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Impacts of Mixed Gaseous and Particulate Pollutants on Secondary Particle Formation during Ozonolysis of Butyl Vinyl Ether

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ABSTRACT: To clarify how coexisting atmospheric pollutants affect secondary organic aerosol (SOA) formation, we investigated the effects of mixed gaseous pollutants (CO and SO_2) and mixed organic–inorganic (MOI) particles on SOA formation during *n*-butyl vinyl ether (BVE) ozonolysis. Higher CO levels (90 ppm) were found to significantly change the chemical composition of SOA (prompting monomers while reducing oligomer formation) without causing much change in the overall SOA mass. Based on the positive matrix factorization (PMF) analysis, heterogeneous chemical conversions between preformed and newly formed SOA were the major pathways of SOA formation in the presence of MOI particles. Furthermore, MOI particles had an enhancing effect on SOA formation at 1% relative humidity (RH) but a negligible effect at higher RH (10 and 55%). The enhancing effect was attributed to the formation of multifunc-



tional products resulting from high functionalization of preformed and newly formed SOA. The negligible effect observed was ascribed to the cleavage of unstable oligomers as a result of the reversible oligomerization of preformed and newly formed SOA. Even so, MOI particles could still affect the composition of newly formed SOA. These results highlight the need to account for the significant effect of mixed gaseous and particulate pollutants on both SOA constituents and their evolution.

INTRODUCTION

Secondary organic aerosol (SOA) contributes to at least onethird of the fine particle mass during severe haze pollution events in many megacity regions.^{1–3} Despite intense research efforts aimed at understanding the formation and atmospheric evolution of SOA,^{4–9} current models severely underestimate its formation due to a lack of knowledge on their complicated constituents, structures, and formation pathways.^{10–15}

To further explore the related mechanisms, recent studies have focused on the effects of anthropogenic gas pollutants, such as NO_x, SO₂, and NH₃, on SOA formation. Such research has shown that anthropogenic SO₂ and NH₃ can enhance SOA formation during both daytime and nighttime oxidation of volatile organic compounds (VOCs) during the day and night.^{16–21} Furthermore, a high level of NO_x tends to reduce SOA formation during daytime photooxidation or ozonolysis of VOCs but enhance SOA formation via the NO_3 radical reaction pathway at night.^{22–24} In addition, mixed anthropogenic pollutants (SO₂ and NH₃ or NO_x) are also reported to have a positive synergetic impact on the formation of anthropogenic SOA.^{18,20} However, although carbon monoxide (CO) is a known, albeit indirect, greenhouse gas pollutant,²⁵ its role in SOA formation remains poorly studied. Recent research reported that CO-rich conditions can significantly reduce SOA formation derived from the photooxidation of monoterpenes by suppressing the formation of highly oxygenated organic molecules (HOMs).²⁶ However, the effect of mixed anthropogenic pollutants containing CO on secondary particle formation remains unclear and needs further exploration.

In addition to mixed gases, air pollutants also contain many mixed particulates consisting of organic and inorganic matter. Mixed organic—inorganic (MOI) particles are a major contributor to fine particulate pollution under highly complex conditions in urban areas.^{27–31} Thus, several recent studies have focused on the effects of MOI heterogeneous processes on SOA formation. For instance, the presence of ammonium sulfate (AS) and ammonium bisulfate (ABS) seeds coated with α -pinene-derived SOA can reduce the uptake of intermediate species (i.e., isomeric isoprene epoxydiols) on MOI particles and inhibit subsequent SOA formation.^{32–34} In contrast, the heterogeneous reaction of aldehydes with preformed particulate hydroperoxides forming peroxyhemiacetals can lead to a large increase in SOA mass in the presence of dodecane SOAcoated AS particles under dry conditions.³⁵ This indicates that the heterogeneous reactions involving MOI particles for SOA

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formation can differ and also imply that the different effects of MOI particles may be closely related to the SOA precursors and the composition and acidity of MOI particles.

