Multigeneration Production of Secondary Organic Aerosol from Toluene Photooxidation

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ABSTRACT: Photooxidation of volatile organic compounds (VOCs) produces secondary organic aerosol (SOA) and light-absorbing brown carbon (BrC) via multiple reaction steps/pathways, reflecting significant chemical complexity relevant to gaseous oxidation and subsequent gas-to-particle conversion. Toluene is an important VOC under urban conditions, but the fundamental chemical mechanism leading to SOA formation remains uncertain. Here, we elucidate multigeneration SOA production from toluene by simultaneously tracking the evolutions of gas-phase oxidation and aerosol formation in a reaction chamber. Large size increase and browning of monodisperse submicrometer seed particles occur shortly after initiating oxidation by hydroxyl radical (OH) at 10−90% relative humidity (RH). The evolution in gaseous products and aerosol properties (size/density/optical properties) and chemical speciation of aerosol-phase products indicate that the aerosol growth and browning result from earlier generation products consisting dominantly of dicarbonyl and carboxylic functional groups. While volatile dicarbonyls engage in aqueous reactions to yield nonvolatile oligomers and light-absorbing nitrogen heterocycles/heterochains (in the presence of NH3) at high RH, organic acids contribute to aerosol carboxylates via ionic dissociation or acid−base reaction in a wide RH range. We conclude that toluene contributes importantly to SOA/BrC formation from dicarbonyls and organic acids because of their prompt and high yields from photooxidation and unique functionalities for participation in aerosol-phase reactions.

KEYWORDS: secondary organic aerosol, photooxidation, toluene, aerosol-phase reactions, functionality

1. INTRODUCTION

Secondary organic aerosol (SOA) produced from photochemical oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) represents a dominant constituent of tropospheric fine aerosols,1,2 with profound implications for air quality, human health, weather, and climate.3−6 Photochemical oxidation of VOCs yields various condensable oxidized organics with distinct functionality, volatility, and reactivity.7−9 Currently available mechanisms of VOC oxidation leading to SOA formation include condensation of low- or nonvolatile products, equilibrium gas-particle partitioning of intermediate-volatile products, and aerosol-phase reactions of volatile products to form nonvolatile compounds.10,11 Understanding the chemical mechanisms leading to SOA formation represents a significant challenge in atmospheric chemistry research. Atmospheric models consistently underestimate SOA mass concentrations measured in field studies.12−14 Moreover, light-absorbing brown carbon (BrC) represents one type of organic aerosol that scatters and absorbs solar radiation and is produced from various primary and secondary sources. Secondary BrC is formed by a variety of atmospheric chemical processes, including multiphase reactions and cloud processing.15−17

Aromatic hydrocarbons account for about 20−30% of VOCs under urban environments and are emitted primarily from anthropogenic sources, i.e., from motor vehicles and industrial activities.18−20 Toluene is the most abundant aromatic hydrocarbon in the urban atmosphere, for which its photochemical oxidation is mainly initiated by the hydroxyl radical (OH) via multiple reaction stages/pathways.21−23 An experimental–theoretical study showed that the most favorable pathway for toluene oxidation corresponds to OH addition to the aromatic ring to yield the OH-toluene adduct, which subsequently reacts via H-extraction by O2 to form cresol, rather than O2 addition to form primary peroxy radicals (RO2).24 Typically, SOA formation from toluene photo-
oxidation is believed to be dominated by condensation/partitioning of the oxidation products,1,2,10 including organic acids and low-volatility polyhydroxy organics (LVO) such as hydroxyl/dihydroxy/trihydroxy methyl benzoquinones and dihydroxy/trihydroxy/tetrahydroxy/pentahydroxy toluenes.5,26 Also, multistage autoxidation of RO2 from aromatics likely yields highly oxygenated organic molecules (HOMs) with low volatility and a high ratio of oxygen to carbon atoms (O/C), and previous studies detected HOMs in the gas phase.27–29 However, the reported yield for HOMs from toluene oxidation is small (about 0.1%)27,29 and HOMs have yet to be detected in the aerosol phase to confirm their contribution to SOA formation. Note that LVOs differ from HOMs in terms of the oxidation pathways (i.e., OH addition versus RO2 autoxidation) and the O/C ratio, while both possess low volatility. In addition, toluene-derived SOA formation involves aqueous chemistry relevant to cloud processing and aqueous aerosols.30 A recent experimental study found that NH4 enhances the SOA mass loading from toluene photooxidation in the presence of nitrogen oxides (NOx = NO + NO2) especially under wet conditions, attributable to the formation of carboxylates and organic nitrates.31 Another recent smog chamber study on toluene photooxidation observed an increasing SOA yield with increasing NOx under low-NOx conditions but a suppressed SOA yield under high-NOx conditions.32 Also, the latter study showed an increase in the particle number concentration, diameter, and extinction/scattering coefficients relevant to the formation of ammonium nitrate and nitrogen-containing compounds by adding ammonia (NH4).32 Several studies revealed that small α-dicarbonyls (i.e., glyoxal and methylglyoxal), which are the major products of toluene oxidation, produce low-volatility oligomers and light-absorbing BrC via aqueous reactions.33,34,35 Moreover, a recent theoretical study established a carbenium ion-mediated oligomerization mechanism for methyglyoxal to produce SOA.36 In addition, increased light absorption was detected when toluene-derived SOA was exposed to gas-phase NH4, indicative of BrC formation.37,38

However, previous studies have been unable to assess temporally resolved SOA production from multigeneration VOC oxidation.25–32 For example, no previous work has measured time-dependent production of condensable oxidized organics and variations in the aerosol properties, and there lacks chemical speciation for the aerosol-phase products from toluene oxidation. The available chemical mechanisms have yet to explain explosive secondary aerosol growth observed under polluted conditions, which is dominated by SOA formation.14 In this work, we elucidate the fundamental chemical mechanisms leading to SOA formation from toluene oxidation by simultaneously tracking the temporal evolutions in gaseous products and aerosol properties.

