with O_2 to yield acylperoxy radical, which could further react with HO_2 to form multifunctional hydroperoxide (Ziemann and Atkinson, 2012). The second channel is the reaction of organic peroxy radical with HO_2 to produce hydroperoxide, terminating directly the radical chain. Acid-driven heterogeneous chemistry of hydroperoxide has been previously adopted to explain the generation of certain OSs (Riva et al., 2016a; Riva et al., 2016b). With the presence of sulfuric acid formed by the oxidation of SO_2 by OH, TMB-derived hydroperoxides can be hydrolyzed by H^+ and then react with inorganic SO_4^{2-} to form organosulfates. The conversion of inorganic sulfates to organosulfates could cause changes in aerosol growth, multiphase chemistry, and acidity (Zhang et al., 2019; Riva et al., 2019).

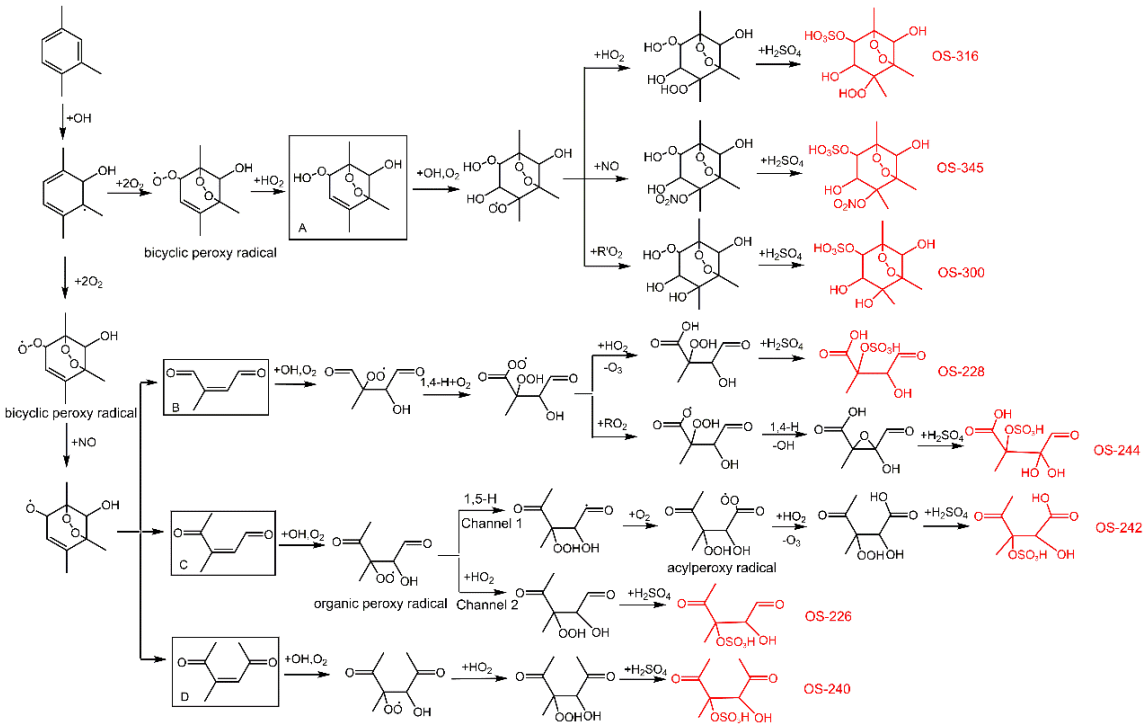

Figure 6. Proposed mechanisms for organosulfate formation from the photooxidation of TMB in the presence of SO_2. The black boxes mark the ring-opening and ring-retaining products suggested in previous studies (Li and Wang, 2014; Zaytsev et al., 2019). The compounds in red are organosulfates detected by UPLC-HRMS in this work.

