Instantaneous Nitric Oxide Effect on Secondary Organic

Aerosol Formation from *m*-Xylene Photooxidation

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Abstract

Secondary organic aerosol (SOA) formation from aromatic hydrocarbon photooxidation is highly sensitive to NO concentration. The instantaneous effect of NO on SOA formation from *m*-xylene photooxidation is investigated in this work by data mining 10 years of aromatic hydrocarbon chamber experiments conducted in the UC Riverside/CE-CERT chamber. First, the effect of sub-ppb NO concentrations on SOA formation is explored. The relationship of SOA growth rate to 1) NO₂/NO ratio; 2) instantaneous HC/NO; 3) absolute NO concentration; 4) peroxy radical reaction branching ratio and 5) hydroxyl radical concentration are illustrated. Second, continuous and stepwise NO, NO₂ and HONO injection are applied to *m*-xylene photooxidation experiments to simulate continuous NO sources in an urban area. The influence of these reaction scenarios on radical concentrations and SOA formation is explored. [HO₂·]/[RO₂·] shows a strong correlation with SOA yields in addition to [·OH]/[HO₂·], [·OH], [HO₂·] and [RO₂·]. Enhanced SOA formation is observed when low NO levels (<1ppb) are artificially maintained by continuous or step-wise injection; consistent with earlier research, SOA formation is observed to be suppressed by large initial NO injections. It is proposed that NO at sub-ppb level enhances ·OH formation increasing HO₂· and RO₂· and therefore promoting SOA formation. Further, two NO pathways (one promoting and one suppressing SOA formation) and one extremely low NO phase (NO “free”) are used to demonstrate the evolution of NO impact on SOA formation during photooxidation. This study implies that SOA yields from aromatic hydrocarbon and low NO_x photooxidation is previously underestimated due to differences between traditional environmental chamber experiments and atmospheric reactivity.

Key Words

Aromatic hydrocarbon; NO_x; Secondary Organic Aerosol; Kinetic Modeling; Radicals

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34 1. Introduction

35 Aromatic hydrocarbons are major anthropogenic SOA precursors (Calvert, et al., 2002;
36 Kanakidou, et al., 2005) contributing upto 50-70% of SOA formation in urban areas (Na, et
37 al., 2004). However, the mechanism of SOA formation from aromatic hydrocarbons is not
38 explicitly understood (Hallquist, et al., 2009; Calvert, et al., 2002). Previous papers report that
39 SOA formation from aromatic hydrocarbon photooxidation is highly sensitive to the nitric
40 oxide (NO) level during environmental chamber simulations (e.g., Hurley et al., 2001;
41 Johnson et al., 2005; Martín-Reviejo and Wirtz, 2005; Song et al., 2005). Previous chamber
42 studies demonstrate that higher initial NO_x concentration lowers aromatic SOA yields (Song,
43 et al., 2005; Ng, et al., 2007).

44 It is generally accepted that the NO concentration determines the branching ratio of peroxy
45 radical (RO₂·) reaction with NO and the hydroperoxy radical (HO₂·) impacting SOA
46 formation and volatility (Kroll and Seinfeld, 2008). Hurley et al. (2001) suggest that SOA
47 yield decreases when O₃ and nitrate radical (NO₃·) are suppressed by high NO concentration.
48 Cao and Jang (2008) assert that NO_x directly reacts with intermediate radicals, thus increasing
49 organic nitrate formation and leading to less SOA formation. Song et al. (2005) suggest that
50 NO_x concentration also affects the ring-opening and ring-retaining oxidation pathways of
51 aromatics. Ng et al. (2007) further argue that NO would not reduce SOA formation if
52 sufficient hydroxyl radical (·OH) was available. Chan et al. (2010) propose that the
53 RO₂+NO₂ pathway of unsaturated aldehyde photooxidation serves as an additional important
54 route for SOA formation from aromatics.

55 The atmospheric relevance of laboratory studies is critical for development of accurate SOA
56 models. First, ambient-like chamber conditions are preferable to best mimic intermediate and
57 radical concentrations. NO concentrations in recent chamber experiments are much closer to
58 ambient conditions compared with earlier studies (Izumi and Fukuyama, 1990; Odum et al.,
59 1996; Song et al., 2005; White et al., 2014). It should be pointed out that SOA precursors,
60 NO_x (e.g. NO, NO₂ and HONO) and radical sources are typically injected before
61 photooxidation begins (e.g. Forstner et al., 1997; Hurly et al., 2001; Ng et al., 2007).
62 Experiments with only initial precursor and NO or H₂O₂ injection will be referred to as
63 “classic experiments” within this work. Chemical components including SOA precursors, NO,
64 NO₂, O₃, ·OH, HO₂· and NO₃· dramatically change during classic SOA formation experiments
65 (Warren et al., 2008). In a classic low initial NO concentration experiment (e.g., Ng, et al.,
66 2007), NO decreases from dozens of ppb to below detection limit (~0.2 ppb), the SOA
67 precursor exponentially decays, and the instantaneous O₃ production rate (Sillman, 1999) and
68 accumulated O₃ concentration change (Fig. S1). However, the ambient atmosphere usually