2. MATERIALS AND METHODS

A 1 m3 environmental chamber (Teflon PFA) with 18 black light lamps (18 × 30 W, F30T8/350BL, Sylvania) was used in our experiments (see the Methods section and Figure S1 in the Supporting Information (S1)), similar to our previous studies.33,39–41 Briefly, monodispersed seed particles were exposed to the products from OH-toluene oxidation in the reaction chamber. Photooxidation of toluene was initiated by turning on the black light lamps when OH radicals were produced from photolysis of hydrogen peroxide (H2O2). The initial concentration for toluene and the steady-state concentration for OH were estimated to be 6.6 ppm and 2.7 × 106 molecules cm−3, respectively (see the Methods section in S1). A water bubbler at a temperature of 30°C was used to humidify the chamber from 10 to 90% relative humidity (RH), and all experiments were performed at 298 K. A N2 flow of 5 standard liter per minute (slpm) was used to atomize 0.06 M solution of ammonium sulfate—(NH4)2SO4 or AS, ammonium bisulfate—NH4HSO4 or ABS, and sodium chloride—NaCl to produce seed particles. Seed particles were dried to RH of ~2% by a Nafion Gas Dryer, charged by a bipolar charger, and analyzed by an integrated aerosol analytical system.33 Monodispersed seed particles with an initial size of 100 nm were size-selected by a differential mobility analyzer (DMA) with an initial particle concentration of 1.5 × 104 cm−3 measured by a condensation particle counter (CPC). The three different types of seed particles, i.e., (NH4)2SO4, NH4HSO4, and NaCl, were selected to represent distinct particle acidity and interfacial electric fields.34,42 The acidity of seed particles was estimated using a thermodynamic model,33 with the pH value of 3–5 in the presence of gaseous NH3 and 0–1 in the absence of gaseous NH3 for (NH4)2SO4, 0.5 for NH4HSO4, and 7 for NaCl. Also, there likely exists an electric field induced from net charge separation of soluble ions at the air–water interface, which is strongly positive for (NH4)2SO4, negligible for NH4HSO4, and slightly negative for NaCl.42 The particle size growth, density, and light scattering/absorption were simultaneously and continuously monitored, after monodispersed seed particles were exposed to the products of toluene-OH oxidation in the reaction chamber. The particle size increase was quantified by a growth factor, GF, which is defined by Dp/D0, where Dp is the diameter after exposure and D0 = 100 nm is the initial diameter measured by DMA. Note both Dp and D0 correspond to the dry particle diameter measured after passing through the Nafion dryer (about 2% RH). An aerosol particle mass (APM) analyzer was used to derive the particle density.39–41 An ion drift-chemical ionization mass spectrometer (ID-CIMS)43 and a thermal desorption-ion drift-chemical ionization mass spectrometer (TD-ID-CIMS)40 using hydronium reagent ions (H3O+) analyzed and quantified gases and aerosol-phase chemical composition, respectively. An integrating nephelometer and a cavity ring-down spectrometer were employed to measure light scattering (bsca) and extinction (beca) coefficients at 532 nm, respectively.47 The absorption coefficient (bagb) was determined from (beca − bscat), and the single scattering albedo (SSA) was calculated from bscat/bext. Measurements of gaseous concentrations of the oxidation products and aerosol properties (i.e., GF, SSA, density, and chemical composition) were made simultaneously throughout the experiments. While the gaseous concentrations of oxidation products, GF, SSA, and density were temporally resolved in our experiments, the particle chemical composition was analyzed after seed particles were exposed for 20 min to toluene photooxidation and collected for two additional hours by TD-ID-CIMS, reflecting an overall aerosol chemical makeup during an experiment. Similar to GF, SSA, density, and chemical composition were measured under dry conditions, whereas measurements of oxidation products were made directly by analyzing gases from the chamber using ID-CIMS. To assess the effects of different seed particles, RH, and NH3 on SOA and BrC formation, we compared the measured GF and SSA after 90 min exposure to the OH-toluene oxidation.
Wall loss of reactive gases represents a major challenge in investigating SOA formation from VOC oxidation using environmental chambers.\textsuperscript{48−51} For example, previous studies typically determined the SOA yield in the absence/presence of polydisperse seed particles, which is largely subject to the effect of wall loss. However, such a deficiency was remedied from synchronized measurements of gas-phase products and changes in the aerosol properties (i.e., size, density, and optical properties), when monodisperse seed particles were exposed to toluene oxidation products. While wall loss results in reduced concentrations of gaseous oxidation products and particles, the variations in the measured particle properties directly reflect gas-to-particle conversion from toluene oxidation, which is linked to the production of condensable oxidized organics, the interfacial process (accommodation), equilibrium partitioning (solubility), and aerosol-phase diffusion, and reactions.\textsuperscript{35} Specifically, we derived the uptake coefficient ($\gamma$) for condensable oxidized organics from the measured gaseous concentrations and particle size growth (see the Methods section in the SI), which is independent of wall loss and commonly employed to represent SOA formation in atmospheric models.\textsuperscript{1,2,10} Also, we quantified wall loss of reactive gases at different RH from the measured concentrations of oxidation products by ID-CIMS.