Alkyl vinyl ethers are increasingly produced in the chemical industry and widely used as fuels and fuel additives. In the present study, we use *n*-butyl vinyl ether (BVE) as a proxy of alkyl vinyl ethers to investigate the effects of mixed gaseous pollutants (CO and SO₂) and the MOI particles formed in the absence of seed particles on SOA formation derived from BVE ozonolysis. The evolution of SOA composition was further studied by applying positive matrix factorization (PMF) to explore the heterogeneous conversion of organic products and their contribution to SOA formation. This work will help improve our understanding of the different effects of mixed gas pollutants containing CO and SO₂ and mixed particles composed of H₂SO₄ and complex organics on secondary particle formation.

EXPERIMENTAL SECTION

The BVE ozonolysis experiments were carried out in an indoor chamber at ambient temperature (~295 K) and atmospheric pressure (~1 atm) under different relative humidities (RHs). Details of the smog chamber and instruments used in this study have been described in detail previously.^{36,37} In brief, we used a 30 m³ Teflon reaction chamber surrounded by stainless steel housing to maintain a constant temperature. A stirring fan placed in the middle of the chamber was used to ensure the homogeneous mixing of reactants and products. A scanning mobility particle sizer (SMPS) system incorporating a differential mobility analyzer (TSI model 3081) and a condensation particle counter (model 3022) was used to measure aerosol size distributions and particle volume concentrations inside the chamber. All SMPS data were corrected for wall loss by monitoring the particle mass for approximately 2 h after the addition of AS seed particles. Nonrefractory submicron aerosol particle composition, including organics, sulfate, nitrate, and ammonium, was simultaneously measured in situ by high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) with 2 min time resolution, calibration with pure ammonium nitrate, and operation in alternating V-mode and W-mode every 2 min.³⁸ The W-mode data were analyzed to determine the average aerosol carbon oxidation state (OSc) and temporal evolution of SOA. The V-mode data were analyzed for higher-molecularweight ions with m/z > 200. The measured particle concentration was corrected based on the deposition rate of $(NH_4)_2SO_4$ ($k_{dep} = 4.15 \times 10^{-7} \times D_p^{1.89} + 1.39 \times D_p^{-0.88}$; D_p (nm) is the particle diameter).²⁰ Gaseous species, including NO_x (model 42i), SO₂ (model 43i), CO (model 48i), and O₃ (model 49i), were also simultaneously measured at the ppb level with various gas analyzers (Thermo Scientific).

Prior to the start of each experiment, the chamber was flushed with clean zero air for >24 h. Chamber background aerosol concentrations were monitored before all experiments to ensure that particle concentration in the chamber was less than 20 particles cm⁻³. Ozone supplied to the chamber was produced in situ using an ozone generator equipped with two ultraviolet lamps. The initial reaction conditions of all experiments are listed in Table 1. At the start of the experiments, O₃, CO, and SO₂ were added to the chamber in sequence. The chamber was then allowed to equilibrate for 10 min prior to the addition of BVE. Finally, ~20 μ L of BVE (~100 ppb) was injected into a heated three-way tube (80 °C)

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Table 1. Experimental Conditions

exp	[BVE] (ppb)	[O ₃] (ppb)	[SO ₂] (ppb)	seed	CO (ppm)	RH (%)
#1	100	205	0		0.5	10
#2	100	203	0		33	10
#3	100	208 ± 6	155 ± 3		0.55 ± 0.1	10
#4	100	202	152		90	10
#5	100	205 ± 6	150 ± 5	MOI	36 ± 2	1-2
#6	100	200 ± 5	148 ± 3	MOI	34 ± 1	10-11
#7	100	205	150	MOI	34	30-32
#8	100	207 ± 3	142 ± 5	MOI	36 ± 1	54-56