has continuous NO and NO₂ sources, especially in urban areas with heavy traffic (Rattigan et al., 2010) where average NO concentrations exceed 0.2 ppb (Cusack et al., 2013). Excess NO has been used in a previous study to suppress O₃ and NO₃· formation during photooxidation (Hurly et al., 2001). However, the high initial NO_x (>250 ppb) and hydrocarbon concentrations (>2 ppm) still do not accurately mimic the ambient condition. Hence, more field relevant experimental scenarios are needed to improve the reliability of atmospheric model inputs.

Further, reliable methodologies of data interpretation, in view of the differences between laboratory and ambient conditions, are needed to more accurately explore aerosol formation processes directly applicable to the atmosphere. Traditional SOA yield curves (Odum et al., 1996) rely on smog chamber experiments conducted under a variety of conditions and are extensively used in current atmospheric models (e.g., Binkowski and Roselle, 2003; Jenkin et al., 2003). It is worth noting that final fractional aerosol yield (Odum et al., 1996), an averaged SOA growth potential throughout a chamber oxidation process, is currently used to generate SOA yield curves (Ng et al., 2006). However, the average [$\cdot$ OH]/[HO₂·] ratio in traditional chamber experiments are lower than typical atmospheric conditions with the exception of the initial [$\cdot$ OH]/[HO₂·] ratio (Kanaya et al., 2012). The initial [$\cdot$ OH]/[HO₂·] ratio is driven by the high initial NO concentration, which promotes $\cdot$ OH concentration from the NO-O₃-NO₂ photolytic cycle. It indicates that continuous NO_x injection scenarios during photooxidation could improve the similarity between chamber experiments and the atmosphere. Further, changes to the SOA growth curve induction period or time to the onset of aerosol formation in a classic chamber experiment (Hurley et al., 2001; Ng et al., 2007), directly influences the measured overall SOA yield. It is also useful to incorporate instantaneous SOA growth curves into analyses of SOA formation in order to improve model mechanisms. In this work, we use SOA growth curves of 56 classic *m*-xylene photooxidation experiments to investigate the instantaneous NO_x effect on SOA growth. Stepwise and continuous NO_x injection scenarios are also utilized during chamber photooxidation experiments to simulate continuous NO_x sources in urban areas and to bridge the NO influence principle from laboratory observations to the atmosphere. The main goal of the study is to shed insight on the mechanism of NO effect on SOA formation from aromatic hydrocarbons.

2. Method

2.1 Environmental chamber

102 The UC Riverside/CE-CERT indoor dual 90 m³ environmental chambers were used in this
103 study and are described in detail elsewhere (Carter et al., 2005). Experiments were all
104 conducted at dry conditions (RH<0.1%), in the absence of inorganic seed aerosol, and with
105 temperature controlled to 27±1°C. Two movable top frames were slowly lowered during each
106 experiment to maintain a slight positive differential pressure (~0.02" H₂O) between the
107 reactors and enclosure to minimize dilution and/or contamination of the reactors. 276 115 W
108 Sylvania 350BL blacklights are used as light sources for photooxidation.

109 2.2 Gas-phase analysis

110 Decay of *m*-xylene was measured by a pair of Agilent 6980 (Palo Alto, CA) gas
111 chromatographs (GC) equipped with flame ionization detectors (FID). A Thermal
112 Environmental Instruments Model 42C chemiluminescence NO_x analyzer was used to
113 monitor NO, NO_y-NO and NO_y. O₃ was monitored by a Dasibi Environmental Corp. Model
114 1003-AH O₃ analyzer.

115 2.3 Particle phase analysis

116 Aerosol growth was measured using an in-house built scanning mobility particle sizer
117 (SMPS). The differential mobility analyzer is located inside the chamber enclosure to ensure
118 that aerosol sizing was conducted at a temperature identical to the chamber temperature.
119 Particle volume was corrected for particle wall loss assuming a first order wall loss decay as
120 described in Cocker et al (2001a).