The MW 228 and 230 organic sulfonates were assigned as sulfonates containing an aromatic ring based on accurate mass measurements and comparison of mass fragmentation patterns with other aromatic sulfonates (Riva et al., 2015a). MS/MS spectra and the proposed fragmentation schemes of sulfonates are reported in Fig. S8. For MW 228 sulfonate, the MS/MS spectra showed the fragment ions at *m/z* 79.95721 ($SO_3^{\cdot-}$), 118.96625 ($C_8H_7O^{\cdot}$, M - $SO_3^{\cdot-}$ - CO), and 163.04025 ($C_9H_7O_3^-$, M - SO_2) as presented in Fig. S8. For the MW 230 sulfonate, the fragment of parent ion

at *m*/*z* 229.01706 could occur by the loss of 44 mass units to give the product ion at *m*/*z* 185.02777 (Fig. S8). The loss of 79.95747 mass units as sulfite radical is in accord with the MS/MS spectra of aromatic sulfonates generated from the photooxidation of polycyclic aromatic hydrocarbons (Riva et al., 2015b). A recent field measurement demonstrated that aromatic organosulfur compounds account for a substantial fraction of total organosulfur compounds in Shanghai, China, highlighting the importance of aromatic organosulfur compounds (Ma et al., 2014). Aromatic sulfonates formation from the photooxidation of TMB in the presence of SO_2 was unexpected and the exact formation pathway of the aromatic sulfonates warrants further investigation.

3.2 Effects of NH_3

3.2.1 Particle formation and growth in NH_3-involved photooxidation

High-NO_x photooxidation experiments were carried out in the presence/absence of NH_3. The average OH concentrations were similar for each experiment within 300 min of irradiation (Table 1). Figure 7 displays the volume and number concentrations of aerosols as a function of time in different photooxidations (Exps. 5, 8–12). TMB was oxidized to produce many secondary aerosols under continuous UV irradiation. The volume concentrations of aerosol particles have a clear positive correlation with NH_3 initial level for all conditions. However, the effect of NH_3 on particle formation was not as pronounced as that of SO_2 with similar concentration (Fig. 7). In TMB/NO_x/NH_3 photooxidation, the net SOA yield increased slightly from 3.5% to 5.1% as NH_3 initial level increased from 0 to 200 ppb (Table 1). Our result is consistent with the finding of Chen et al. (2020a), who showed that NH_3 did not significantly affect SOA formation from toluene/NO_x photooxidation under dry condition. Interestingly, SMPS measurements demonstrated that the coexistence of SO_2 and NH_3 can considerably promote secondary aerosol formation (Fig. 7). After subtracting the inorganic components, it was seen that the net SOA yield could increase to 13.7% with the introduction of 200 ppb NH_3 and 234 ppb SO_2, indicating the synergetic effects of NH_3 and SO_2 (Chu et al., 2016). The flux of the gas-phase products diffusing to a particle partly depends on the surface area of the particle. The coexistence of SO_2 and NH_3 promoted the increase in particle surface area concentrations (Table 1). The ability of particle formation originating from gas-to-particle conversion may be significantly stronger with SO_2 and NH_3 introduction, leading to the enhancement in particle formation. The total number concentrations of aerosol particles increased rapidly in all experiments after nucleation was initiated as shown in Fig. 7 (b). After reaching the maximum concentration, the number density of particles declined gradually because of particles coagulation and deposition to the chamber walls. Increasing the NH_3 level to 200 ppb enhanced the particle maximum number concentration by factors of 2.0 and 1.7 under SO_2-free and SO_2-involved conditions, respectively. Our results are valuable in terms of the potential of NH_3 emission reductions to improve air quality by decreasing total particle number concentrations.