and subsequently carried into a smog chamber by zero air with a flow rate of 20 L min⁻¹. The injection of BVE including the injecting and mixing process took ~ 10 min. In the time series plots, 0 min means the commencement of experiment preparation, including the addition of O₃, CO, and SO₂. MOI particles were prepared by the in situ formation method, that is, by the ozonolysis of BVE in the presence of SO_2 following the first injection. To explore how preformed MOI particles affected SOA formation, BVE with the same concentration was injected once again into the chamber after the MOI particle concentration peaked and stabilized. At the time of the second BVE injection, there should be no residual BVE in the chamber as excess amounts of O₃ were added during MOI particle formation. To make sure that results are reliable and to rule out potential artifacts, such as the adding sequence of CO, O₃, and SO₂ during experimental preparation, the proportional control of dry air and wet air during adding water, and both the injection process and mixing process of BVE, some parallel experiments under part of experimental conditions were conducted (Table 1). Both SO₂ (520 ppm in N_2) and CO (0.05% in N_2) were purchased from Beijing Huayuan Gas Company in China. BVE (99%) was purchased from Sigma-Aldrich.

RESULTS AND DISCUSSION

Effects of Mixed Gas Pollutants (CO and SO₂) on Secondary Particle Formation. In the absence and presence of SO₂, secondary particle formation (SOA and sulfate) from BVE (100 ppb) ozonolysis was investigated under both COpoor and CO-rich conditions. As shown in Figure 1, as soon as BVE was added to the chamber prefilled with ~ 200 ppb O₃, the mass concentrations of secondary particles, especially sulfate in the presence of SO_2 , began to increase rapidly under both CO-poor and CO-rich conditions. This suggests that BVE ozonolysis produced many reactive intermediates (such as stabilized Criegee intermediates [sCI] in Scheme S1 and OH radicals), and the subsequent interaction between SO2 and reactive intermediates dominated sulfate formation during BVE ozonolysis in the presence of SO_2 .³⁹⁻⁴² The highest fraction of sCI reacted with SO₂ also supported that the sCI + SO₂ reaction dominates sulfate formation (Table S2). BVE was degraded completely in the presence of excess O_3 (Figure S1 and S2) by the end of the experiment.

In the absence of SO₂ (Figure 1A), the SOA mass reached a maximum of 8 and 5 μ g m⁻³ under CO-poor and CO-rich conditions, respectively, after 80 min. Obviously, ozonolysis of BVE under CO-poor conditions resulted in a relatively higher SOA mass than that under CO-rich conditions, consistent with recent findings.²⁶ McFiggans et al. demonstrated that CO-rich conditions suppressed SOA yield of α -pinene photooxidation



Figure 1. Time-dependent growth curves of both SOA and sulfate in the absence (A) and presence of SO_2 (B) under CO-poor (0.5 ppm) and CO-rich (90 ppm) conditions at 10% RH.

in the absence of SO₂ by reducing the formation of HOMs and oligomers due to OH radical scavenging.²⁶ No significant difference in the mass spectra (m/z > 100) between CO-poor and CO-rich conditions in the absence of SO₂ (Figure S3) may result from the very low SOA concentration and the harsh ionization conditions of HR-ToF-AMS. In the presence of SO₂ (Figure 1B), maximum concentrations of secondary particles (SOA and sulfate) between CO-poor and CO-rich conditions were almost equal. In contrast to the CO-poor experiments, the CO-rich conditions had a negligible effect on the formation of both SOA and sulfate during the ozonolysis of BVE in the presence of SO₂. To explore this, we compared the mass spectra of SOA under CO-poor and CO-rich conditions in Figure 2A. The total amounts of monomers and oligomers from the two different experiments were first normalized to 1 prior to subtracting for better comparison. As shown in Figure 2A, based on the different mass spectra under both CO states, CO-rich conditions were found to suppress oligomer formation (negative mass spectra) but promote monomer formation (positive mass spectra) simultaneously. Thus, the CO-rich conditions significantly reduced the oligomerization of monomers with little change in overall secondary particle mass. Here, for sulfate formation, both the sCI and OH radical oxidation pathways contributed to SO₂ consumption and subsequent sulfate formation during BVE ozonolysis under CO-poor conditions. However, the CO-rich conditions may have decreased OH radical concentration by scavenging OH radicals and promoting BVE ozonolysis in the chamber. This would favor sCI formation and its subsequent interaction toward SO₂. Thus, the CO-rich conditions may have suppressed sulfate formation resulting from the $OH + SO_2$ reactions via scavenging OH radicals, whereas the enhancement of sulfate formation through the $sCI + SO_2$ reaction pathway may have simultaneously offset the loss of sulfate caused by the decrease in OH oxidation. Moreover, the simplified model quantitatively showed that approximately 55.2% of OH radicals were consumed by the CO + OH reaction (Table S2), which demonstrates that the CO + OH reaction reduces the reaction of BVE and OH radicals and dominates OH radical consumption.

