1   **Functionality-Based Formation of Secondary Organic Aerosol from *m*-Xylene**

2   **Photooxidation**

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12   **ABSTRACT**. Photooxidation of volatile organic compounds (VOCs) produces condensable

13   oxidized organics (COOs) to yield secondary organic aerosol (SOA), but the fundamental chemical

14   mechanism for gas-to-particle conversion remains uncertain. Here we elucidate the production of

15   COOs and their roles in SOA and brown carbon (BrC) formation from *m*-xylene oxidation by

16   simultaneous monitoring the evolutions of gas-phase products and aerosol properties in an

17   environmental chamber. Four COO types with the distinct functionalities of dicarbonyls,

18   carboxylic acids, polyhydroxy aromatics/quinones, and nitrophenols are identified from early-

19   generation oxidation, with the yields of 25%, 37%, 5%, and 3%, respectively. SOA formation

20   occurs via several heterogeneous processes, including interfacial interaction, ionic

21   dissociation/acid-base reaction, and oligomerization, with the yields of $(20 \pm 4)\%$ and $(32 \pm 7)\%$

22   at 10% and 70% relative humidity (RH), respectively. Chemical speciation shows the dominant

23   presence of oligomers, nitrogen-containing organics, and carboxylates at high RH and

24   carboxylates at low RH. The identified BrC includes N-heterocycles/N-heterochains and

25   nitrophenols, as evident from reduced single scattering albedo. The measured uptake coefficient

26   (γ) for COOs is dependent on the functionality, ranging from 3.7×10^{-4} to 1.3×10^{-2}. A kinetic

27   framework is developed to predict SOA production from the concentrations and uptake

28   coefficients for COOs, and this functionality-based approach well reproduces SOA formation from

29 *m*-xylene oxidation. Our results reveal that photochemical oxidation of *m*-xylene represents a

30 major source for SOA and BrC formation under urban environments, because of its large

31 abundance, high reactivity with OH, and high yields for COOs.

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34 **1.   Introduction**

35   Photooxidation of anthropogenic and biogenic volatile organic compounds (VOCs)

36 produces tropospheric ozone, secondary organic aerosol (SOA), and brown carbon (BrC), with

37 profound implications for air quality, human health, and climate (Pope et al., 2002; Li et al., 2007;

38 IPCC, 2013; NASEM, 2016; Molina, 2021; Zhang et al., 2021). For example, SOA contributes to

39 the Earth energy budget, directly by scattering solar radiation and indirectly by serving as cloud

40 condensation nuclei to influence cloud formation and precipitation (IPCC, 2013; Wang et al., 2014;

41 Zhu et al., 2017). Also, light absorbing BrC interferes with solar radiation transfer, contributing to

42 positive radiative forcing (Wang et al. 2013; NASEM, 2016). VOC oxidation is initiated by various

43 oxidants (e.g., OH, O_3, NO_3, etc.) and proceeds via multiple pathways and stages (Atkinson, 2000;

44 Suh et al., 2001; Zhang et al., 2002; Zhao et al., 2004; Wennberg et al., 2018), yielding condensable

45 oxidized organics (COOs) to form SOA and BrC via gas-to-particle conversion (Finlayson-Pitts

46 and Pitts, 2000; Moise et al., 2015; Seinfeld and Pandis, 2016). Currently, the enormous chemical

47 complexity for VOC oxidation and gas-to-particle conversion represents one of the greatest

48 challenges in atmospheric chemistry research (Ravishankara, 1997; Zhang et al., 2015; NASEM,

49 2016). Aromatic hydrocarbons (e.g., benzene, toluene, xylenes, and trimethylbenzene) account for

50 20-30% of the total VOCs and are the major anthropogenic SOA precursors in the urban

51 atmosphere (Calvert et al., 2002; Ng et al., 2007; Song et al., 2007; Guo et al., 2014; Seinfeld and

52 Pandis, 2016). For example, *m*-xylene or $C_6H_4(CH_3)_2$ represents an important type of aromatic

53 hydrocarbons, which is emitted primarily from industrial and traffic sources. The concentration of

54   *m*-xylene ranges in a level from sub part per billion (ppb) up to several tens of ppb under urban

55   environments (Calvert et al., 2002; Fortner et al., 2009). Photooxidation of *m*-xylene is primarily

56   initiated by OH with a rate constant of 2.4×10^{-11} cm^3 molecule^{-1} s^{-1}, which is nearly four times

57   higher than that of toluene (Fan and Zhang, 2008; Ji et al., 2017). A laboratory study identified *m*-

58   tolualdehyde, *m*-dimethylphenols, and dicarbonyls (i.e., glyoxal, methylglyoxal, unsaturated

59   dicarbonyls, and epoxy carbonyls) as the main gas-phase products from OH-initiated oxidation of

60   *m*-xylene (Zhao et al., 2005).

61   Several types of condensable oxidized organics (COOs) with distinct functionality and

62   volatility are produced form *m*-xylene photooxidation, contributing to aerosol nucleation and grow

63   (Zhang et al., 2004; Zhang et al., 2015; Guo et al., 2020). SOA formation is conventionally

64   considered to be mainly resulted from equilibrium gas-particle partitioning of semi-, intermediate-,

65   or low-volatile products (Shrivastava et al., 2017). Aromatic oxidation by OH yields low-volatile

66   polyhydroxy aromatics/quinones (denoted as PAQ hereafter), which condense to the aerosol-phase

67   (Schwantes et al., 2017). Also, chain autoxidation reactions of RO$_2$ from aromatics photooxidation

68   likely yield highly oxygenated molecules (HOMs) with low volatility (Molteni et al., 2018;

69   Garmash et al., 2020; Wang et al., 2020), although the reported yield of HOMs from *m*-xylene

70   oxidation is small (1.0-1.7%) (Molteni et al., 2018). Several key oxidation products of aromatic

71   oxidation have been shown to readily engage in multiphase reactions and contribute to SOA

72   formation (Ji et al., 2020, Li et al., 2021a). A recent experimental study demonstrated that SOA

73   formation from toluene photooxidation is mainly contributed by volatile dicarbonyls and organic

74   acids (Li et al., 2021b). Moreover, the aqueous reactions between small α-dicarbonyls and base

75   species (e.g., ammonia and amines) produce light-absorbing brown carbon (BrC) (De Haan et al.,

76   2011, 2017; Marrero-Ortiz et al., 2019; Li et al., 2021a,b). Previous experimental studies identified

77 the presence of hydroxy (C-OH), carbonyl (C=O), and acetal (C-O-C) functional groups in

78 aromatic-derived SOA formed via aqueous reactions, implicating a role of oxygenated organics in

79 SOA formation (Jia and Xu, 2014; Jia and Xu, 2018; Zhang et al., 2019). Also, laboratory

80 experiments showed that coating of *m*-xylene SOA on black carbon particles significantly

81 enhances scattering, absorption, and single scattering albedo (SSA) (Guo et al., 2016).

82   Current atmospheric models mainly parameterize SOA formation based on equilibrium

83 partitioning for semi- to low-volatile COOs (Shrivastava et al., 2017). However, gas-to-particle

84 conversion corresponds to decreasing entropy (i.e., $\Delta S \ll 0$), represents non-equilibrium chemical

85 processes (Peng et al., 2021). Moreover, the occurrence of particle-phase reactions significantly

86 alters the physiochemical properties (including volatility, hygroscopicity, and optical properties)

87 for COOs (Tan et al., 2012; Faust et al., 2017; Ji et al., 2020; Li et al., 2021a,b; Liu et al., 2021).

88 Notably, the volatility-based approach consistently under-predicts SOA formation (Heald et al.,

89 2005; Zhang et al., 2015; Hodzic et al., 2016), particularly during haze formation under polluted

90 conditions (Guo et al., 2014; Peng et al., 2021). Here we investigate the production of COOs with

91 different functionalities and assess their roles in SOA formation from *m*-xylene oxidation. A

92 primary objective of this work is to establish a functionality-based framework to predict SOA

93 formation from VOC photooxidation.