### 3. RESULTS AND DISCUSSION

#### 3.1. Temporally Resolved SOA Production

To assess the contribution of condensable oxidized organics to SOA formation, we measured the evolution of gaseous products from toluene-OH oxidation using ID-CIMS. The formation of multigeneration products, typically delineated by the sequence of reactions with OH, is identifiable from their temporal variations (Figures 1a and S2). The first-generation products (G1) include cresol ($m/z = 109$) and benzaldehyde ($m/z = 107$), which are produced via OH addition (about 90%) to the aromatic ring and H-extraction (10%) from the methyl group, respectively (Figure 1b).\textsuperscript{21,22} The second-generation (G2) products consist of $\alpha$-dicarbonyls, i.e., glyoxal ($m/z = 59$) and methylglyoxal ($m/z = 73$), $\gamma$-dicarbonyls (butenedial and methylbutenedial at $m/z = 99$), benzoic acid ($m/z = 123$), epoxide, and dihydroxy toluene (Figures 1c and S3), which are produced from the subsequent reactions of the G1 products with OH. The third-generation (G3) products contain mainly multifunctional organic acids (Figure 1d), including pyruvic acid ($m/z = 89$) and 4-oxo-2-pentenic acid ($m/z = 115$),

![Figure 1](https://pubs.acs.org/doi/10.1021/acs.est.1c02026)
which are formed from the reactions of the G2 products with OH. The G1 products appear shortly upon the initiation of photooxidation by ultraviolet light, reaching the peak mixing ratios of $\sim 16$ ppb for cresol and $\sim 5$ ppb for benzaldehyde (Figure 1b). The G2 products rise subsequently after the G1 products, with the peak mixing ratios from 1 to 5 ppb (Figures 1c and S3a). Note that benzoic acid exhibits a much slower growth than those of the other G2 products because of a smaller branching ratio for the H-extraction pathway.22 The G3 products start to increase at around 20 min and reach peak mixing ratios ranging from sub-ppb to 2 ppb (Figures 1d and S3b). Cresol exhibits the highest mixing ratio among all products, consistent with its dominant yield from toluene oxidation,24 and the peak concentrations of the oxidation products decrease consecutively from G1, G2, to G3 (Figure 1b–d). The time-dependent concentrations of the earlier generational products (G1 and G2) exhibit a decline at longer reaction times, reflecting the conversion from the earlier to later generational (G2 and G3) products (Figure 1b–d). In contrast, the toluene concentration shows a continuous decay throughout the experiments (Figure S3c).

The temporal evolution of GF, SSA, and density of (NH$_4$)$_2$SO$_4$ seed particles exposed to toluene-OH oxidation in the presence of 19 ppb NH$_3$ and at 90% RH is depicted in Figure 1e–g. The size growth factor, GF, exhibits an initial delay ($\sim 5$ min) and then increases monotonically, reaching 2.56 at 90 min (Figure 1e). The initial hysteresis in GF is consistent with the delayed formation of the G2/G3 products (Figure 1c,d), which are mainly responsible for the measured particle growth. While the low-volatility G2/G3 products engage in gas-particle conversion (for epoxide and dihydroxy toluene) or ionic dissociation/acid–base reaction to form carboxylates (for organic acids), the volatile G2 products (i.e., $\alpha$-dicarbonyls and $\gamma$-dicarbonyls) undergo aerosol-phase reactions to form oligomers (Figure S4).33–36,52,53 In addition, $\alpha$-dicarbonyls and $\gamma$-dicarbonyls react with NH$_3$ to yield nitrogen-containing organics (NCO), including nitrogen heterocycles and nitrogen heterochains (Figure S5),35 which are characteristic of light-absorbing BrC.15,16 The measurement of SSA shows a steady decline throughout the exposure and reaches 0.94 at 180 min (Figure 1g), confirming BrC production. Our measured SSA is comparable to another study of toluene-derived SOA, which showed a decrease of SSA from