In addition, the size distributions of secondary particles as a function of time under both CO-poor and CO-rich conditions in the presence of SO₂ were also compared. As shown in Figure 2B,C, the maximum particle concentrations monitored by SMPS were 2.4×10^6 particle cm⁻³ under the CO-poor state and 1.3×10^6 particle cm⁻³ under the CO-rich state. The particle concentration of secondary particles under CO-poor conditions was obviously higher than that under CO-rich conditions in the presence of SO₂. A similar phenomenon was also observed in the absence of SO₂ (Figure S4). Recent studies have indicated that the formation of oligomers significantly contributes to new particle formation.⁴³⁻⁴⁵ Thus, the lower oligomer concentration observed under CO-rich conditions was likely responsible for the reduced new



Figure 2. Different mass spectra (signal_(90 ppm CO) – signal_(0.5 ppm CO)) between the two different CO levels in the presence of SO₂ (A); size distribution of secondary aerosol as a function of time under CO-poor (B) and CO-rich conditions (C) at 10% RH.

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Figure 3. Time-dependent growth curves of SOA and sulfate at 1% RH (A) and 10% RH (B) in the presence of preformed MOI particles. Size distribution of secondary aerosol as a function of time at 1% RH (C) and 10% RH (D).



Figure 4. Three-factor solutions for PMF analysis of SOA in the presence of MOI particles at 1% RH.

particle formation. These results indicate that mixed gas pollution (CO and SO₂) had a negligible effect on secondary particle formation but a significant impact on new particle formation and SOA constituents. Recent studies demonstrated that ambient SOA particles can exist as amorphous glasses and in a highly viscous state under very dry condition (<10% RH).^{46,47} The existence of glassy states may have profound consequences for the properties of atmospheric aerosol particles.⁴⁸ Thus, this work further implied that the effect of mixed gas pollutants (CO and SO₂) on ambient secondary

particles with glassy states needs to be seriously considered in future study.

Effects of MOI Particles on Secondary Particle Formation. MOI particles are major contributors to fine particulate pollution in the atmosphere, especially in urban areas during severe haze pollution.^{36,49} To investigate their effects on secondary particle formation, MOI particles containing H_2SO_4 and SOA were first produced via ozonolysis of BVE in the presence of SO_2 under different RH conditions. As shown in Figure 3A,B, the maximum mass concentrations of SOA and sulfate in the MOI particles were approximately 4 and 10 μ g m⁻³ at 1% RH and 25 and 150 μ g m⁻³ at 10% RH, respectively. A higher RH significantly promoted sulfate formation via enhancing nucleation and growth of H₂SO₄ particles.^{50,51} And more H₂SO₄ particles further caused SOA formation via providing a higher surface area and volume for condensation of low-volatility oxidized species, consistent with our recent work.⁵² When MOI particle concentrations reached the maximum stability, another 100 ppb BVE was added to the chamber to investigate the effects of preformed MOI particles on secondary particle formation. To exclude the effects of the decrease in O₃ and SO₂ concentrations on secondary particle formation, both O₃ and SO₂ were replenished in the chamber to ensure the same initial concentrations during ozonolysis of the first and second injections of BVE (Figure S5).