121 2.4 Radical Analysis

122 The gas-phase reaction model SAPRC-11 developed by Carter and Heo (2012) was utilized to
123 predict radical concentrations ($\cdot$ OH, HO₂ $\cdot$, RO₂ $\cdot$ and NO₃ $\cdot$). SAPRC-11 uses updated chemical
124 mechanisms designed to address NO_x impacts on aromatic photooxidation. The model
125 accurately simulated data within the UCR/CE-CERT environmental chamber experiments
126 within acceptable biases (Carter and Heo, 2012) for 14 different types of aromatic
127 hydrocarbons and for a variety of reactant concentrations and NO_x levels.

128 2.5 Data mining

129 Data mining was conducted on 56 previous classic *m*-xylene photooxidation experiments
130 conducted in the UCR/CE-CERT environmental chamber with blacklights (k_t =0.13 min⁻¹
131 Warren et al., 2008) and initial HC/NO ranging from 1.3 to 591.2 (ppbC:ppb) (Table S1).

132 2.6 Reaction scenarios

133 Five reaction scenarios (RS) were used to study the NO influence on SOA formation: 1)
134 Classic RS; 2) H₂O₂ RS; 3) Stepwise HONO RS; 4) Stepwise or continuous NO RS and 5)

Stepwise NO₂ RS (Table 1). NO and *m*-xylene were initially injected in all five scenarios. H₂O₂ was also injected initially in RS2, RS4 and RS5. In RS4 and RS5, NO or NO₂ was injected at 5-15 ppb·hr⁻¹ either stepwise (once per hour) or continuously. HONO was injected at ~20-60 ppb·hr⁻¹ injected stepwise in RS3. *m*-Xylene, NO, NO₂ and hydrogen peroxide (H₂O₂) injection followed previous work (Song, et al., 2005; Qi et al., 2010; Nakao et al., 2011a). Nitrous acid (HONO) was prepared by adding 1 wt % aqueous NaNO₂ dropwise or by syringe (250 µl) into 20 mL of 10 wt % sulfuric acid in a glass bulb (Kautzman et al., 2009) and flushed into chamber with ~2 LPM nitrogen for 15 minutes each time along with the NO and NO₂ side products formed as part of the HONO preparation. Perfluorohexane was used as an inert tracer for each experiment to monitor reactor dilution. Dilution of the inert tracer was observed to be <2% during the course of all experiments.

3. Results

3.1 NO effect on SOA growth curve during classic *m*-xylene photooxidation

The traditional SOA growth curve (ΔM_0 vs. ΔHC) is used to represent SOA formation (Kroll and Seinfeld, 2005). The slope of the SOA growth curve provides instantaneous SOA growth rates as reactivity conditions evolve. SOA growth curves for 56 classic *m*-xylene photooxidation experiments (black lights, $k_I=0.13 \text{ min}^{-1}$; SOA density = 1.4 g cm^{-3} (Song et al., 2007b, Ng et al., 2007, Malloy et al., 2009)) with initial HC/NO_x ranging from 1.3 to 591.2 (ppbC:ppb) are displayed in Fig. S2.

The induction period, measured in this work as the amount of aerosol precursor consumed between lights on and initial aerosol formation, varies widely for the 56 experiments. The hydrocarbon consumption during the induction period directly affects SOA yield (aerosol mass formed/hydrocarbon reacted) calculations (Henze et al., 2008; Kroll et al., 2007). Hurley et al. (2001) previously shifted the x-axis (hydrocarbon consumed) of their SOA growth curve by a fixed fraction of the initial hydrocarbon ($[HC]_i$) to remove the induction period and group their SOA growth curves. However, in the current study, $[HC]_i$ alone cannot explain variations in the induction period length for experiments with similar $[HC]_i$ and different NO (e.g. 368A and 368B) and therefore NO concentration is considered critical to induction period. By defining significant SOA growth as instantaneous SOA yield (Jiang, 2003) higher than 0.01, experimental parameters including initial HC concentration, instantaneous SOA yield, $[NO]$, $[NO_2]/[O_3]$, $[NO_2]/([NO]*[\cdot OH])$ and $[NO_2]/([NO]*[HC])$ were correlated to induction period (Table S2) with NO₂/NO ratio identified as the best indicator of induction-period length. Therefore, the experimental hydrocarbon consumed is offset (Fig. S4) in this work by the hydrocarbon consumed when NO₂/NO=70 (first of three consecutive

169 10-minute average measurements above threshold) based on the statistical analysis (Table S2)
170 for the 56 classic *m*-xylene experiments with initial NO ranging from 0-433 ppb. $\Delta\text{HC}'$
171 represents the hydrocarbon decay after the NO_2/NO threshold is achieved (Fig. S3 a) and b)).
172 $\Delta\text{HC}'$ is zero if the threshold is never achieved, which occurs for experiments with extreme
173 low initial NO_x ($\text{NO}_x < 1\text{ppb}$) or HC/NO_x . The curve color (Fig. S4) corresponds to the fraction
174 of hydrocarbon consumption at threshold ($f_t = \Delta\text{HC}'/\Delta\text{HC}_t$). ΔHC_t stands for the total
175 hydrocarbon decay during photooxidation.