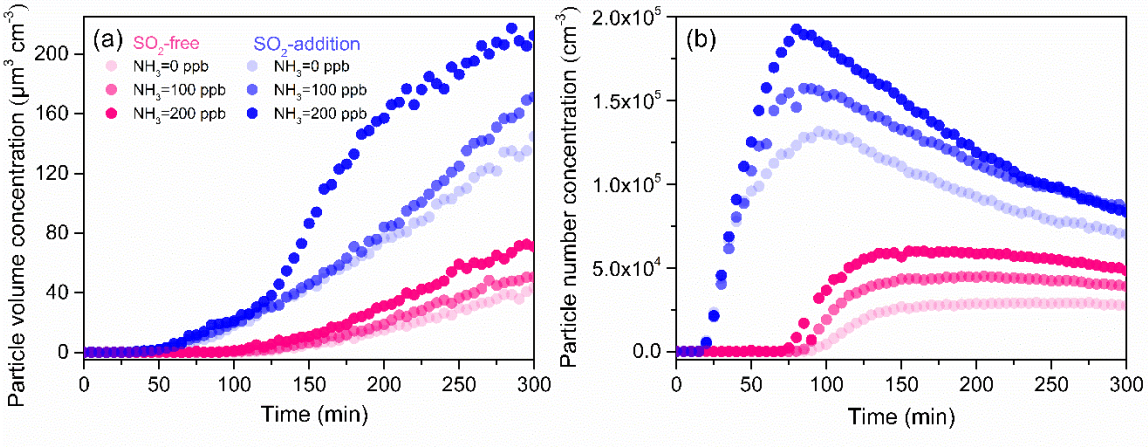

Figure 7. Time evolutions of the volume (a) and number (b) concentrations of aerosol particles from TMB photooxidation with different initial NH_3 levels under SO_2-free and SO_2-addtion (~ 230 ppb) conditions.

Once generated, aerosol particles need to grow to a larger size (> 50–100 nm) before they exert significant impact on global climate and public health. To explore the effects of NH_3 on particle growth, the initial growth rate of aerosol particles from different experiments are also compared in Fig. S9. In SO_2-free experiments, the increase in NH_3 initial concentrations led to remarkable increase of the initial growth rate of aerosol particles. High initial growth rates were also found in the photooxidation of other aromatics such as toluene and o/m/p-xylene with NH_3 addition (Li et al., 2018). This result may be explained by the fact that under SO_2-free condition, NH_3 mainly reacts with acids to produce ammonium salts. Previous studies have reported that ammonium salts could partition into the initial growth process of new secondary aerosol particles and thus increase the particle initial growth rate (Li et al., 2018; Zhu et al., 2014). More interestingly, NH_3 level did not substantially affect the initial growth rate of particles in the presence of SO_2 (Fig. S9). The results in Fig. 7 have demonstrated that the synergetic effects of NH_3 and SO_2 can promote new particle formation (Lehtipalo et al., 2018). In SO_2-involved experiments, NH_3 molecules tend to promote new particles formation rather than particles growth. Note that these effects of NH_3 on particle initial growth might be more complex in the ambient air with high levels of SO_2, NH_3, NO_x, VOCs than current smog chamber experiments.

3.2.2 Particle chemical composition in NH_3-involved photooxidation

The ATR-FTIR spectra of aerosol particles from NH_3-added experiment are also given in Fig. 5. A previous study suggested that the absorbances at 3310–3360 cm^{-1} and 1550–1650 cm^{-1} can be assigned to N-H stretch and C-N-H bend in secondary amine molecules, respectively (Babar et al., 2017). However, no evidence of secondary amine formation was detected and no clear FTIR spectra