By comparison, the maximum concentrations of SOA and sulfate increased 2 and 5 times, respectively, relative to that in the MOI particles formed during ozonolysis of the first injection of BVE at 1% RH. However, the maximum concentrations of SOA and sulfate formed during ozonolysis of the second injection of BVE were almost equal to that observed in the MOI particles at 10% RH. These results indicate that the presence of MOI particles formed under different RHs had different effects on secondary particle formation. Numerous studies have indicated that the effect of seed particles on secondary particle formation is generally closely related to new particle formation and heterogeneous processes.^{32,53-56} Parallel experiments under both of the RHs are shown in Figure S6.

As shown in Figure 3C,D, the size distributions of the suspended particles as a function of time under both experimental conditions were also compared. Significant but similar new particle events were observed following the second injection of BVE in both experiments. However, it is worth noting that the concentrations of newly formed particles (4 \times 10^5 for 1% RH and 1.9×10^5 particle cm⁻³ for 10% RH) were apparently lower than the concentrations of preformed MOI particles at both 1% RH (8.5×10^5 particle cm⁻³) and 10% RH $(1.1 \times 10^6 \text{ particle cm}^{-3})$. This is consistent with recent studies, in which the presence of higher initial seed aerosol (SOA-coated seed particles) reduced the nucleation of particles during the photooxidation of toluene and ozonolysis of α -pinene.^{32,57,58} In the current study, the presence of MOI particles also allowed newly formed nucleated species (lowvolatile organic compounds or sulfuric acid) to partition more effectively into preformed MOI particles.

Effects of Heterogeneous Reactions on Secondary Particle Formation at 1% RH. To further explore whether heterogeneous reactions also contributed to SOA formation and caused different effects at different RH, the chemical evolution and conversions of SOA under continued reaction were investigated by applying PMF to analyze the AMS data.⁵⁹ Each resolved PMF factor represented a group of molecules with similar chemical/physical properties. The methodology of PMF analysis is presented in the Supporting Information (Figures S7–S10).

As indicated in Figure 4, three factors were identified following PMF analysis of BVE-SOA. The temporal evolution of SOA with reaction time was first analyzed at a very low RH (1%). As shown in Figure 4A, factor 1 increased substantially during early aerosol growth, peaked after 10 min, and subsequently decreased gradually. Its evolution indicates the rapid transformation of precursors to first-generation products (such as hydroxylated or oxygenated monomers) and

condensation on H₂SO₄ particles during early aerosol growth. Monomers in the mass range of 120–200 Da (Figure 4B), representing functionalized components (monomers), were formed primarily in factor 1. Factor 2 was generated later than factor 1 and gradually increased with the decrease in factor 1 as the reaction continued (Figure 4A). Thus, factor 2 was characterized as second-generation products due to the further heterogeneous conversion (such as oligomerization) of functionalized products in factor 1. An increase in the abundance of functionalized compounds in the mass range of 120-250 Da from 4.6% (Figure 4B) to 5.3% (Figure 4C) and clusters in the mass range of 250-500 Da from 3.7% (Figure 4B) to 4.7% (Figure 4C) provided evidence for the above conclusion. The cluster of peaks separated by a mass unit of 74 Da (Figure 4B,C) was a characteristic of the copolymer system (oligomers). These results indicate that both functionalization and oligomerization contributed to the increase in factor 2. In the latter half of the experiment (Figure 4A) during the ozonolysis of second-injected BVE, both factors 1 and 2 showed similar time trends as observed in the MOI particles. Interestingly, a profound increase in factor 3 accompanied by a sharp decrease in factor 2 was observed in the first reaction stage of the ozonolysis of second-injected BVE. This implies that the heterogeneous chemical conversion of factor 2 likely contributed to the increase in factor 3. The higher fraction of functionalized compounds (8.6%) and the lower fraction of oligomers (3.7%) shown in Figure 4D suggest that functionalization processes were more important than oligomerization processes during the chemical conversion of factor 2 to factor 3. Based on the above PMF analysis, the homogeneous formation of factor 1 followed by the partitioning and heterogeneous chemical conversion among the factors further confirmed that both homogeneous and heterogeneous reactions will contribute to the differences in chemistry.