176 $M_0 - M_0'$ (new Y-axis) is then defined as the SOA formed only after crossing the NO_2/NO
177 threshold (Fig. S3c). It is obtained by subtracting the minimal aerosol formation (M_0') at the
178 time the NO_2/NO threshold is reached. The modified SOA growth curves of the 56 classic
179 experiments are shown (Fig. 1). Violet curves (154A, 223A, 223B and 820B) located in the
180 lower right region of the figure are experiments that did not reach the NO_2/NO threshold.
181 These four experiments have initial HC/NO_x lower than 3 ppbC:ppb and the lowest SOA
182 formation rate among all 56 experiments and will not be further discussed in this section.
183 Three regions (Region 1, 2 and 3) are used to categorize the remaining 52 curves (Fig. 1,
184 Table S1; the four experiments that never reached the NO_2/NO threshold are marked as
185 Region 4). Different regions suggest different SOA growth rates since all curves are modified
186 to start from the origin of new coordinate $M_0 - M_0'$ vs. $\Delta\text{HC} - \Delta\text{HC}'$ and have approximately
187 linear trends.

188 Green and blue curves (Fig. 1) in Regions 1 and 2 are sandwiched by red and orange curves in
189 Regions 2 and 3 indicating that factors other than NO_2/NO ratio also affect SOA growth rate.
190 Therefore, the HC/NO ratio, NO and NO_2 influence on SOA growth rate are also investigated.
191 Table S1 lists HC/NO ratio, NO and NO_2 concentration at the time the NO_2/NO threshold is
192 reached. The relationship between SOA growth rate and NO_2 or HC/NO concentration are
193 shown in Fig. 2. Curves in Region 1 have NO_2 concentrations below 20.6 ppb when the
194 NO_2/NO threshold are reached. Region 3 curves are related to smaller HC/NO (< 164
195 ppbC:ppb) at the NO_2/NO threshold. Curves in Region 2 (Fig. 1) with medium NO_2
196 concentration and high HC/NO ranks at the top in SOA growth rate among the three regions.
197 This indicates that low NO or NO_2 concentration promotes SOA formation (comparing
198 Region 2 with Region 1) particularly when the NO is below ppb level. Since curve colors are
199 well organized red to blue from higher to lower SOA growth rate, it is also possible that the
200 fraction of hydrocarbon consumption before the threshold or the average $\cdot\text{OH}$ concentration
201 related to hydrocarbon consumption also affects SOA growth rate after the threshold (see
202 Section 4.1). Second, it is demonstrated that sub-ppb level NO promotion of aerosol growth
203 rate depends on instantaneous HC/NO when comparing curves in Region 3 to Region 2. For
204 example, experiments (e.g. 247A and 247B) that start with high initial NO and hydrocarbon
205 concentrations have significant SOA formation even for relatively high NO concentrations

206 (5.80 and 5.02 ppb). Significant SOA formation is attributed to the high HC/NO ratios (32.2
207 and 36.6 ppb: ppb) at elevated NO concentrations thus confirming the importance of
208 instantaneous HC/NO.

209 3.2 Radical analysis of classic *m*-xylene photooxidation experiments

210 HO₂· plus RO₂· reaction has been considered as a major pathway of SOA formation under low
211 NO_x conditions (Kroll and Seinfeld, 2008). Instantaneous relationships between SOA growth
212 rate, fraction of RO₂· reacting with HO₂· and ·OH concentration are studied by using the
213 modified SOA growth curve (Section 3.1). First, it is assumed that RO₂· reacts only with
214 HO₂· and NO (Kroll and Seinfeld, 2008). The fraction of RO₂· reacting with HO₂· is then
215 defined as f_2 (eq. 3-1)

$$216 \quad f_2 = k_3[\text{HO}_2\cdot]/(k_3[\text{HO}_2\cdot] + k_1[\text{NO}\cdot]). \quad (3-1)$$