94 **2.   Experimental Methodology**

95 **2.1   Chamber experiments**

96   The production of COOs and their roles in SOA formation from *m*-xylene oxidation were

97 investigated using a 1 m^3 chamber (Teflon® PFA, Fig. S1 in the Supplementary Information or

98 SI), similar to our previous studies (Li et al., 2021a,b). The environmental chamber was equipped

99 with eighteen black light lamps (18 × 30W, F30T8/350BL, Sylvania). A water bubbler at a

100 temperature of 30°C was used to humidify the chamber to 10%, 30%, 50%, or 70% relative

101 humidity (RH), and all experiments were performed at 298 K. Three types of seed particles were

102 produced using a constant output atomizer (Model 3076, TSI) to represent various chemical

103 compositions, i.e., NH_4HSO_4 - ammonium bisulfate (ABS), $(NH_4)_2SO_4$ - ammonium sulfate (AS)

104 in the presence and absence of NH_3, and NaCl - sodium chloride. Seed particles were dried to RH

105 of ~2% by a Nafion drier (PD-070−18T-12SS, Perma Pure) and size-selected for an initial size of

106 100 nm by a differential mobility analyzer (DMA, Model 3081, TSI). Size-selected particles were

107 injected into the chamber with an initial particle concentration of 1.5×10^4 cm^{-3} measured by a

108 condensation particle counter (CPC, Model 3760A, TSI). The acidity of seed particles was

109 estimated using a thermodynamic model (Fountoukis and Nenes, 2007; Wang et al., 2018), with

110 the pH value of 3~5 in the presence of gaseous NH_3 and 0~1 in the absence of gaseous NH_3 for

111 $(NH_4)_2SO_4$, -0.5 for NH_4HSO_4, and 7 for NaCl. To investigate the effects of NH_3 and NO_x,

112 commercially available gaseous NH_3 (2000 ppm NH_3 in N_2) and NO_2 (500 ppm NO_2 in air) was

113 injected into the chamber with a flow of 100 sccm. 600 μL H_2O_2 (35 wt%, Sigma-Aldrich) and 10

114 μL *m*-xylene (99.5%, Sigma-Aldrich) were injected into a glass reservoir, which was then flushed

115 into the chamber by a 10 slpm flow from a pure air generator (Aadco 737-11, Aadco Inc.) for 10

116 min. The gases were then mixed by a fan inside the chamber. Once desired concentrations were

117 established, the black light lamps were turned on to initiate H_2O_2 photolysis to generate OH

118 radicals. The initial concentration for *m*-xylene and the steady-state concentration for OH were

119 estimated to be 1.9 ppm and 2.1×10^6 molecules cm^{-3}, respectively (Fig. 1a). The experimental

120 conditions are summarized in Table 1.

121 **2.2   Analytical instruments**

122   The particle size growth, density, light scattering/absorption were simultaneously and

123 continuously monitored, after monodispersed seed particles were exposed to the products of *m*-

124 xylene-OH oxidation in the reaction chamber. A scanning mobility particle sizer (SMPS)

125 consisting of a DMA and a CPC was used to continuously measure the particle size growth factor,

126 GF = D_p/D_0, where D_p is the diameter after exposure and D_o = 100 nm is the initial diameter. Note

127 both D_p and D_0 correspond to the dry particle diameter measured after passing through a Nafion

128 dryer (~2% RH). An aerosol particle mass analyzer (APM, Model 3600, Kanomax) was used to

129 derive the particle density throughout the experiments (Li et al., 2021b). The density for the SOA

130 materials (ρ_{SOA}) is calculated by,

$$\rho_{SOA} = \frac{\rho \times GF^3 - \rho_0}{GF^3 - 1} \qquad (1)$$

131 where ρ and GF are measured particle density (g cm^{-3}) and growth factor at t (min), respectively.

132 ρ_0 is the initial density of seed particles. The uncertainty in the density measurements was

133 estimated to be $\pm$ 0.03 g cm^{-3}.

134   To measure the optical properties of exposed particles, a 1-slpm flow from the chamber

135 was diluted by 4-slpm N_2 and introduced into a commercial integrating nephelometer (TSI 3563)

136 and a home-built cavity ring-down spectrometer (CRDS) throughout the experiment. Light

137 scattering (b_{sca}) and extinction (b_{ext}) at 532 nm were determined by the nephelometer and CRDS,

138 respectively. The nephelometer was calibrated by comparing measured b_{sca} with b_{ext} from CRDS

139 when measuring ammonium sulfate particles with diameters of 100 nm, 150 nm, 200 nm, 250 nm,

140 and 300 nm. The absorption coefficient (b_{abs}) was determined from ($b_{ext} - b_{sca}$), and SSA was

141 calculated from b_{sca}/b_{ext}.

142   The ID-CIMS using the hydronium reagent ion (H_3O^+) was employed to analyze gaseous

143 concentrations with a sample flow rate of 0.5 slpm from the chamber. The sample line was heated

144   to 70°C to reduce wall loss. Gas-phase concentrations of m-xylene and its oxidation products were

145   quantified by ID-CIMS. Briefly, the concentration of species A from the proton transfer reaction

146   ($H_3O^+ + A \rightarrow H_2O + HA^+$) is determined by,

$$[A] = \frac{S_A}{k_{PTR} \times \Delta t \times S_{RI}} \qquad (2)$$

147   where S_A and S_{RI} are the mass spectrum intensities for A and reagent ions, respectively. k_{PTR} is the

148   proton-transfer rate constant between A and H_3O^+ (Zhao and Zhang, 2004). $\Delta t = \frac{l}{U_i}$ is the retention

149   time of ions, which is determined by the length of the drift tube $l = 8$ cm and the ion drift velocity

150   U_i. The ion drift velocity U_i is determined from:

$$U_i = u_0 \left(\frac{760 \; torr}{p}\right)\left(\frac{T}{273 \; K}\right)E \qquad (3)$$

151   where $u_0 = 2$ cm^2 V^{-1} s^{-1} is the reduced ionic mobility (Dotan et al., 1976), $p = 3.0$ torr, $T = 298$ K,

152   and $E = 133$ V cm^{-1} is the voltage gradient in the drift tube. Alternatively, the concentrations of m-

153   xylene, dicarbonyls, and organic acids were also calibrated by preparing the vapors of m-xylene,

154   methylglyoxal with known mixing ratios in N_2, and using a permeation tube of propanoic acid,

155   respectively (Li et al., 2021a). The detection limit (defined as 3 times of the ratio of signal to noise)

156   for the oxidation products from m-xylene-OH reactions was estimated to be 50 ppt by the ID-

157   CIMS.

158   The steady-state OH concentration was determined by exponential fitting ($y = ke^{-bx}$) of

159   the decay of m-xylene concentration (Fig. 1a),

$$[OH] = \frac{b}{k_1} \qquad (4)$$

where $k_1 = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is the second-order rate constant for m-xylene-OH oxidation (Fan and Zhang, 2008). The estimated concentration of OH was 2.1×10^6 molecules cm^{-3} in our experiments.

We also estimated loss of condensable vapors to the chamber wall using the first-order wall-loss coefficient, kw (s^{-1}), by considering gas-phase transport within the chamber (Zhang et al., 2014)

$$kw = \left(\frac{A}{V}\right) \frac{\alpha_w \bar{c}}{4 + \frac{\pi}{2}\left(\frac{\alpha_w \bar{c}}{\sqrt{k_e D_g}}\right)} \tag{5}$$

where A/V is the surface to volume ratio of the chamber (equal to $6/L$ for a square chamber, where $L = 1$ m is its dimension), α_w is the mass accommodation coefficient of vapors onto Teflon chamber walls, $\bar{c}$ is the mean thermal speed of the molecules, k_e is the coefficient of eddy diffusion, which is estimated to be 0.5 based on the loss rate of particles (McMurry and Rader, 1985),

$$k_e = \frac{(\frac{\pi L \beta_0}{12})^2}{D_b} \tag{6}$$

where β_0 is the fractional loss rate of particles,

$$\beta_0 = \frac{\Delta N}{N \times \Delta t} = \frac{15000 \text{ cm}^{-3} - 7500 \text{ cm}^{-3}}{15000 \text{ cm}^{-3} \times 7200 \text{ s}} = 1.4 \times 10^{-5} \text{ s}^{-1} \tag{7}$$

where N is the particle number concentration, $D_b = 6.75 \times 10^{-10}$ m^2 s^{-1} is the Brownian diffusion coefficient for particles. D_g is the gas-phase diffusion coefficient. For NH$_3$, the mass accommodation coefficient of vapors onto the chamber wall is 0.05 (Zhang et al., 2014). Gas-phase diffusion constant D_g is 1.98×10^{-5} m^2 s^{-1}. The mean thermal speed $\bar{c}$ is 603 m s^{-1}. The first-order wall-loss coefficient of NH$_3$ was calculated to be 1.2×10^{-2} s^{-1}.

The average concentration of NH$_3$ or NO$_x$ (noted as X) is estimated by,

$$\overline{[X]} = \frac{(1 - e^{-k_w \times \Delta t_i})}{k_w \times \Delta t_i} [X]_0 \qquad (8)$$

177   For initial injection of 400 ppb NH_3, the average concentration of NH_3 was estimated to be 19 ppb.

178   The first-order wall-loss rate of NO_x was measured to be $2.5 \times 10^{-3}\,h^{-1}$, leading to negligible wall-

179   loss (Qi et al., 2020).

180   The particle-phase chemical composition was analyzed by thermal desorption (TD) - ID -

181   CIMS (TD-ID-CIMS) (Wang et al., 2010). Seed particles after 20 min of exposure to

182   photooxidation were collected for 2 hours by a platinum filament (with a collection voltage of

183   about 3000 V) in a 2.5 slpm flow from the reaction chamber, and the analytes were evaporated by

184   heating the filament to 350°C for 2 s and detected by ID-CIMS using H_3O^+ as the reagent ions.

185   The mass resolution of TD-ID-CIMS was about 0.5 amu. The desorption signal was represented

186   by the relative intensity (RI) of the integrated peak area during heating. The uncertainties of TD-

187   ID-CIMS measurements arose from the flow rate, voltage, collection time, evaporation voltage,

188   and mass spectrometer ionization/detection efficiencies during particle collection and were

189   represented by the standard deviation of three repeated measurements. In both ID-CIMS and TD-

190   ID-CIMS configurations, an ion drift- tube was used. An electric field of E/N = 138 Td was applied

191   for ID-CIMS at high RH (i.e., 70%), and E/N = 110 Td was used for TD-ID-CIMS at low RH (<

192   1%). Formation of cluster ions was effectively suppressed, since a uniform electrical field in the

193   drift tube decomposed weakly-bonded cluster ions. Fragmentation using ID-CIMS or TD-ID-

194   CIMS was minimal, and all gaseous and particle-phase products were detected at their respective

195   parent-peaks, indicating little dissociation effect from either thermal desorption or ionization by

196   H_3O^+(Yuan et al., 2017). For example, the major molecules detected by TD-ID-CIMS at high RH

197   from *m*-xylene oxidation were acetal/hemiacetal oligomers, consistent with a previous study

198   showing intact oligomers with thermal desorption (Claflin and Ziemann, 2019).