differences between aerosols from TMB/NO_x experiment and aerosols from TMB/NO_x/NH_3 photooxidation were found in this work (Fig. 5). It has been recently discovered that the conversion of oxidized organics to nitrogen-containing compounds in the presence of NH_3 is more likely to occur in high RH condition (Zhang et al., 2020). NH_3 uptake by TMB-derived aerosol particles may be limited to the aerosol surface under low RH condition (RH < 20%) (Bell et al., 2017). The amounts of secondary amine compounds formed from the NH_3 uptake by aerosol may be small, resulting in no characteristic peaks of secondary amine in ATR-FTIR spectra. Surprisingly, the effects of NH_3 on aerosol chemical compositions were increasingly important under SO_2-rich condition. As displayed in Fig. 5(e), the strong C=O band at 1720 cm^{-1} converted to a shoulder upon NH_3 addition to the TMB/NO_x/SO_2 reaction system. In addition, the C-N stretch at 1332 cm^{-1} was observed in TMB/NO_x/SO_2/NH_3 photooxidation (Fig. 5). The particle-phase C-N stretch has been also characterized in m-xylene photooxidation experiments with NH_3 addition and was suggested to account for nitrogen-containing compounds (Liu et al., 2015b). A smog chamber study also found that the coexistence of SO_2 and NH_3 substantially enhanced the formation of nitrogen-containing compounds from the photooxidation of toluene (Chu et al., 2016). In the current work, the presence of SO_2 could promote the increase in particle acidity. Elevating particle acidity could facilitate the reaction of NH_3/NH_4^+ with carbonyl-containing compounds, leading to the formation of nitrogen-containing organic compounds (Liu et al., 2015b).

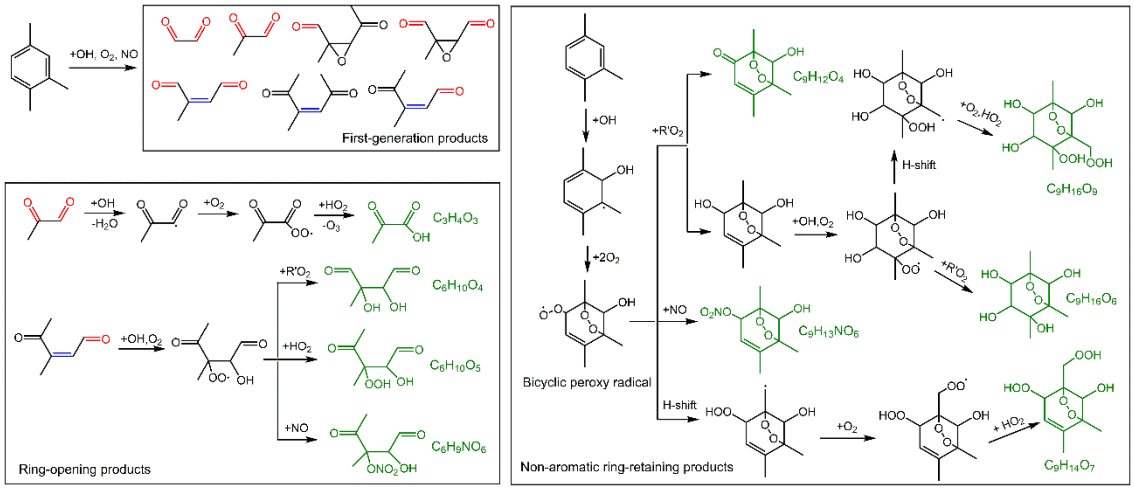

Figure 8. Simplified formation mechanism of the detected products in SOA formed from NH_3-involved photooxidation. Some observed products are produced through same chemical mechanism and for simplicity, only one product is drawn in this figure as an example.

The MS measurement results are consistent with FTIR analysis. As shown in the MS spectra of aerosol samples (Fig. S10), under SO_2-free condition, the presence of NH_3 did not result in considerable changes in peak numbers and abundance for both positive ion mode and negative ion mode. NH_3 could slightly enhance SOA formation in SO_2-free experiment as mentioned in Sect. 3.2.1. Therefore, the NH_3-induced changes in the absolute concentrations of organic components