Figure 2. Variation in SOA growth with seed particles. (a) Time-dependent growth for (NH$_4$)$_2$SO$_4$ particles in the presence (AS w/o NH$_3$, blue) and absence (AS w/o NH$_3$, purple) of 19 ppb NH$_3$ and for NH$_4$HSO$_4$ (ABS, red) and NaCl (green) particles in the absence of NH$_3$. (b) GF (black) and SSA (red) at 90 min of exposure. (c) SOA density for seed particles of (NH$_4$)$_2$SO$_4$ in the presence (blue) and absence (purple) of 19 ppb NH$_3$, ABS (red), and NaCl (green). The color legend is similar to that in (a). (d) Aerosol-phase relative intensity (RI) for carboxylates (black), oligomers (green), and NCO (brown) on different seed particles. (e) GF (black) and SSA (red) at $t = 90$ min with varying NH$_3$ concentrations between 0 and 74 ppb. (f) Aerosol-phase relative intensities (RI) for carboxylates (black square), oligomers (green square), and N-heterocycles (brown square) from $\alpha$-dicarbonyls, oligomers (blue open square), and N-chains (brown open square) from $\gamma$-carbonyl with varying NH$_3$ concentrations between 0 and 74 ppb. Initiation of photooxidation by ultraviolet light occurred at $t = 0$. The error bar denotes 1σ of three replicated measurements.
The reaction between NaCl and organic acids yields sodium and methylglyoxal reach 1.71 respectively, while the densities for the oligomers of glyoxal (Table S1), and increases throughout the experiment, reported previously (1.4 g cm$^{-3}$). The evolution in density clearly reflects variation in the chemical composition during particle growth because of distinct material densities for the condensable oxidized organics from G2/G3 products as well as aerosol-phase oligomeric products (Table S1). For example, the densities of benzoic acid, monomers of glyoxal and methylglyoxal, and imidazoles are 1.27, 1.05–1.27, and 1.03–1.23 g cm$^{-3}$ respectively, while the densities for the oligomers of glyoxal and methylglyoxal reach 1.71–1.90 g cm$^{-3}$ (Table S1). The initial decline in the total density corresponds to a chemical composition dominated by organic acids and smaller oligomers from the G2 products, while the continuous increase in the SOA density is a characteristic of increasing aqueous-phase reactions to yield larger oligomeric products (Figure 1g). In addition, the evolutions in the measured GF and density correlate closely with those of the G2 products (including benzoic acid and dicarboxyls) (Figure 1c,e,g), confirming their role in the initial decline of the total particle density.

To further unravel the identity of the condensable oxidized organics responsible for the measured GF, SSA, and density, we analyzed chemical composition by collecting particles after exposure to toluene-OH oxidation using TD-ID-CIMS (Figure 1h). The composition measurements reveal the dominant abundances of three functional groups in the aerosol phase, i.e., oligomers, NCOs, and carboxylates, along with a small amount of LVO (including hydroxyl toluene/benzoquinone). Assuming comparable sensitivity to proton-transfer reactions for the aerosol-phase organics, we estimated the contributions of oligomers, NCOs, carboxylates, and LVO to the total SOA formation from the measured mass intensities, with the values of 26, 26, 40, and 8%, respectively (Table S2). The identified mass peaks shown in Figure 1h are summarized in Tables S3–S5, and the corresponding reaction pathways leading to the formation of oligomers and NCOs are illustrated in Figures S4 and S5, respectively.

3.2. SOA Formation on Different Seed Particles. The temporal evolution of SOA on different types of seed particles shows similarly a rapid, continuous increase in GF, after a short initial hysteresis (Figure 2a). Among the different seed particles, (NH$_4$)$_2$SO$_4$ in the presence of NH$_3$ exhibits the largest GF and lowest SSA at 90 min (Figure 2b) because of efficient oligomer and NCO production. The calculated SOA density ranges from 1.19 to 1.28 g cm$^{-3}$ at 10 min (Figure 2c), which are characteristic of an initial composition dominated by organic acids and smaller oligomers from the G2 products (Table S1), and increases throughout the experiment, consistent with increasing oligomerization. (NH$_4$)$_2$SO$_4$ particles with NH$_3$ exhibit the highest density (1.60 g cm$^{-3}$), similar as the measured GF. The density of 1.60 g cm$^{-3}$ for the toluene-derived SOA is higher than that of common organics reported previously (1.4 g cm$^{-3}$). Comparison of the chemical composition on different seed particles reveals increased carboxylates from NH$_4$HSO$_4$, (NH$_4$)$_2$SO$_4$ without NH$_3$, (NH$_4$)$_2$SO$_4$ with NH$_3$, to NaCl seed particles, consistent with an increasing acid–base reaction. Additionally, the reaction between NaCl and organic acids yields sodium carboxylates and leads to evaporation of hydrogen chloride (HCl), explaining the largest carboxylate intensity on NaCl seed particles (Figure 2d). Among the different types of seed particles, the intensities for oligomers and NCOs reach the highest for (NH$_4$)$_2$SO$_4$ particles with NH$_3$ (Figure 2d). No NCO compounds are identified on NaCl seed particles in the absence of NH$_3$. The density trends among different seed particles are similar to that in oligomer intensity (Figure 2c,d), indicating an essential role of oligomerization in regulating the particle density.