From the O₃ profiles at 1% RH (Figure S5A), the consumption of much more O_3 in the latter half of experiments seemed to imply that some unsaturated products may be produced. Recent studies proved that the aldol condensation and the acid-catalyzed dehydration of hemiacetals can produce a class of unsaturated oligomers during SOA formation.^{60,61} Thus, we speculated that more unsaturated aldehyde oligomers should be produced initially at 1% RH. And their further ozonolysis not only resulted in the consumption of more O_3 but enhanced the formation of more oxygenated products via functionalization in the latter half of the experiment. This may explain why the functionalization processes were more important than oligomerization processes at 1% RH. The proposed formation mechanism of unsaturated oligomers is shown in Scheme S2. The isomerization of alkoxy-substituted sCI and the subsequent oxygen-increasing reaction (OIR, isomerization of the alkoxy-O2 addition to the alkyl radicalreaction between RO₂ radicals) sequence repeats to first form two neutral compounds ($C_4H_6O_6[m/z \ 150]$ and $C_5H_8O_4[m/z \ 150]$ z 132]).⁶¹ Then, the multistep hemiacetal pathway of two neutral compounds further produces oligomers with a high MW. In addition, Scheme S3 also gives the possible fragmentation pathway of oligomers with m/z 509.

From the van Krevelen diagrams of the elemental ratios at 1% RH in Figure 5A, the bulk O:C and H:C data points of the preformed and newly formed SOA fell in the chemical region derived by the addition of alcohol or peroxide groups and the addition of carboxylic acids (or simultaneous addition of



Figure 5. Van Krevelen diagrams of elemental ratios in the presence of MOI particles at 1% RH (A) and higher RH (10 and 55%) (B).

carbonyl and alcohol groups), respectively. In particular, the presence of MOI particles at 1% RH resulted in completely different evolutions of H:C and O:C ratios. In the first injection, the increase in bulk O:C with stable H:C implied oxidation without significant loss of hydrogen. This was consistent with several recent studies on unsaturated hydrocarbons, in which reaction occurs by autoxidation, leading to the formation of organic peroxides via peroxy radical isomerization and the Baeyer–Villiger reaction between hydroperoxides and ketones.^{62–66} Thus, it could be concluded that functionalization involving hydroperoxide may dominate the formation of functionalized components and subsequent oligomers. In the second injection, however, the evolutions of

the H:C and O:C ratios were consistent with the classical path in which O:C increases when H:C decreases.⁴ As the reaction continued, the bulk O:C was gradually close to carboxylic acid (or simultaneous addition of carbonyl and alcohol groups). This further proves that highly oxygenated organic compounds dominated in factor 3. However, further oligomerization involving acids and alcohol oxides, such as esterification, could not explain the increase in the O:C ratio and the oxide state of SOA as esterification reduces the O:C ratio and oxidation state of SOA accompanied by loss of H₂O.⁶⁷ Based on recent studies, we found that oligomerization between sCI and functionalized components with aldehyde, carboxyl, and hydroxyl led to an increase in the average O:C ratio and oxidation state of SOA.^{68,69} Thus, we concluded that the formation of multifunction components resulting from heterogeneous reactions between newly formed and preformed intermediates mainly contributed to the formation of highly functionalized compounds in factor 3, as well as the oxidation of preformed low functionalized compounds. Based on the changes in the mass spectra during the whole experiments (Figure S11A), the higher increasing proportion of monomers (320%) relative to oligomers (186%) also implied that the formation of multifunctional products mainly contributed to the enhancing effect following the second injection at 1% RH. Thus, the significant effect of MOI particles on SOA formation could be attributed to complex heterogeneous chemical conversion. The preformed MOI particles primarily enhanced SOA formation by further high multifunctionality at very low RH (1%).