199   While the gaseous concentrations of the oxidation products, GF, SSA, and density were

200   temporally resolved in our experiments, the particle chemical composition reflected an overall

201   aerosol chemical makeup during an experiment. To assess the effects of different seed particles,

202   RH, and NH_3 on SOA and BrC formation, we compared the measured GF and SSA values after

203   120-min exposure to the *m*-xylene-OH oxidation.

204   **2.3 Uptake coefficient (γ) determination**

205   The uptake coefficient (γ) for COOs is calculated by,

$$\gamma = \frac{4 \times FR \times kp}{\bar{c} \times S} \qquad (9)$$

206   where FR is the percent contributions of the COO species from *m*-xylene-OH oxidation to the

207   particle-phase mass intensity measured by TD-ID-CIMS. kp is measured first-order particle uptake

208   rate constant for COOs (i.e., glyoxal, methylglyoxal, γ-dicarbonyls, organic acids, PAQ, and

209   nitrophenols), which is calculated from the measured growth rate of seed particles,

$$kp = \frac{\pi \times \left(D_p^3 - D_0^3\right) \times \rho \times \bar{N} \times N_A}{6 \times MW \times [A] \times \Delta t} \qquad (10)$$

210   where D_p and D_0 are the final and initial diameters of the particles during the time-period of,

211   respectively, ρ is the density of total SOA, $\bar{N} = 11250$ cm^{-3} is the average particle number

212   concentration during 120 min, $\Delta t = 120$ min is the exposure time, N_A is Avogadro constant, MW

213   is the molar weight of species A, and [A] is the average gas phase concentration of species A. $\bar{c}$ is

214   the mean thermal speed of A. S is the average surface area of aerosols (cm^2 surface/cm^3 air) during

215   the period of $\Delta t = 120$ min,

$$S = \frac{\pi \int_{t=0}^{120 \, min} D^2 \times HGf^2 \times \bar{N} dt}{\Delta t} \qquad (11)$$

216 where D is the time-dependent particle diameter, HGf is the hygroscopic growth factor of particles

217 (Seinfeld and Pandis, 2016). The error bars of reactive coefficients are derived from the

218 propagation of uncertainties for the parameters in eqs. 9-11 (i.e., 1 σ of at least three repeated

219 measurements for each parameter).

2.4 Simulation of gaseous oxidation products

221 The gas-phase concentration of m-xylene-OH oxidation products were simulated by a tri-

222 exponential kinetic model to account for the gas-phase oxidation, chamber wall loss, and particle

223 uptake. The precursor A with an initial concentration of $[A]_0$ undergoes multiple steps of oxidation

224 to yield multi-generation products, P_n (where $n = 1, 2, 3, \ldots$). Once formed, each product engages

225 in further oxidation with a pseudo first-order rate constant of $k_{n+1}' = k_{n+1}[OH]_{ss}$, particle uptake

226 with a rate of kp_n, and wall loss with a rate of kw_n. The forward rate constants, k_{n+1}, were taken

227 from MCM 3.3.1 (Jenkin et al., 2003). The rate of uptake kp_n is expressed by,

$$kp_n = \frac{1}{4}\gamma_n \bar{c} S \tag{12}$$

228 and the first-order wall loss rate constants were estimated by eq. 5 with the mass accommodation

229 coefficients α_w constrained by the measured time-dependent concentration. The gas-phase

230 concentrations of P_1 to P_3 are calculated by,

$$[P_1] = \frac{k_1'[A]_0}{k_2' + kw_1 + kp_1 - k_1'}(e^{-k_1't} - e^{-(k_2'+kw_1+kp_1)t}) \tag{13}$$

$$[P_2] = C_1 e^{-(k_3'+kw_2+kp_2)t} + C_2 e^{-k_1't} - C_3 e^{-(k_2'+kw_1+kp_1)t} \tag{14}$$

$$[P_3] = C_4 e^{-(k_4'+kw_3+kp_3)t} + C_5 e^{-(k_3'+kw_2+kp_2)t} \\ + C_6 e^{-k_1't} - C_7 e^{-(k_2'+kw_1+kp_1)t} \tag{15}$$

231 where C_1 to C_7 are constants, and k'_n denotes the pseudo-first order rate constant,

$$k'_n = k_n[OH] \tag{16}$$

232   The rate constants and values for C_1 to C_7 are summarized in Table S1.

2.5   COO yield

234   The COO yield (Y_{COO}) from *m*-xylene oxidation is determined from,

$$Y_{COO} = [COO_i]/\Delta[C_6H_4(CH_3)_2] \tag{17}$$

236   where *i* represents the type of COO species, and $\Delta[C_6H_4(CH_3)_2]$ denotes the concentration of *m*-

237   xylene consumed due to OH oxidation. There were four types of COOs identified from our

238   experiments, i.e., dicarbonyls for $i = 1$, carboxylic acids for $i = 2$, PAQ for $i = 3$, and nitrophenols

239   for $i = 4$. The measured gaseous concentration for each COO is corrected for wall-loss and

240   unreacted earlier generation products,

$$[COO_i] = \{[COO_{i,f}] + (\frac{1}{4}\gamma_i \bar{c} S + kw_i)\overline{[COO_i]}\Delta t\}/(1 - \frac{[A_f]}{[A_t]}) \tag{18}$$

241   where $[COO_{i,f}]$ and $\overline{[COO_i]}$ are the final and time-averaged gas-phase concentrations of COO_i at

242   120 min, respectively. $[A_f]$ and $[A_t]$ are the unreacted and the total production of the earlier

243   generation species A, respectively.

2.6   SOA mass concentration and yield

245   The measured SOA mass concentration is calculated based on the aerosol size growth and

246   density,

$$M_{SOA,meas.} = \frac{1}{6}\pi(D_p^3 \times \rho_t - D_0^3 \times \rho_0) \times \bar{N} \tag{19}$$

247   where ρ_t and ρ_0 are the final and initial particle density during 120 min, respectively.

248   Alternatively, by categorizing COOs in accordance with the functional groups, we established a

249   framework to predict SOA formation from the measured production and reactivity. The SOA mass

250   concentration (M_{SOA}) is predicted from the measured uptake coefficients and average gas-phase

251   concentrations of COOs,

$$M_{\text{SOA}} = \sum_i^4 \frac{1}{4} \gamma_i \bar{c}_i S[\text{A}_\text{i}] MW_i \tag{20}$$

252 where MW_i is the molar weight of species i. γ_i is averaged over all identified species for each type

253 (i) of COOs, and $[\text{A}_i]$ is the sum of the measured concentrations of all identified species for type i

254 (time-averaged). The SOA mass yield is expressed by,

255 $$Y_{SOA} = M_{\text{SOA}}/\{\Delta[C_6H_4(CH_3)_2] \times MW_m\} \tag{21}$$

256 where MW_m is the molar weight of m-xylene.

257   To compare the measured and predicted SOA formation at RH = 10% and 70%, we

258 corrected the increased vapor wall loss and reduced particle surface area at RH = 70% compared

259 to 10% RH. A correction factor is determined from the average measured gas concentration ratios

260 (R_c) between 10% and 70% RH for each type of COOs. Additionally, a hygroscopic volume

261 enhancement factor (HVE) of 1.2 between 10% and 70% RH is adopted. The RH-corrected SOA

262 mass for each COO is estimated by,

$$M_{i,corr} = R_c \times M_{SOA} \times \frac{S_1}{S_2} \times \text{HVE} \tag{22}$$

263 where S_1 and S_2 are the particle surface areas at 10% and 70% RH, respectively.

264 **3.   Results and Discussions**

265 **3.1   Evolution of oxidation products**

266   To elucidate the production of COOs, we measured time-dependent gaseous concentrations

267 of m-xylene oxidation products. The OH-m-xylene reactions occur via dominantly OH-addition to

268 the aromatic ring to yield m-xylene-OH adducts and minorly H-abstraction from the methyl group

269 to form methylbenzyl radicals (about 4%) (Fan and Zhang, 2008). The m-xylene-OH adducts then

270 react with O_2 to form dimethylphenol via H-extraction or OH-m-xylene-O_2 peroxy radicals (RO_2)

271 via O_2 addition (Fig. S2a). While the m-xylene mixing ratio exhibits an exponential decay

272 throughout the experiments (Fig. 1a), the formation of the gas-phase oxidation products follows

273 the rate-determining steps involving successive OH-oxidation with three major generations (Fig.