might be small in SO_2-free experiments, leading to similar mass spectra for Fig. S10(a) and Fig. S10(b). In addition, the major products (Table S4) are likely generated by similar chemical mechanisms (Fig. 8), which are not sensitive to the change in initial NH_3 levels under current experimental conditions. First, the photooxidation of TMB in the presence of NO can result in the formation of bicyclic oxy radicals that could decompose to a series of ring-opening products including biacetyl, epoxy-dicarbonyl, and carbonylic products (Li and Wang, 2014). As depicted in Fig. 8, the first-generation products could be further oxidized by OH. For example, oxidation of methylglyoxal by OH can proceed through abstraction of the aldehydic hydrogen to form the $CH_3C(O)C(O)^{\cdot}$ radical, which may react with O_2 and then with HO_2 to form pyruvic acid. Second, bicyclic peroxy radical (BPR) is a key intermediate for the formation of non-aromatic ring-retaining products. Reactions of BPR with $R'O_2$ can form either bicyclic carbonyl and bicyclic alcohol, which further undergoes OH oxidation to yield the $C_9H_{16}O_6$ and $C_9H_{16}O_9$ compounds. BPR can produce bicyclic organonitrates by reaction with NO, and can also undergo intramolecular H-shift followed by O_2 addition to form a new bicyclic peroxy radical. The new bicyclic peroxy radical reacts with HO_2 to generate highly oxygenated organic molecules, consistent with a recent study (Wang et al., 2020b). To our knowledge, NH_3 does not basically affect the reaction of free radicals in gas-phase during the photooxidation of TMB. Generally, NH_3 levels play a negligible role in the aerosol organic composition in TMB photooxidation without SO_2 addition. In contrast, under SO_2-rich condition, the increase in NH_3 level led to a significant increase in the abundance of organic compounds (especially for compounds with $m/z > 200$) in both positive and negative ion modes (Fig. S11). The introduction of SO_2 and NH_3 lead to the formation of ammonium sulfate (Fig. S12), which is an attractive condensation sink for organic vapors. High particle surface area concentration in TMB/NO_x/SO_2/NH_3 experiments may increase the abundance of organic compounds in the bulk phase. To better explain this effect, the saturation mass concentrations of detected products were predicted based on a previous method (Li et al., 2016) and the calculated results are shown in Fig. 9 and Table S4. During the photooxidation of TMB, the fates of organic compounds are mainly governed by the competition between fragmentation and functionalization. Losing carbon atoms increases product volatility, which could be partly compensated by functionalization. Among the compounds present in aerosol particles formed from NH_3-added systems, fourteen products were C9 or smaller multifunctional oxidation products. From Fig.9, the range of product saturation mass concentration spanned approximately 8 orders of magnitude, indicating that the measured particle-phase products are considerably different regarding volatility. The products in the particle-phase are classified into three classes in Fig. 9: low-volatility organic compound, intermediate volatility organic compounds, and semi-volatility organic compounds. The measured products might not be responsible for homogenous nucleation but these compounds can gradually condense onto nucleation particles (i.e., ammonium sulfate) to contribute to aerosol formation and growth, which highlights the role of ammonium sulfate in this case.