Effects of Heterogeneous Reactions on Secondary Particle Formation at 10% RH. The three factors at 10% RH exhibited very similar temporal evolutions in the first



Figure 6. Three-factor solutions for PMF analysis of SOA in the presence of MOI particles at 10% RH.

experiment as was observed at 1% RH. During the formation of MOI particles, factor 1 first increased, then reached a maximum, and finally decreased; factor 2 increased with the decrease in factor 1; and only a small amount of factor 3 was observed (Figure 6A). Even so, a significant distinction was observed in the latter half of the experiment. First, unlike the re-formed products in factor 1 at 1% RH, a sharper decrease in factor 1 was observed at 10%. Second, although a significant amount of factor 3 was likewise quickly formed during the initial reaction period in the latter half of the experiment as found at 1% RH, this factor decreased gradually after reaching its peak as the reaction continued, which differed from that observation at 1% RH. Thus, we concluded that the condensed chemical conversions of both factors 1 and 2 mainly contributed to the formation of factor 3 due to their simultaneous dramatic decrease in the early period of the latter half of the experiment at 10% RH. Finally, as the reaction continued, the increase in factor 2 at 10% RH mainly resulted from the condensed chemical conversion of factor 3 rather than that of factor 2 observed at 1% RH. To understand the different effects of MOI particles on SOA formation and evolution, we further analyzed the mass spectra of the three factors shown in Figure 6B–D. The decrease in the abundance of functionalized compounds (100-250 Da) from factor 1 (16.6%) to factor 3 (11%) suggested that oligomerization processes likely dominated the heterogeneous chemical conversions at 10% RH. Based on the changes in mass spectra during the whole experiments (Figure S11B), the lower increasing proportion of monomers (5%) relative to oligomers (29%) also implied that the formation of oligomerization mainly contributed to heterogeneous chemical conversions at 10% RH. However, this was inconsistent with the lower abundance of oligomer found in factor 3 compared to that in factor 1. Thus, some unknown mechanism may occur at 10% RH

The apparent difference between SOA composition at both of RH following the first injection of BVE was observed in van Krevelen diagrams (Figure 5). Relative to that at 10% RH following the first injection (Figure S13), the higher mass fraction of m/z 44 (CO₂⁺) in the three factors indicated that several more oxygenated organic species were produced in MOI particles at 1% RH (Figure S12). These results suggested that SOA composition in MOI particles formed at different RHs is profoundly different and the same factor at different RHs was not similar. The significant difference in both the temporal evolution and mass concentration of every factor between low and high RH also supported the above conclusion in the whole PMF solution (Figure S14). The unknown chemical conversion among the factors at 10% RH may be related to the SOA composition. As shown in Figure 5B, newly formed SOA was due to increasing carbonylation/carboxvlation that led to an increase in O:C and a simultaneous decrease in H:C ratio. This implies that reversible oligomerization possibly occurred in the latter half of the experiments.⁷⁰⁻⁷⁵ The further reaction of newly formed reactive intermediates with preformed functionalized components in factor 1 and oligomers in factor 2 of the MOI particles may produce stable oligomers and some unstable oligomers during the early reaction period in the latter half of the experiment. These unstable oligomers could subsequently dissociate to stable oligomers and other high-volatility oxidation products. The re-formation of stable oligomers likely resulted in the highest oligomer abundance found in factor 2. These highvolatility oxidation products did not condense significantly on the particle. As a result, the presence of MOI particles did not significantly promote the increase in SOA at 10% RH. This may explain why the MOI particles had no effect on SOA formation at 10% RH.