274 1b-e). The first-generation products (P_1) include dimeththylphenol (m/z = 123) and

275 methylbenzaldehyde (m/z = 121), corresponding to OH addition to the aromatic ring (~96%) and

276 hydrogen extraction (~4%) from the methyl group, respectively (Fan and Zhang, 2008; Li et al.,

277 2021b). The second-generation products (P_2) mainly consist of methylglyoxal (m/z = 73),

278 methylbutenedial (m/z = 99), toluic acid (m/z = 137), and dimethylresorcinol (Fig. 1f and Fig. S2b),

279 which are produced from the P_1 reactions with OH/HO_2. For example, methylglyoxal and

280 methylbutenedial are formed from OH oxidation of dimeththylphenol and subsequent ring-

281 opening or from the primary peroxy radical. The latter undergoes cyclization to form the bicyclic

282 radical, which then reacts with O_2 to form the secondary peroxy radical, followed by reactions

283 with HO_2 and subsequent ring-cleavage (Fan and Zhang, 2008). The third-generation products (P_3)

284 contain mainly multi-functional organic acids, including pyruvic acid (m/z = 89), 4-oxo-2-

285 pentenoic acid (m/z = 115), and 3-methyl-4-oxo-2-pentenoic acid (m/z = 129) produced from the

286 subsequent reactions of dicarbonyls with OH. Note that P_n in Fig. 1b denotes the lumped product

287 of the nth generation, which is related the sequence of OH addition for m-xylene oxidation and

288 accounts for the various species detected by ID-CIMS (Fig. S2b).

289   The P_1 concentrations rise immediately upon initiating photooxidation and reach the peak

290 mixing ratios of about 20 ppb for dimeththylphenol and 9 ppb for methylbenzaldehyde. There is a

291 slight decline in P_1 concentrations after 70 to 100 mins, reflecting their consumption from further

292 OH oxidation (Fig. 1c). The P_2 concentrations follow those of P_1 (Fig. 1d and Fig. S3a) and reach

293 the peak mixing ratios ranging from 0.4 to 2.4 ppb, dependent on their subsequent oxidation by

294 OH as well as loss to the chamber wall and aerosols. Note that the concentration of toluic acid

295   rises later than those of the dicarbonyls, attributable to the slower rates for H-abstraction by OH

296   from the methyl group than OH-addition to the aromatic ring (Fan and Zhang, 2008). The P_3

297   concentrations increase monotonically after a delay of 10-20 mins and reach a mixing ratio from

298   sub-ppb to 2.5 ppb at 120 min (Fig. 1e and Fig. S3b). The initial concentration of *m*-xylene (e.g.,

299   1940 ppb) in our experiment is higher than that in the atmosphere, potentially inducing self- and

300   cross-reactions of RO_2 to form alkoxy radicals (RO) or dialkyl peroxides (ROOR') leading to

301   HOMs. However, negligible products relevant to HOMs were detected in our experiments,

302   indicating a minor importance for the self- and cross-reactions of RO_2 compared to the competing

303   reactions between RO_2 and $HO_2/NO/RO_2$ to form ring-opening products. Our results for

304   insignificant contribution of HOMs to SOA formation from m-xylene oxidation are consistent with

305   a small yield of HOMs reported in a previous study (Molteni et al., 2018).

306   We simulated the time-dependent evolution of the gaseous products by employing a tri-

307   exponential kinetic model (Fig. 1b and Table S1). Multi-generation oxidation of *m*-xylene occurs

308   via consecutive reaction steps to produce a multi-generation product, P_n (where *n* denotes the

309   sequence of OH oxidation), which subsequently engages in additional OH oxidation, wall loss,

310   and aerosol loss. Fig. 1b-d indicates that the simulated concentrations well reproduce those

311   measured for P_1 to P_3 by adopting our measured γ (to be discussed below) and estimated wall loss

312   rates (see Methods and Table S1 in SI).

313   **3.2   Particle size growth, SSA, and chemical speciation**

314   To evaluate SOA and BrC formation from COOs, we measured the time-dependent GF,

315   SSA, and density, after $(NH_4)_2SO_4$ seed particles are exposed to the *m*-xylene oxidation products

316   in the presence of 19 ppb NH_3 and at 70% RH (Fig. 2a-c, Exp. 1). The GF increases monotonically

317   and reaches a value of (2.41 ± 0.03) at 120 min (Fig. 2a), while the SSA declines steadily

318 throughout the exposure and reaches the value of (0.91 ± 0.01) at 120 min (Fig. 2b). The latter is

319 indicative of the production of light-absorbing BrC. The measured SSA for m-xylene is lower than

320 that previously reported for toluene under comparable experimental conditions (Li et al., 2021b).

321 The difference in SSA/BrC formation between toluene and m-xylene is explained by a higher yield

322 of methylglyoxal from m-xylene than from toluene (Jenkin et al., 2003; Nishino et al., 2010), since

323 methylglyoxal produces BrC more efficiently via aqueous reaction than glyoxal (Li et al., 2021a).

324 Analysis of particle chemical composition using TD-ID-CIMS reveals high abundances of

325 oligomers, nitrogen-containing organics (NCO) consisting of N-heterocycles/N-heterochains,

326 carboxylates, along with a small amount of dimethylresorcinol/benzoquinone (Fig. 2c). The

327 identified mass peaks are summarized in Tables S2 to S4. Assuming similar sensitivity to proton-

328 transfer reactions for the aerosol-phase organics, i.e., with the proton transfer reaction rate

329 constants of $(2 \text{ to } 4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (Zhao and Zhang, 2004), the contributions of

330 oligomers, NCO, carboxylates, and dimethylresorcinol/benzoquinone to the total SOA formation

331 are estimated to be 22%, 23%, 47%, and 8%, respectively, at 70% RH (Table S5). Note that the

332 TD-ID-CIMS method preserves the identify for all organic species without fragmentation,

333 providing unambiguous chemical speciation for the aerosol-phase products.

334 **3.3   Effects of seed particles, NH$_3$, RH, and NO$_x$**

335   We assessed the dependence of SOA/BrC formation from m-xylene-OH oxidation on

336 different seed particles (Exp. 1-4), NH$_3$ concentration (Exp. 1-12), RH (Exp. 1,13-15), and NO$_x$

337 concentration (Exp. 1,16-18). Fig. 3a shows that $(NH_4)_2SO_4$ in the presence of 19 ppb NH$_3$ exhibits

338 the largest GF and lowest SSA at 120 min, which are explained by the chemical mechanisms

339 leading to the formation of the observed aerosol-phase products. While dicarbonyls undergo

340 aqueous phase reactions to form oligomers (Fig. S4) (Ji et al., 2020; Li et al., 2021a), organic acids

341 engage in ionic dissociation and acid-base reaction to yield carboxylates (Fig. 3b). In addition, the

342 reaction of dicarbonyls with NH_3 produces N-heterocycles/N-heterochains (Fig. S5), which are

343 light-absorbing (Marrero-Ortiz et al., 2019; Li et al., 2021a). Oligomerization of dicarbonyls

344 involves protonation, hydration, and deprotonation, which are mediated by carbenium ions via

345 nucleophilic addition (Ji et al., 2020; Li et al., 2021a). While protonation of dicarbonyls to yield

346 carbenium ions is promoted by hydrogen ion activity, high acidity hinders hydration and

347 deprotonation, explaining the largest GF and the smallest SSA on weakly acidic $(NH_4)_2SO_4$

348 particles in the presence NH_3 (Fig. 3a). In addition, uptake of dicarbonyls, organic acids, and PAQ

349 is likely facilitated on aqueous $(NH_4)_2SO_4$ particles, because of surface propensity of charge-

350 separation at the interface (Hua et al., 2011; Shi et al., 2020). Specifically, surface-abundant NH_4^+

351 cations arising from interfacial charge separation of $(NH_4)_2SO_4$ likely exert electrostatic attraction

352 to gaseous oxygenated species (with a negative charge character) to enhance uptake for

353 dicarbonyls, organic acids, and PAQ (Li et al., 2021a,b). The most efficient formation of SOA and

354 BrC on $(NH_4)_2SO_4$ particles in the presence of NH_3 are also consistent with the measured highest

355 intensities for oligomers and NCO (Fig. 3b). On the other hand, ionic dissociation and acid-base

356 reaction to yield carboxylates occur efficiently in the presence of NH_3/NaCl, as evident from the

357 increasing carboxylate intensity from NH_4HSO_4 to NaCl (Fig. 3b). The GF and SSA increase and

358 decrease, respectively, with NH_3 from 0 to 27 ppb for all three types of seed particles (Fig. 4a,b),

359 relevant to the reactions of NH_3 with dicarbonyls to form NCO and with organic acids to form

360 ammonium carboxylates. The analysis of the particle composition confirms that the intensities of

361 oligomers, NCO, and carboxylates increase with the NH_3 concentration (Fig. 4c-e).