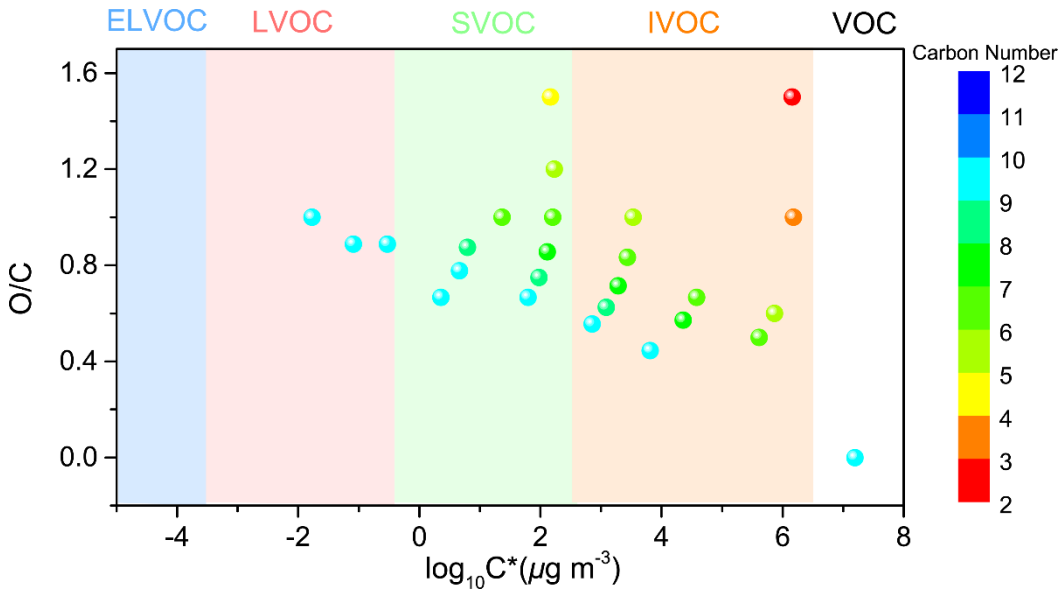

Figure 9. TMB and detected products (Table S4) displayed in the two-dimensional volatility-oxidation space. Based on the method of Li et al. (2016), we grouped the detected compounds in the classes of extremely low-volatility organic compound (ELVOC), low-volatility organic compound (LVOC), semi-volatility organic compound (SVOC), intermediate volatility organic compounds (IVOC), and volatility organic compound (VOC).

4 Conclusions

In summary, we explored the detailed effects of SO_2 and NH_3 on secondary aerosol formation from TMB photooxidation. Our results demonstrate a substantial increase in ultrafine particle (< 100 nm) number concentrations resulting from SO_2 addition. Significant increases in SOA yields were found in TMB/NO_x/SO_2 photooxidation, due to acid-driven heterogeneous reaction. The laboratory characterization of SOA composition confirmed the formation of new organosulfates at MW 214, 226, 228, 240, 242, 244, 268, 300, 316, and 345. The MS data give experimental evidence that the MW 214 and 242 organosulfates could account for organosulfates previously designated as unknown origin in ambient $PM_{2.5}$, while some of them that were observed in TMB/NO_x/SO_2 photooxidation are isomers of recognized biogenic organosulfates. This indicates that care must be taken in the identification of TMB-derived organosulfates in ambient aerosols. More laboratory and field studies with organosulfate authentic standard should be carried out to determine the accurate yield of the measured organosulfates and the contribution of TMB-derived organosulfate to total atmospheric organosulfate. In addition, the composition of secondary aerosol could determine the physicochemical properties of aerosol particles (e.g. viscosity and phase state). Changes in SO_2 emissions in different regions all over the world have great implications for the physicochemical properties of aromatics-derived SOA and, thus, highly influence the global climate.

The presence of NH_3 also increased the number and volume concentration of secondary aerosol particles, especially under SO_2-rich condition. We characterized a series of multifunctional ring-retaining and ring-opening organic compounds containing one and even more carbonyl and alcohol. The predicted volatility distributions of products suggested that the measured later-generation products progressively condense onto nucleation particles to enhance particle formation in NH_3-added photooxidation. Current models that are used to assess aerosol-climate interactions should fully take into account the influence of NH_3 on secondary aerosol formation, which is especially significant in regions with strong NH_3 emissions.

Data availability. Experimental data are available upon request to the corresponding author.

Supplement. The supplement related to this article is available online at:

Author contribution. Zhaomin Yang: Conceptualization, Methodology, Investigation, Validation, Visualization, Writing – original draft preparation. Li Xu: Investigation. Narcisse T. Tsona: Visualization, Writing – review & editing. Jianlong Li: Visualization, Writing – review & editing. Xin Luo: Methodology, Resources. Lin Du: Conceptualization, Investigation, Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing – review & editing.

Competing interests. The authors declare that they have no conflict of interest.

Financial support. This work was supported by National Natural Science Foundation of China (91644214), Youth Innovation Program of Universities in Shandong Province (2019KJD007), and Fundamental Research Fund of Shandong University (2020QNQT012).

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