The dependencies of the measured GF, SSA, and density on different seed particles are explainable by the mechanisms leading to the formation of the observed aerosol-phase products (Figure 2d). Gas-particle conversion of organic acids from the G2/G3 products likely includes ionic dissociation to form carboxylates or acid–base reactions to form ammonium (sodium) carboxylates in the presence of NH$_3$ (NaCl), as evident from the increasing carboxylate intensity (Figure 2d). On the other hand, dicarboxyls engage in oligomerization, which is mediated by carboxylic acids. Protonation, hydration, and depolymerization of dicarboxyls produce carboxonium ions and diols/tetrols, and subsequent nucleophilic addition to the carbenium cation by the negative hydroxyl O-atom of diols/tetrols or the negative N-atom of NH$_3$ results in the formation of oligomers and NCOs, respectively. While protonation is favored under acidic conditions, high proton concentration inhibits hydration and depolymerization to form diols/tetrols, resulting in most efficient oligomerization under moderate acidic condition, i.e., on (NH$_4$)$_2$SO$_4$ particles with NH$_3$. Also, oligomerization is likely promoted by an electric field on (NH$_4$)$_2$SO$_4$ particles because of net charge separation from ion distributions at the interface. The interfacial electric field is strongly positive for (NH$_4$)$_2$SO$_4$ solutions and is likely enhanced on submicrometer particles due to high ionic strength. A positive electric field exerts interfacial attraction to carboxyl and carboxylic functional groups, which possess negatively charged characteristics. Hence, the most efficient nucleophilic addition involving carbenium ions and the strongest interfacial attraction jointly explain the largest GF and highest intensities for oligomers and NCOs on (NH$_4$)$_2$SO$_4$ particles with NH$_3$. Recent measurements of SOA and BrC formation from glyoxal and methylglyoxal showed that the formation of oligomers and NCOs occurs over a wide acidity range and is most efficient on (NH$_4$)$_2$SO$_4$ particles with NH$_3$, consistent with our present results.

We further examined the dependence of GF, SSA, and chemical composition on gaseous NH$_3$ (Figure 2e). For (NH$_4$)$_2$SO$_4$ particles, GF initially increases with NH$_3$ but decreases when the NH$_3$ concentration exceeds 19 ppb. On the other hand, SSA decreases with NH$_3$ but increases slightly when the NH$_3$ concentration exceeds 37 ppb. These dependencies of GF and SSA on NH$_3$ reflect the competition in the formation between oligomers and NCOs from $\alpha$- and $\gamma$-dicarbonyls. NH$_3$ is involved in aerosol-phase reactions with dicarboxyls to form NCOs and with organic acids to form ammonium carboxylates, responsible for the increasing GF and decreasing SSA with initially increasing NH$_3$. However, an elevated NH$_3$ concentration likely converts dicarboxyls to diimine compounds, resulting in fewer carboxyl functional groups to form larger NCO. Small NCO is subjected to evaporation back to the gas phase, leading to a reduced GF and slightly increased SSA at subsequently increasing NH$_3$. Analysis of the particle composition confirms that NCOs and
carboxylates initially increase with NH₃ but become invariant when NH₃ exceeds 19 ppb, while there are slightly decreasing oligomers when NH₃ exceeds 19 ppb. We performed additional experiments by exposing NH₄HSO₄ and NaCl seed particles to toluene-OH oxidation products by varying NH₃. For NH₄HSO₄ seed particles, the addition of NH₃ converts NH₄HSO₄ to (NH₄)₂SO₄, resulting in a similar GF as that of (NH₄)₂SO₄ (Figure S6). For NaCl seed particles, GF increases considerably with NH₃ and becomes independent on NH₃ at a concentration exceeding 19 ppb (Figure S7a), similar to the measured carboxylate intensity (Figure S7b). Also, the intensities for oligomer and NCO decrease and increase, respectively, with increasing NH₃, consistent with the competition in the formation between oligomers and NCOs (Figure S7b).

3.3. Effects of RH and Gaseous Reactants. We carried out additional experiments by varying RH from 10 to 90% (Figure 3). Comparison of the measured evolutions in GF, SSA, and density shows noticeable RH effects. At low RH (10%), the particle growth exhibits an elongated hysteresis, as evident from the evolution in the GF. Compared to 90% RH with a delay of ~5 min, the increase in GF only occurs after a hysteresis of 10–15 min at 10% RH (Figure S8). These differences in the particle density imply that the condensable oxidized organics contribute distinctly to the particle growth under high and low RH conditions. Also, the measured SSA at 90 min is equal to unity at 10% RH and decreases with increasing RH (Figure 3c), indicating that NCO formation is negligible at low RH and occurs only at high RH.

To gain further understanding on the cause for the variability in GF, SSA, and density, we performed measurements of the chemical composition at varying RH. At low RH (10%), carboxylates represent dominantly the aerosol-phase products (about 86%), while the contributions of oligomers, NCOs, and LVO to the total SOA formation are estimated as 3, 2, and 9%, respectively (Table S7). With increasing RH from 10 to 90%, contributions to the total SOA formation consecutively increase and decrease for oligomers/NCOs and carboxylates, respectively, while the fraction for LVO is nearly invariant. These dependencies of GF, SSA, and density on RH are relevant to the aerosol-phase chemistry to form carboxylates, oligomers, and NCOs. For (NH₄)₂SO₄ particles, the deliquescent and efflorescent points occur, respectively, at 80 and 36% RH. At low RH (10%), aqueous reactions to yield oligomers/NCOs are considerably suppressed below the efflorescent point, attributable to hindered protonation, hydration, and deprotonation of dicarboxylic acid. Also, the measured gaseous concentrations of sub-ppb to a few ppb levels for organic acids are much smaller than their corresponding equilibrium vapor pressures (Table S8), rendering implausible gas-to-particle conversion by condensation alone. On the other hand, the equilibrium vapor pressures of organic acids are likely reduced in a multicomponent system.
via the analogous Raoult’s Law. In addition, water molecules inevitably play a key role in stabilizing carboxylates in the aerosol phase because of their dominant abundance even at 10% RH, i.e., with a gaseous concentration of $6 \times 10^{16}$ molecules cm$^{-3}$ or $3.3 \times 10^7$ parts per million (ppm). Particles consisting of organic acids retain water even at very low RH (i.e., with a $\text{H}_2\text{O}$ mass fraction of 17% at 5% RH), which facilitates the formation of carboxylates via ionic dissociation or acid–base reactions below the efl orescent point. The equilibrium vapor pressures of hydroxyl toluene/benzoquinone are much lower than those for organic acids (Table S8), favoring gas-to-particle conversion for LVOs. 