362   We carried out additional experiments by varying RH from 10% to 70% in the presence of

363 19 ppb NH_3 (Fig. 5). The GF decreases with increasing RH from (3.10 ± 0.06) at RH = 10% to

364   (2.41 ± 0.03) at RH = 70% (Fig. 5a). The measured SSA at 120 min is close to unity at 10% and

365   30% RH and decreases with increasing RH (Fig. 5a), indicating negligible NCO formation at low

366   RH but significant NCO formation at RH above 50%. Carboxylates represent the dominant

367   constituent throughout the RH range (i.e., 85% at 10% RH to 47% at 70% RH), while the

368   contributions of oligomers and NCO are small at low RH (2-5% at RH < 40%) and become

369   increasingly significant at high RH (15-23% at RH > 50%) (Fig. 5b). The fraction for PAQ (8%)

370   is nearly invariant with RH. For $(NH_4)_2SO_4$ particles, the deliquescent and efflorescent points are

371   at 80% and 36% RH, respectively (Li et al., 2021b). At low RH (10% and 30%), aqueous reactions

372   to yield oligomers/NCO are minimal because of small water activity and significantly suppressed

373   protonation and oligomerization. On the other hand, carboxylic acids readily undergo ionic

374   dissociation or acid-base reaction, since organic acids efficiently retain water even at low RH (Xue,

375   2009). The equilibrium vapor pressures for PAQ are much lower than those for organic acids

376   (Table S6), facilitating more efficient condensation. Additionally, wall-loss of COOs is more

377   pronounced at high RH (Li et al., 2021b), explaining the decreased GF with increasing RH.

378   Measurement of gaseous concentrations for COOs shows that wall-loss is 1.5 to 4.6 times more

379   efficient at 70% RH than at 10% RH, while wall loss of m-xylene is negligible at both RH levels

380   (Table S7).

381   We determined the total density and the density of the SOA fraction for $(NH_4)_2SO_4$ seed

382   particles exposed to m-xylene oxidation (Fig. 5 c,d). The measured densities are distinct between

383   10 and 70% RH. At 10% RH, the total density decreases monotonically, while the SOA density

384   increases slightly with reaction time, i.e., from 1.27 to 1.39 g cm^{-3} (Fig. 5c), indicating minor

385   oligomers and dominant carboxylic acids at low RH. At 70% RH, the total particle density initially

386   decreases from 1.77 g cm^{-3} to 1.41 g cm^{-3} (at a GF of 1.24) and subsequently increases steadily to

387   1.56 g cm^{-3} at 120 min. The SOA density on $(NH_4)_2SO_4$ particles increases from 1.26 g cm^{-3} at 10

388   min to 1.55 g cm^{-3} at 120 min (Fig. 5d). The evolution in the densities reflects the variation in the

389   chemical composition. The initial particle growth is dominated by small oligomers, imidazoles

390   from methylglyoxal/methylbutenedial, and early-generation organic acids (e.g., toluic acid), with

391   the densities from 0.98 to 1.27 g cm^{-3} (Table S8). Subsequent particle growth from

392   methylglyoxal/methylbutenedial yields large oligomers, with the densities of 1.71-1.90 g cm^{-3}

393   (Table S8).

394   To evaluate the NO_x effects, we performed experiments on $(NH_4)_2SO_4$ seed particles by

395   varying the initial NO_x concentration from 0 to 500 ppb (Fig. 6). Three major nitrophenols are

396   identified from NO_2 addition to the OH-*m*-xylene adduct, i.e., 4-methyl-2-nitrophenol ($m/z = 154$),

397   dimethyl nitrophenol ($m/z = 168$), and dimethyl-4-nitrocatechol ($m/z = 184$) (Fig. 6a). The

398   production of nitrophenols is much smaller than those for dicarbonyls and organic acids, consistent

399   with a smaller yield (less than 7%) for nitrophenols (Fan and Zhang, 2008). The GF on $(NH_4)_2SO_4$

400   seed particles with NH_3 decreases from 2.41 ± 0.03 to 2.18 ± 0.03 with 0 to 500 ppb NO_x (Fig. 6b).

401   The SSA decreases significantly from 0.911 ± 0.006 to 0.839 ± 0.003 with increasing NO_x (Fig.

402   6b), because of the formation of light-absorbing nitrophenols (Hems and Abbatt, 2018; Li et al.,

403   2021b). Analysis of particle composition reveals that the decreasing GF with increasing NO_x

404   correlates with simultaneous decreases of carboxylates, oligomers, and NCOs and with increasing

405   nitrophenols in the aerosol-phase (Fig. 6c). Overall, nitrophenols contribute 2% to 4% to the SOA

406   formation. Addition of NO_x not only produces nitrophenols and but also alters the cycling between

407   RO_2 and alkoxy (RO) radicals, leading to re-distributions of COOs. The presence of NO_x decreases

408   dicarbonyls and organic acids, as evident from decreased intensities for oligomers, NCO, and

409   carboxylates in the aerosol-phase with increasing NO_x (Fig. 2h).

3.4   COO and SOA Yields

From the measured GF and COO concentrations, we derived the γ, which is widely employed to represent aerosol formation in atmospheric models (Zhang et al., 2015). The measured γ varies with the functionality of COOs and RH on $(NH_4)_2SO_4$ seed particles (Fig. 7a). Results of the γ values for COOs are also summarized in Table S9. The γ for dicarbonyls is the highest (from 3×10^{-3} to 1.3×10^{-2}) at 70% RH but is significantly reduced (from 3.7×10^{-4} to 1.0×10^{-3}) at 10% RH, while the γ's for organic acids, PAQ, and nitrophenols are slightly higher at 70% RH. Among the organic acids, the γ correlates with the acid dissociation constant and solubility, which are the highest for pyruvic acid and the lowest for toluic acid. The standard variation in γ (within one σ) among each COO type is within 50%, 40%, 30%, and 15% for dicarbonyls, organic acids, PAQ, and nitrophenols, respectively. From the measured concentrations of COOs and m-xylene, we determined the COO yields (Y_{COO}) using eq. 17, by considering four COO species, i.e., dicarbonyls for $i = 1$, carboxylic acids for $i = 2$, PAQ for $i = 3$, and nitrophenols for $i = 4$ (Table S7). The Y_{COO} values for dicarbonyls, organic acids, PAQ, and nitrophenols are 25%, 37%, 5%, and 3%, respectively (Fig. 7b), indicating significant production of COOs from m-xylene oxidation.

Our work shows significant increase in particle size (Fig. 2a) and constantly varying particle properties, i.e., SSA (Fig. 2b) and density (Fig. 5c,d), which closely correlate with the gaseous COO production (Fig. 1). These results imply a highly nonequilibrium kinetic process leading to SOA formation from m-xylene oxidation, which cannot be described by equilibrium partitioning. The gas-to-particle conversion from m-xylene oxidation is dominated by several volatile COO species (i.e., organic acids and dicarbonyls) and with minor contribution from condensation of low-volatility COO (i.e., polyhydroxy aromatics/quinones, and nitrophenols) (Fig.

433   5b). In our study, the vapor pressures of the detected gaseous oxidation products for organic acids

434   and dicarbonyls are too large to explain the measured particle growth via equilibrium partitioning

435   (Table S6). Specifically, the saturation vapor pressures of organic acids detected in the particle-

436   phase range from 1.9×10^{-3} to 6.6×10^{-6} atm, while their gas-phase concentrations range from 0.5

437   to 2.5 ppb. Similarly, the saturation vapor pressures of dicarbonyls detected in the particle-phase

438   range from 1.6×10^{-1} to 3.9×10^{-4} atm, while their gas-phase concentrations range from 0.5 to 2.2

439   ppb. The high saturation vapor pressures and low gas-phase concentrations for those COOs render

440   equilibrium partitioning implausible in our experiments. Also, the detection of the particle-phase

441   products confirms that organic acids and dicarbonyls directly participate in heterogeneous

442   reactions to yield low-volatility products. Moreover, volatility-based equilibrium partitioning

443   cannot not explain the variations in the particle size growth, SSA, and chemical compositions on

444   different seed particles (Fig. 3). Clearly, the gas-to-particle conversion from *m*-xylene oxidation

445   involves several distinct heterogeneous processes, including the interfacial interaction, ionic

446   dissociation/acid-base reaction, and nucleophilic oligomerization (Li et al., 2021a,b).

447   We establish a functionality-based SOA formation to predict the aerosol mass

448   concentration (M_{SOA}) from the measured gaseous concentrations and γ's for COOs using eq. 20.

449   The M_{SOA} is calculated using the averaged γ (Fig. 7a and Table S10) and the measured time-

450   averaged concentrations for each COO type (Table S7). While the production of COOs is

451   dependent on the VOC types and photooxidation, the aerosol-phase reactivity of COOs, as

452   represented by γ, is only dependent on the functionality for a given aerosol type. Thus, SOA

453   formation from various VOC types can be predicted from the production and reactivity for COOs

454   based on the experimental measurements, by categorizing COOs in accordance with their

455   functional groups. In our study, the measured uptake coefficient for each COO type (γ_i) is derived

456 from the measured particle growth (eqs. 9 and 10), which implicitly accounts for non-continuum

457 diffusion, imperfect accommodation, and evaporation (Zhang et al., 1994; Ravishankara, 1997).

458   To assess the consistency of our approach, we compared the predicted and measured SOA

459 mass yields (Y_{SOA}), according to eq. 21. The predicted Y_{SOA} is $(11 \pm 3)\%$ and $(6 \pm 1)\%$,

460 respectively, at 10% and 70 % RH, comparable to the measured values of $(14 \pm 0.4)\%$ and $(6.3 \pm$

461 $0.2)\%$ on $(NH_4)_2SO_4$ seed particles (Fig. 7c). The slight differences between the predicted and

462 measured Y_{SOA}'s are explainable by the uncertainties related to lumping each COO type (i.e.,

463 averaging the γ values) as well as unaccounted low-abundant COO species. To account for the

464 RH-dependent wall loss for COOs, we corrected Y_{SOA} from the measured gaseous concentrations

465 at varying RH (see Methods and Table S7). Such correction results in an increase of about one to

466 four times for Y_{SOA} at 10% and 70% RH, yielding the values of $(20 \pm 4)\%$ and $(32 \pm 7)\%$,

467 respectively (Fig. 7c). Under atmospheric conditions, SOA/BrC formation from m-xylene is

468 expected to be enhanced at high RH, because of significantly enhanced aqueous reaction, larger

469 aerosol surface-area, and higher water activity. Field measurements showed significantly enhanced

470 SOA formation with increasing RH during severe haze evolution (Guo et al., 2014; Peng et al.,

471 2021).