Under higher ambient RH, the maximum concentrations of newly formed SOA and sulfate following the second injection of BVE were also almost equal to that observed in the MOI particles at either 30% RH or 55% RH (Figure S15-S16). A slightly reversible reaction between factors 1 and 3 was also observed at 55% RH (Figure S17). As shown in Figure 5B, the different evolutions of H:C and O:C ratios were also observed at 55% RH. Together with that at 10% RH, these results implied that the preformed MOI particles have a negligible impact on SOA yield when RH exceeded 10% but could affect the composition of newly formed SOA to some extent via the heterogeneous reaction between SOA components in MOI particle and newly formed reactive species. In addition to the preformed MOI components, we speculated that the different effects of MOI particle on SOA formation may be related to the particle acidity and water content. Thus, particle acidity and liquid water content for MIO experiments were also estimated using the E-AIM model (model II: H⁺-NH₄⁻- $SO_4^{2}-NO_3^{-}-H_2O)$ based on the maximum concentration of the chemical components.^{76–78} The particle acidity (\sim 1.6 μ mol m⁻³) and water content (~4.4 μ mol m⁻³) at 10% RH were profoundly higher than those (~0.079 μ mol m⁻³ and ~0.12 μ mol m⁻³, respectively) at 1% RH. Thus, we concluded that the reversible reactions among different SOA components may occur easily under higher particle acidity and higher water content, consistent with recent work.^{70,74,79} In addition, based on the method of the fragmentation pattern of $H_xSO_y^+$ reported by Chen et al.,⁸⁰ changes in the fragmentation pattern of $H_x SO_v^+$ between the first and second injections were also observed (Figure S18), which implies that MOI particles could also affect the organosulfate formation in this study.

Atmospheric Implications. Air pollutants consist of a complex combination of gases and particulate matter, especially under highly complex pollution conditions in urban areas. In this study, we studied the effect of both mixed gas and mixed particulate pollutants on secondary particle formation from BVE ozonolysis. The presence of mixed gaseous pollutants (CO and SO_2) exhibited a negligible effect on secondary particle formation but had a significant impact on SOA composition and subsequent chemical conversion. Based on the experimental study and global model calculations, McFiggans et al. demonstrated that the presence of oxidants and product scavengers, such as CO and isoprene, can effectively suppress both particle number and mass of α -pinene-derived SOA in the absence of SO₂.²⁶ Our study further highlights that the significant effect of oxidant and product scavengers on SOA composition in the presence of SO₂ should also be seriously considered during the future study of atmospheric SOA. Moreover, the presence of MOI particles was shown to enhance secondary particle formation at 1% RH but exhibit a negligible effect at 10% RH. Combined PMF solution and van Krevelen diagram shows that the heterogeneous chemical conversion between the preformed and newly formed oxidation products dominated SOA formation at both 1% RH and 10% RH. The enhancement of SOA observed at 1% RH could be attributed to the formation of a significant amount of highly functionalized components. In contrast, reversible condensed oligomerization

resulted in conversion from unstable oligomers to highvolatility oxidation products with little change in overall SOA mass. This section highlights the important effects of mixed particulate pollution on both the chemical composition and formation of SOA.

Recent studies demonstrated that ambient SOA particles can exist as amorphous glasses and in a highly viscous state under very dry condition (<10% RH).^{46,47} Although most experimental results on SOA were obtained under very dry condition in this work, these results still may help to improve our understanding of the role of heterogeneous chemistry in SOA with a highly viscous state in the atmosphere. Recently, a high-resolution time-of-flight chemical-ionization mass spectrometer (HR-ToF-CIMS) coupled with a different chemicalionization reagent (i.e., HNO3 and iodine) has also been widely used to detect highly oxidized multifunctional organic compounds (HOMs) and oligomers during secondary particle formation.^{26,81} Thus, we believe that the combination of HR-TOF-AMS and HR-ToF-CIMS would provide more knowledge of the category and structures of SOA composition, which would help to further investigate the role of complex MOI particles in the formation and chemical conversion of SOA in the atmosphere.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b07650.

Kinetic model reactions of BVE ozonolysis; proposed oligomerization pathway; discussion of the effect of MOI particle on SOA formation at higher RH and organosulfate; and the methodology of PMF analysis (PDF)

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