Interestingly, the particle growth is weakly dependent on (slightly decreasing with) RH from 10 to 90% (Figure 3d). Such a RH dependence is related to gas-particle conversion, aqueous reactions, and wall loss of the oxidation products. Specifically, wall loss of the precursors for oligomers, NCOs, and carboxylates are more pronounced at high RH, as evident from the measured concentrations of the various condensable oxidized organics. Wall loss is 1.3–4.3 times more efficient at 90% RH than at 10% RH, leading to reduced gaseous concentrations of the condensable oxidized organics at high RH (Table S9). The larger wall loss at higher RH is explained by increasing aqueous reactions of the condensable oxidized organics onto the Teflon chamber wall via oligomerization (for dicarbonyls) and ionic dissociation/acid–base reaction (for organic acids). Hence, the weak dependence of GF on RH is attributed to a canceling effect between increased aqueous reactions to form oligomers, NCOs, and carboxylates but decreased gaseous concentrations of the condensable oxidized organics due to larger wall loss at higher RH. At 10% RH, GF increases slightly (i.e., from 2.53 to 2.65) with NH$_3$ and the GF increase correlates with increased carboxylates in the aerosol phase (Figure S9). The GF increase with NH$_3$ at low RH is smaller than that at high RH (Figures S6 and S7), indicating a hindered acid–base reaction. Furthermore, the evidence for the occurrence of oligomerization and acid–base reaction at low RH (10%) unambiguously indicates an indispensable role of H$_2$O to form oligomers, NCOs, and carboxylates (Figure 3d and Table S7), albeit to a lesser extent.

The measured size growth of particles and the corresponding gas-phase concentrations of the condensable oxidized organics were employed to derive the uptake coefficient on ammonium sulfate in the presence of 19 ppb NH$_3$ at 10 and 90% RH (Tables 1 and S6). The $\gamma$ value for dicarbonyls is the highest at 90% RH (from $3 \times 10^{-3}$ to $1.2 \times 10^{-3}$) but is significantly reduced (from $3.4 \times 10^{-4}$ to $9.0 \times 10^{-4}$) at 10% RH, while the $\gamma$ value for organic acids and LVOs is only slightly higher at RH (90%). The measured $\gamma$ appears to correlate with the acid dissociation constant ($K_a$) and solubility among the organic acids, i.e., being the highest for pyruvic acid and the lowest for benzoic acid. For comparison, our derived $\gamma$ values for glyoxal and methylglyoxal are consistent with those recently reported at 90% RH (within 20%).

To evaluate the effects of NO$_x$ on SOA formation from toluene oxidation, we performed additional experiments using (NH$_4$)$_2$SO$_4$ seed particles in the presence of NH$_3$ by varying NO$_x$ concentrations from 0 to 300 ppb (Figure 4a–c). Measurements of time-dependent gas-phase concentrations show the formation of three major nitrophenols from NO$_x$ addition to the OH-toluene adduct in the presence of NO$_x$, i.e., 2-nitrophenol ($m/z = 140$), methyl nitrophenol ($m/z = 154$), and dihydroxy nitrotoluene ($m/z = 170$) (Figure 4d). The evolution in gas-phase concentrations clearly illustrates the multigeneration production of nitrophenols. The concentrations of first-generation nitrophenols (i.e., 2-nitrophenol and methyl nitrophenol) increase instantaneously upon initiation of photooxidation, while the second-generation nitrophenol (i.e., dihydroxy nitrotoluene) appears with a significant delay of about 30 min. The decrease in the concentrations of 2-nitrophenol and methyl nitrophenol at a longer reaction time (60 min) reflects their consumption to form dihydroxy nitrotoluene. The production of nitrophenols is much smaller than those for dicarbonyls and organic acids from toluene oxidation (Figures 1 and 4), consistent with a small yield of less than 7% under high-NO$_x$ conditions. Addition of 100 ppb NO$_x$ causes a slight decrease in the measured GF (at 90 min) compared to that without NO$_x$ in the RH range of 10–90% (Figure 4a). At a constant RH level (70%), the GF value decreases monotonically from 2.58 ± 0.04 to 2.40 ± 0.05 from 0 to 300 ppb NO$_x$ (Figure 4b). Analysis of the particle composition reveals that the decreasing size growth correlates with simultaneous decreases of carboxylates, oligomers, and NCOs but an increase of nitrophenols in the aerosol phase (Figure 4c). The contribution of nitrophenols to SOA formation ranges from 3 to 6% and is the largest from methyl nitrophenol. The production of gas-phase nitrophenols and their corresponding volatility decrease and increase, respectively, with increasing functionality, explaining the largest contribution to SOA formation from methyl nitrophenol. The effects of NO$_x$ on toluene oxidation include the production of nitrophenols and the cycling between RO$_2$ and alkox (RO) radicals, altering the product distributions for the condensable oxidized organics. Specifically, the presence of NO$_x$ impacts the competing RO$_2$ reactions, and the formation of nitrophenols decreases the production of dicarbonyls and organic acids, as reflected by decreased oligomers, NCOs, and carboxylates in the aerosol phase with increasing NO$_x$.