472 **4.**   **Conclusions**

473   In this work we have elucidated the production of COOs and their roles in SOA formation

474 from m-xylene oxidation. The major advantages of our analytical methodologies lie in

475 simultaneous monitoring of the evolutions of gaseous oxidation products and aerosol properties

476 when seed particles are exposed to the oxidation products, which allows for assessment of multi-

477 generation production of SOA and BrC. Also, our experimental approach remedies the deficiency

478 of wall loss of reactive gaseous and particles, which represents a main obstacle in experimental

479 investigation using environmental chambers (Zhang et al., 2014; Huang et al., 2018). OH-initiated

480 oxidation of *m*-xylene produces four distinct COO types consisting of dicarbonyls, carboxylic

481 acids, polyhydroxy aromatics/quinones, and nitrophenols from early-generation (P$_2$ and P$_3$), with

482 the yields of 25%, 37%, 5%, and 3%, respectively. SOA formation occurs via several

483 heterogeneous processes, including interfacial interaction, ionic dissociation/acid-base reaction,

484 and oligomerization, with the yields of (20 ± 4)% at 10% RH and (32 ± 7)% at 70% RH. The

485 identified aerosol-phase products include dominant oligomers, N-heterocycles/N-heterochains,

486 and carboxylates at high RH and dominant carboxylates at low RH, along with small amounts of

487 PAQ and nitrophenols (in the presence of NO$_x$). The nitrogen-containing organics consisting of

488 N-heterocycles, N-heterochains, and nitrophenols are light-absorbing, characterized by low SSA.

489 The measured γ for COOs is dependent on the functionality, ranging from 3.7×10^{-4} to 1.3×10^{-2}.

490 A kinetic framework is developed to predict SOA formation from the concentration and γ for

491 COOs. Our results illustrate that SOA formation from *m*-xylene oxidation is accurately quantified

492 from the abundance and reactivity for COOs (i.e., eq. 20). Notably, this kinetic framework

493 accounts for the interfacial process (i.e., mass accommodation) as well as aqueous reactions (i.e.,

494 oligomerization and acid-base reactions) without the assumption of gas-particle equilibrium. We

495 envisage that this functionality-based approach is applicable to predict SOA formation from VOC

496 photooxidation using experiment/field measured or model-simulated COOs, aerosol surface area,

497 and reactivity. We conclude that photochemical oxidation of *m*-xylene represents a major source

498 for SOA and BrC formation under urban conditions, because of its large abundance, high reactivity

499 with OH, and high yields for COOs.

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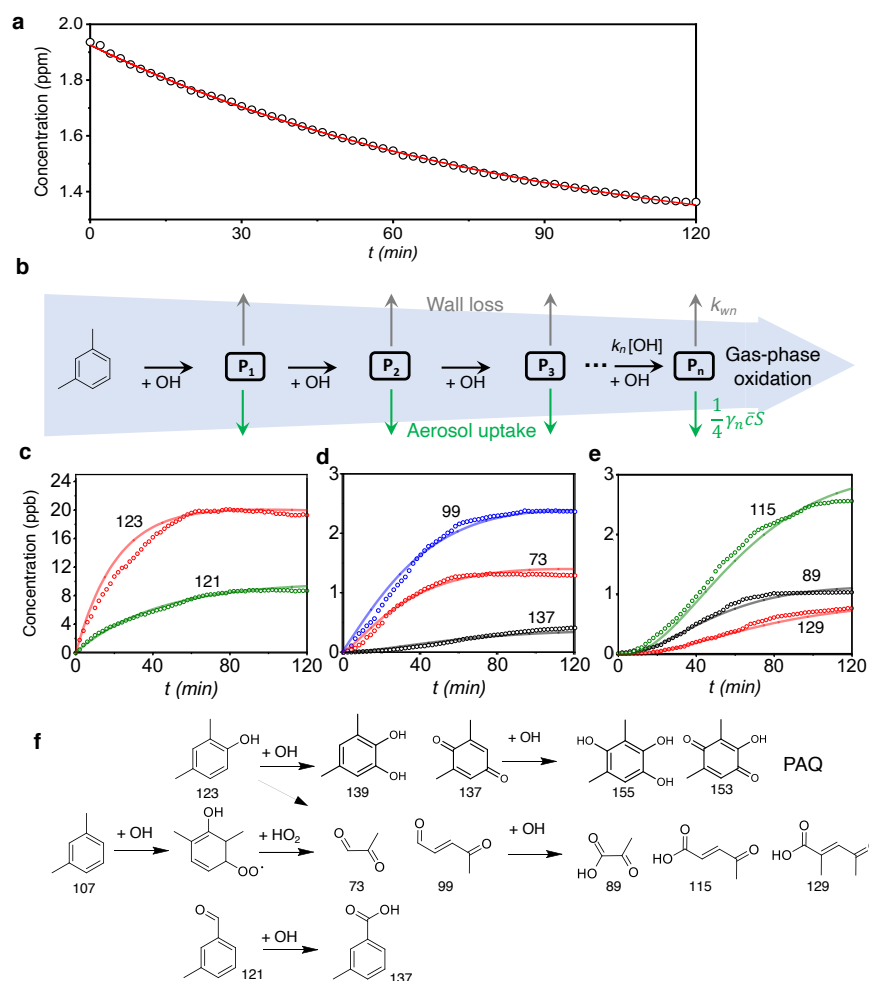
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728 **Figure 1.** OH-initiated photooxidation of *m*-xylene. (a) Time-dependent concentration of *m*-
729 xylene. The symbols are from the measurements, and the red solid line corresponds to exponential
730 fitting of the *m*-xylene concentration. The initial concentration for *m*-xylene and the estimated
731 steady-state concentration for OH are 1940 ppb and 2.1×10^6 molecules cm^{-3}, respectively, with a
732 bimolecular rate constant of 2.4×10^{-11} cm^3 molecule^{-1} s^{-1}. (b) Schematic representation leading to
733 the multi-generation product, P_n, where n denotes the sequence of OH-initiated oxidation. The
734 black, gray, and green arrows denote the gas-phase oxidation, chamber wall loss, and aerosol
735 uptake, respectively. k_n and kw_n are the rate coefficients for the gas-phase oxidation and wall loss,
736 respectively, γ_n represents the aerosol uptake coefficient, $\bar{c}$ is the thermal velocity, and S is the
737 aerosol surface area. (c-e) Time-dependent gas-phase concentrations of P_1 (c), P_2 (d), and P_3 (e)
738 products. The symbols are from measurements, and the solid curves are simulated according to the
739 tri-exponential kinetics. (f) The gaseous oxidation pathways leading to the detected products. The
740 top row corresponds to the pathways leading to polyhydroxy aromatics/quinones (PAQ). The
741 numbers in (c) to (f) represents the mass to charge ratio (*m/z*). All experiments are carried out for
742 (NH$_4$)$_2$SO$_4$ seed particles with 19 ppb NH$_3$ at 298 K and RH = 70%. Initiation of photooxidation
743 by ultraviolet light occurs at $t = 0$.

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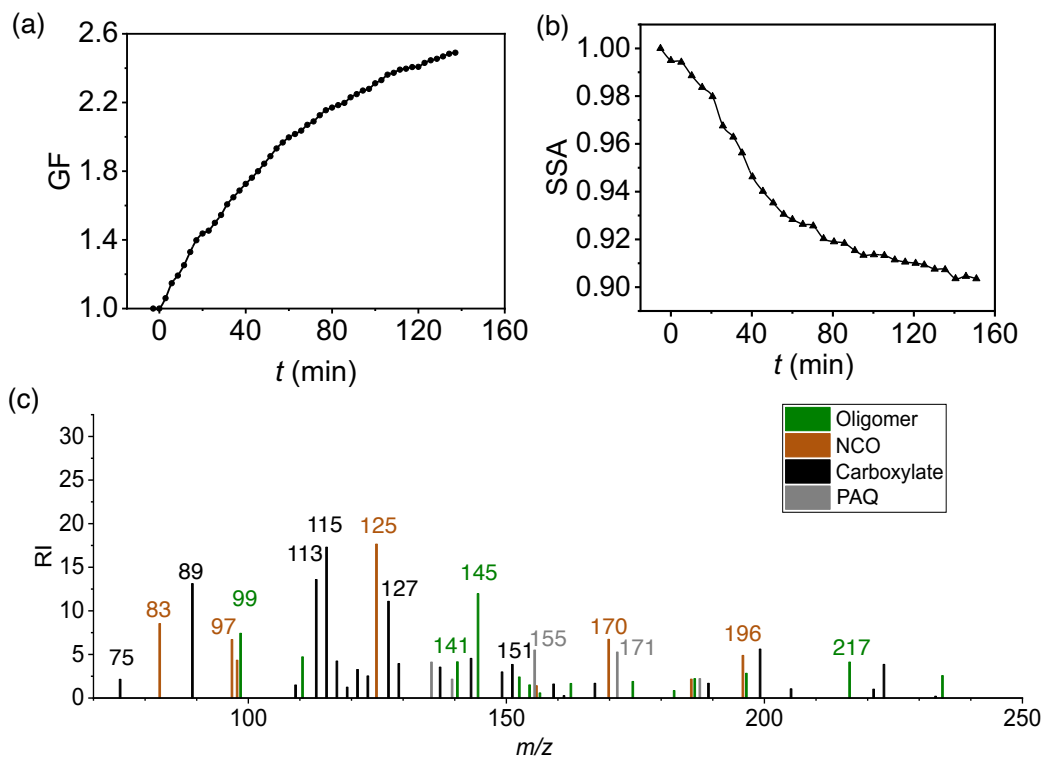
Figure 2. SOA and BrC formation from *m*-xylene photooxidation. Time-dependent growth factor
(GF = D_p/D_0, a) and single scattering albedo (SSA, b) of seed particles exposed to *m*-xylene
oxidation products. (c) Chemical speciation of aerosol-phase products by TD-ID-CIMS. Initiation
of photooxidation by ultraviolet light occurred at $t = 0$. RI denotes the relative intensity for the
integrated peak area during thermal desorption. All experiments are carried out for $(NH_4)_2SO_4$ seed
particles with 19 ppb NH_3 at 298 K and RH = 70%.