We further examined SOA growth by varying the concentrations of gaseous reactants, i.e., toluene and OH (Figure S10). The particle volume growth rate, defined by $G_R = (D_3 - D_1^3)/(D_0^3 \Delta t)$ where $D_0$ and $D_1$ are the diameters after 30 and 10 min of exposure, increases with the concentrations of toluene (Figure S10a). Measurements of chemical compositions show increased carboxylates, oligomers, and NCOs with increasing toluene concentrations (Figure S10b), consistent with increasing production of condensable oxidized organics to contribute to increasing particle growth.
Similarly, there is increased SOA formation, when OH concentration is increased by a factor of up to 6 (Figure S10c). The measured oligomers and NCOs increase initially but then decrease with increasing OH, while there is a monotonic increase for carboxylates (Figure S10d). While increasing photochemical oxidation generally favors the production of condensable oxidized organics, an excessive OH level oxidizes gaseous dicarbonyls to organic acids to shift oligomerization to carboxylate formation, impacting multigenerational SOA formation. The trends in aerosol-phase carboxylates, oligomers, and NCOs with OH are attributed to an increased formation of organic acids at the expense of dicarbonyls because of multigenerational photooxidation (Figure S10d).

3.4. Linking Multigeneration Oxidation to SOA Formation. The experimental methodology developed here allows for differentiation of the contributions of multigeneration products from VOC oxidation to SOA formation. By simultaneously monitoring the concentrations of gaseous products and particle properties (i.e., size, density, optical properties, and chemical composition), we elucidate the chemical mechanisms for multigeneration SOA production from toluene-OH oxidation (Figure 5). Exposure to oxidation products results in large size growth and browning of seed particles (Figures 1e,f and 2a,b). Two major types of condensable oxidized organics consisting of dicarbonyl and carboxylic functional groups are identified from toluene oxidation, along with a small amount of LVOs (Figures 1h, 2d, and S10c).
Multigeneration photooxidation is clearly illustrated from the temporally resolved evolution in the gaseous and aerosol-phase products (Figures 1−4 and S3). There exist multiple unimolecular (i.e., isomerization and ring-opening) and bimolecular (i.e., with OH and O₂) reactions leading to condensable oxidized organics (Figure S2). Typically, unimolecular reactions occur on much shorter timescales than bimolecular reactions, and bimolecular reactions with O₂ are faster than those with OH because of high O₂ abundance. 21−23 Our results demonstrate prompt SOA and BrC formation from the G2 (two OH reaction steps) and G3 (three OH reaction steps) products, along with one−two additional steps of reactions with O₂. Also, our results show a negligible contribution to SOA formation for HOMs, which are proposed from multigeneration oxidation, i.e., involving three−four OH and two−four O₂ reaction sequences. 27−29 Specifically, we detected no measurable signals associated with HOMs both in the gas and aerosol phases. The formation of primary RO₂ from initial OH addition to the aromatic ring is thermodynamically and kinetically unfavorable, 23 consistent with the large yield of cresols detected by ID-CIMS in our experiments (Figure 1b). The dominant formation of cresols but the large yield of cresols detected by ID-CIMS in our experiments at ambient-pressure ionization (API) is subjected to considerable electric field that operates at a pressure of 5 Torr and with a controlled electric field, both effectively inhibiting clustering of product ions (see the Methods section in the SI). In contrast, atmospheric-pressure ionization (API) is subjected to considerable interference from the formation of ion clusters. 57 Notably, available detection of gaseous HOMs has been made by API-CIMS using NO₃⁻ reagent ions, 27−29 while HOMs have yet to be confirmed by other CIMS methods, such as proton-transfer reaction-mass spectrometry (PTR-MS), which includes the application of a drift tube to minimize ion clustering. On the other hand, the ID-CIMS is capable of detecting HOMs using H₂O⁺ reagent ions, considering its detection limit (about sub-ppb levels) and large proton affinity for HOMs. 45 Future studies on the detection of HOMs using CIMS are warranted to assess their contribution to SOA formation.

Our experiments show that the condensable oxidized organics with different functionalities contribute distinctly to SOA formation. While organic acids from the G2/G3 products engage in ionic dissociation or acid−base reactions to yield carboxylates, dicarbonyls from the G2 products undergo aqueous reactions to form oligomers and NCOs. Gas-particle conversion for organic acids occurs over a wide RH range (i.e., from 10 to 90%), though to a lesser extent at low RH. Condensation of organic acids is implausible because of their high equilibrium vapor pressures (Table S8), and the occurrence of gas-particle conversion implicates a critical role of H₂O in stabilizing organic acids, 51 by facilitating carboxylate formation. Formation of oligomers and NCOs from dicarbonyls takes place efficiently above the efflorescent point at high RH, corroborating an aqueous mechanism involving carbenium ion-mediated and interfacial electric field-enhanced oligomerization to form oligomers and NCOs. 35,36,42 Such a mechanism also explains the inefficient formation of oligomers and NCOs at low RH because of significantly inhibited protonation, hydration, and deprotonation of dicarbonyls.

The conventional view for SOA formation is that multigeneration photooxidation of VOCs yields products with successively decreasing volatility. 12,16,11 The extent of VOC oxidation is commonly expressed by the O/C ratio, which is also correlated with the volatility of the products. For example, HOMs, which likely consist of a range of chemical functional groups such as peroxy, hydroperoxides, and peroxycarboxylic acids with a high O/C ratio (close to unity), are believed to possess sufficiently low volatility and to represent an important category of oxidation products for SOA formation. 27−29 From chemical composition measurements using TD-ID-CIMS, we determined the O/C ratio for the SOA components consisting of carboxylates, oligomers, NCOs, and LVOs, which varies between 0 and 1.75 (Table S8). Notably, there is little correlation between the O/C ratio and SOA contribution for the aerosol-phase products (normalized by their gaseous concentrations), with a correlation coefficient of R² = 0.015 (Figure S11a). Also, the volatility of organic acids and dicarbonyls is sufficiently high to preclude condensation (Table S7). Similarly, there exists no correlation between the equilibrium vapor pressure and SOA formation for the condensable oxidized organics (i.e., dicarbonyls, organic acids, and LVOs), with a correlation coefficient of R² = 0.052 (Figure S11b). Hence, neither the O/C ratio of the SOA components nor the equilibrium vapor pressure of the condensable oxidized organics accurately reflects SOA formation from toluene oxidation.

In our work, the OH concentration is comparable to the ambient level, while the toluene concentration is much higher than those of urban conditions, which range widely from sub-ppb to several hundred ppb. 14,18−20 Production of the condensable oxidized organics in the atmosphere is dependent on the types/abundances of VOCs as well as the extent of oxidation (i.e., the intensity of solar radiation and the reaction time). 35,38 A latest experimental work showed up to 70% of SOA formation by oligomeric products from the OH-initiated oxidation of trimethylbenzene (at 90% RH), 35 which has a molar yield of 90% for methylglyoxal. Our experimental results provide a plausible explanation for large SOA formation under polluted environments. 1,14 Recent measurements revealed that the hygroscopicity for the SOA component resembles those of organic acids, alkylationmmonium carboxylates, and ammonium carboxylates on clean days with low RH but those of glyoxal and methylglyoxal oligomers on polluted days with high RH, 59 consistent with our observed trends for the contributions of organic acids and oligomers/NCOs to SOA formation at low and high RH conditions, respectively. Another recent study suggested a dominant role of uptake of gas-phase oxidation products in SOA formation in Beijing, which is attributable to nonequilibrium dissolution of simple carboxyls and organic acids and increases with RH. 60 Since the aerosol physiochemical properties (size, mass, density, light absorbing/scattering,
etc.) are dependent on RH, the change in the aerosol properties from field measurements is typically referenced to dry particles at low RH. For example, measurements of the mass concentration for fine particulate matter (size smaller than 2.5 μm or PM2.5) are conducted after 48 h equilibration of sample filters below 35−45% RH in an air-conditioned setting. Drying of aerosols inevitably leads to evaporation of volatile and water-soluble species. Hence, SOA formation or growth in field studies is dominantly contributed by nonvolatile aerosol-phase products similar to our present work.

In summary, we show that dicarbonyls and organic acids contribute dominantly to SOA and BrC formation from toluene oxidation because of their prompt production and large yields. The functionality of the condensable oxidized organics largely regulates their participation in aerosol-phase reactions, i.e., ionic dissociation or acid−base reaction for organic acids to form carboxylates and oligomerization for dicarbonyls to form oligomers/NCOs. Our findings of SOA formation from tolune oxidation reconcile atmospheric measurements of explosive SOA growth under polluted urban conditions and underscore the importance of understanding multigeneration production of condensable oxidized organics and the relationship between the functionality and aerosol-phase reactivity. Future studies are necessary to identify and quantify condensable oxidized organics from the photooxidation of different VOC types, including the production from gaseous oxidation, the relationship between functionality and reactivity in the aerosol phase, and contributions to SOA and BrC formation. In addition, our results corroborate that the synergetic interaction between toluene oxidation and NH3 contributes to BrC formation, which impacts the radiative transfer in the atmosphere. The optical properties of ambient BrC aerosols are dependent on the abundance of the precursor gases, the timescale and extent of their photooxidation, production of NCOs, and the mixing state among various aerosol ingredients.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c02026.

Methods, schematic representation of the experimental setup (Figure S1); multigeneration products from toluene-OH photooxidation (Figure S2); temporal evolutions in products and reactants from toluene oxidation (Figure S3); pathways for oligomerization (Figure S4); pathway for BrC formation (Figure S5); size growth with NH3 (Figure S6); variations in size growth and composition with NH3 (Figure S7); temporal evolution in SOA density (Figure S8); variations in size growth and composition with NH3 (Figure S9); variations in particle growth with reactants (Figure S10); SOA formations versus O/C ratio and volatility (Figure S11); density of identified major SOA components (Table S1); contributions of condensable organic species (Table S2); mass-peak assignments for nitrogen-containing organics (Table S3); mass-peak assignments for organic acids and low-volatile organics (Table S4); mass-peak assignments for oligomeric products (Table S5); measured uptake coefficient (Table S6); relative contributions of condensable oxidized organics (Table S7); oxygen to carbon (O/C) ratio (Table S8); and comparison of measured gaseous concentrations (Table S9) (PDF)

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Notes

The authors declare no competing financial interest.

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