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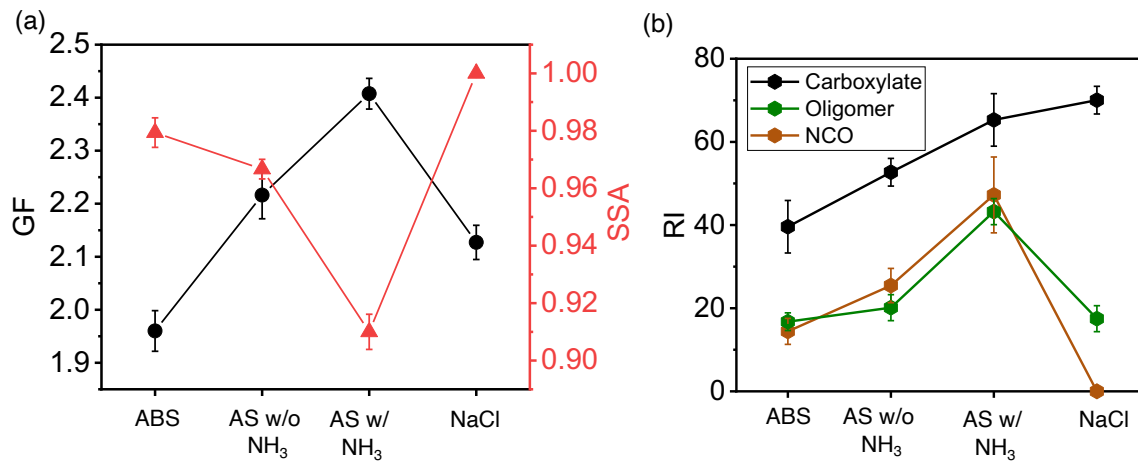
Figure 3. Dependence of SOA/BrC formation on seed particles. (a) GF (black) and SSA (red) at
120 mins of exposure for $(NH_4)_2SO_4$ particles in the presence (AS w/ NH_3) and absence (AS w/o
NH_3) of 19 ppb NH_3 and for NH_4HSO_4 (ABS) and NaCl particles in the absence of NH_3. (b)
Aerosol-phase relative intensity (RI) for carboxylates (black), oligomers (green), and NCO (brown)
on different seed particles. The error bar denotes 1σ of 3 replicated measurements. All particle
properties were measured relevant to dry conditions (less than 5% RH) and were dominantly
contributed by non-volatile aerosol-phase products.

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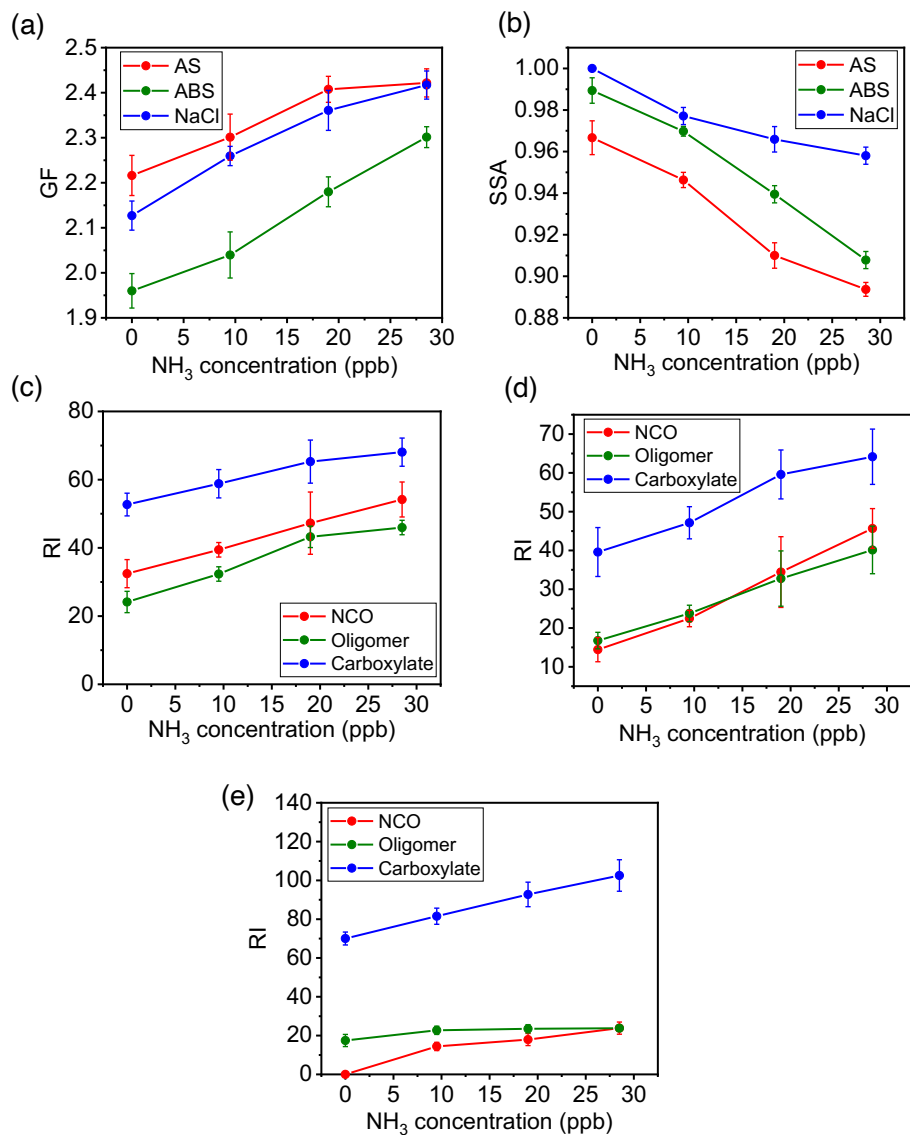
Figure 4. Variation of SOA formation with seed particles and NH_3 concentration. (a,b) growth
factor (a) and SSA (b) at t = 120 min with varying NH_3 concentration between 0 and 27 ppb for
ammonium sulfate (AS, red), ammonium bisulfate (ABS, green), and sodium chloride (NaCl,
blue) seed particles. (c-e) Aerosol-phase mass relative intensity (RI) for NCO (red), oligomers
(green), and carboxylates (blue) on AS (c), ABS (d), and NaCl (e) seed particles. The error bar
denotes 1σ of 3 replicated measurements.

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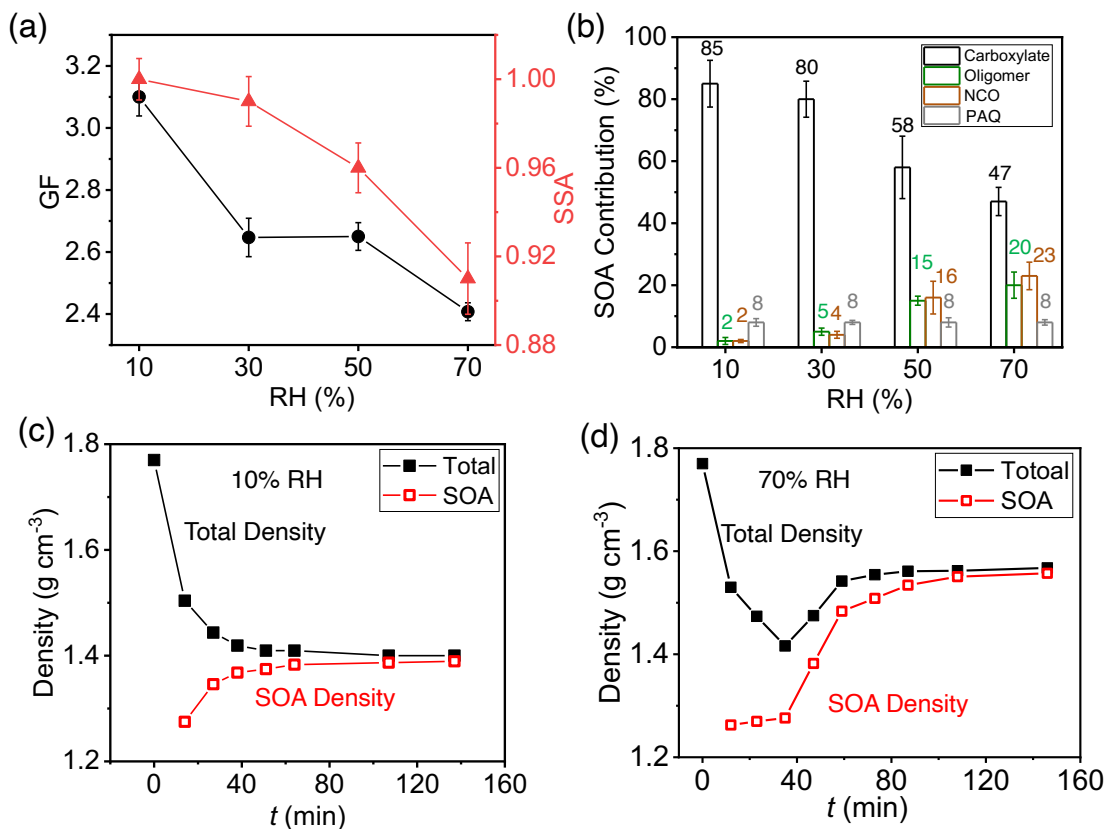
Figure 5. Dependence of SOA/BrC formation on RH. (a) GF (black) and SSA (red) at 120 min with varying RH from 10% to 70%. (b) Contribution of COOs to SOA formation with varying RH from 10% to 70%: carboxylate (black), oligomers (green), NCO (brown), and PAQ (gray) to SOA formation. The number denotes the percentage contribution (%) of each type of aerosol-phase products. (c,d) Time-dependent particle (black) and SOA (red) densities of seed particles exposed to *m*-xylene oxidation products at RH = 10% (c) and 70% (d), respectively. The error bar denotes 1σ of 3 replicated measurements.

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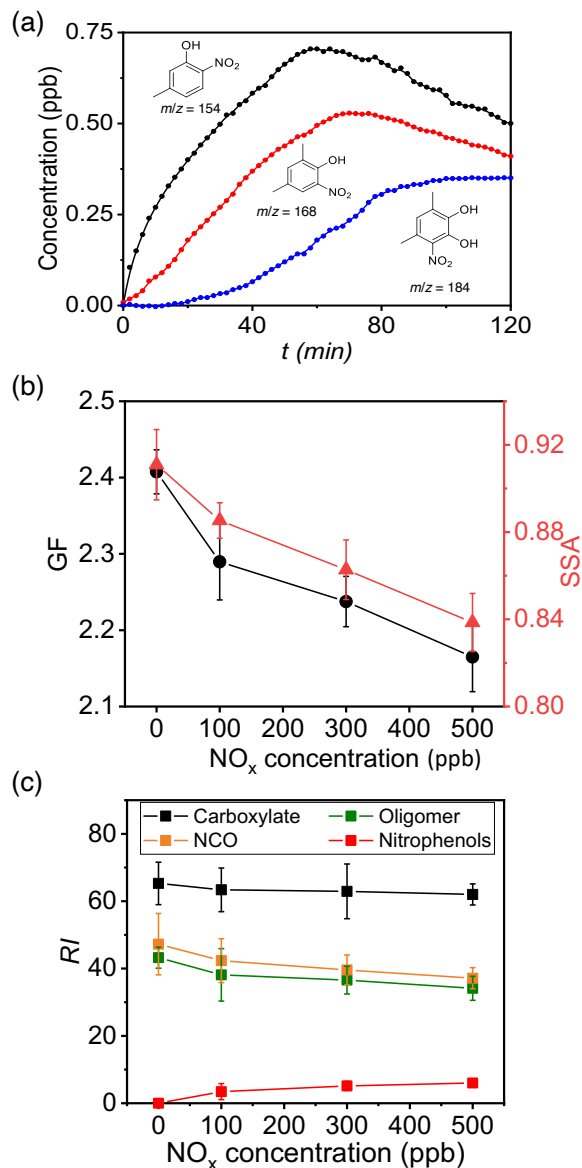
Figure 6. The effects of NO_x. (a) Time-dependent gas-phase concentrations of 5-methyl-2-nitrophenol (black, $m/z = 154$), dimethyl nitrophenol (red, $m/z = 168$), and dihydroxy nitrotoluene (blue, $m/z = 184$). The numbers denote the mass to charge ratio (m/z). Initiation of photooxidation by ultraviolet light occurred at $t = 0$. (b) GF (black) and SSA (red) at 120 min with varying NO_x concentration from 0 to 500 ppb. (h) Dependence of aerosol-phase relative mass intensities (RI) for carboxylates (black), oligomers (green), NCO (brown), and nitrophenols (red) on NO_x concentration for $(NH_4)_2SO_4$ seed particles with 19 ppb NH_3 at RH = 70%. The error bar denotes 1σ of 3 replicated measurements.

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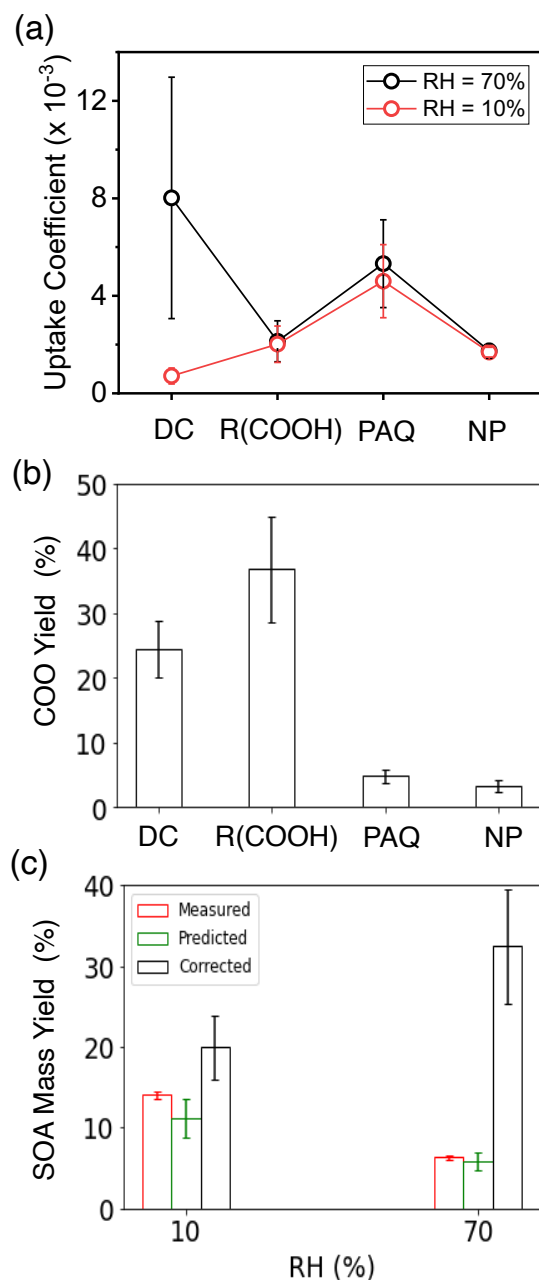
Figure 7. Uptake coefficient, COO yield, and SOA mass yield. (a) Average uptake coefficients (γ) for different types of COOs at 10% (red) and 70% (black) RH for $(NH_4)_2SO_4$ seed particles with 19 ppb NH_3 at 298 K. (b) COO yields: dicarbonyls, organic acids, polyhydroxy aromatics/quinones, and nitrophenols are represented by DC, $R(COOH)_n$, PAQ, and NP, respectively. (c) SOA mass yields at 10% (left columns) and 70% RH (right). The red, green, and black columns represent the measured, predicted, and corrected (for wall loss) SOA mass yields according to eq. 19-22. All experiments are carried out for 14 $\mu g\ m^{-3}$ $(NH_4)_2SO_4$ seed particles with 19 ppb NH_3 at 298 K. The error bars denote the 1σ of 3 replicated measurements or by accounting for error propagation of the measured parameters.

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799   **Table 1. Summary of experimental conditions.**

Experiment #	Seed particle	NH_3 concentration (ppb)	NO_x concentration (ppb)	RH
Exp. 1	AS	19	0	70%
Exp. 2	AS	0	0	70%
Exp. 3	ABS	0	0	70%
Exp. 4	NaCl	0	0	70%
Exp. 5	AS	9.5	0	70%
Exp. 6	AS	28.5	0	70%
Exp. 7	ABS	9.5	0	70%
Exp. 8	ABS	19	0	70%
Exp. 9	ABS	28.5	0	70%
Exp. 10	NaCl	9.5	0	70%
Exp. 11	NaCl	19	0	70%
Exp. 12	NaCl	28.5	0	70%
Exp. 13	AS	19	0	10%
Exp. 14	AS	19	0	30%
Exp. 15	AS	19	0	50%
Exp. 16	AS	19	100	70%
Exp. 17	AS	19	300	70%
Exp. 18	AS	19	500	70%

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