217 where k_3 ($7.63 \times 10^{-12} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$) and k_1 ($9.23 \times 10^{-12} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$) are the
218 reaction rates of RO₂· with HO₂· and NO, respectively (Carter, 2010; Carter and Heo, 2013).
219 [HO₂·] is predicted by SAPRC-11 with [·OH] calculated from *m*-xylene decay. Modified SOA
220 growth curves of 52 classic *m*-xylene photooxidation experiments are colored by f_2 (Fig. 3a).
221 HO₂· and RO₂· reaction and SOA formation are insignificant for experiments with initial
222 HC/NO_x lower than 3 ppbC:ppb. A color gradient of increasing f_2 is observed with increasing
223 SOA growth (Fig. 3a). When NO₂/NO ratios are lower than 70, HO₂· is unable to compete
224 with NO for RO₂· resulting in insignificant SOA formation. It is observed that the medial f_2
225 value (green color, $0.25 < f_2 < 0.5$, Fig. 3a) exists in the initial part of Region 1, end part of
226 Region 3 and most of Region 2. The medial f_2 value represents the value for which the SOA
227 formation mechanism transitions from NO suppression to HO₂· dominant. The large medial f_2
228 in Region 2 indicates SOA formation peaks when NO and HO₂· are in similar concentration
229 rather than when NO is completely depleted. Assuming that SOA originates from RO₂· and
230 HO₂· reactions, it will be shown later (Section 4.2) that RO₂· and HO₂· concentrations can be
231 promoted by NO (especially under sub-ppb NO concentration range). Several red and orange
232 curves in Fig. 1 of Region 2 and Region 3 show lower initial f_2 (blue in Fig. 3a) after the
233 threshold compared with others. Low HC/NO ratio in Region 3 inhibits RO₂· and
234 HO₂· reaction by reducing peroxy radical concentration (Fig. 8a). Further, higher initial NO_x
235 concentrations in Region 3 increase yields of higher volatility organic nitrate species thereby
236 lowering the overall SOA yield. The lower f_2 in Region 2 compared to Region 1 (Fig. 3a)
237 corresponds to the highest SOA growth rate indicating a boundary [NO]/[HO₂·] condition that
238 promotes SOA formation.

239 The $\cdot\text{OH}$ effect on SOA formation is studied by coloring the modified growth curves with the
 240 hydrocarbon decay rate (R_{HC}) (Fig. 3b). By assuming *m*-xylene only reacts with $\cdot\text{OH}$
 241 (Martín-Reviejo and Wirtz, 2005), R_{HC} (min^{-1}) is described by eq. 3-4

$$242 \quad R_{HC} = \frac{\Delta(HC_i)}{[HC_i] \times \Delta t} = k \times [\cdot\text{OH}] \quad (3-4)$$

243 where k ($7.86 \text{ m}^3 \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$ or $2.31 \times 10^{-11} \text{ (cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1})$) (Calvert, et al., 2002) is the
 244 reaction rate constant of the hydrocarbon with $\cdot\text{OH}$, $[HC_i]$ and $[\cdot\text{OH}]$ are the mass
 245 concentration ($\mu\text{g} \cdot \text{m}^{-3}$) of parent hydrocarbon and $\cdot\text{OH}$ at time t , respectively, Δt is the time
 246 change (min) and $\Delta(HC_i)$ is the change of hydrocarbon mass concentration ($\mu\text{g} \cdot \text{m}^{-3}$) during (t ,
 247 $t + \Delta t$). Since *m*-xylene predominantly reacts with $\cdot\text{OH}$ (Atkinson 1989; Calvert, et al., 2002)
 248 faster hydrocarbon decay indicates higher $\cdot\text{OH}$ concentration. High $\cdot\text{OH}$ concentration is
 249 mainly observed in Regions 2 and 3, which have higher NO or NO₂ compared with Region 1.
 250 NO enhances $\cdot\text{OH}$ formation by reaction of NO with HO₂ $\cdot$ to form more $\cdot\text{OH}$ and therefore
 251 higher R $\cdot$ and RO₂ $\cdot$ (Fig. 8a). The change in [RO₂ $\cdot$], [HO₂ $\cdot$] and [HO₂ $\cdot$]/[RO₂ $\cdot$] with $[\cdot\text{OH}]$
 252 directly influences SOA growth rate. SOA growth rate is still low in Region 3 despite
 253 high $\cdot\text{OH}$ concentration due to competition between NO promotion and inhibition effects on
 254 SOA.

255 3.3 SOA formation of *m*-xylene photooxidation for five reaction scenarios

256 Overall aerosol yield (OAY) defined by Odum et al. (1996) and instantaneous aerosol yield
 257 (IAY) introduced by Jiang (2003) are both applied to describe SOA formation. Fig. S5 shows
 258 linear SOA growth after an induction period ($r^2 > 0.97$ after $M_0 > 0.5 \mu\text{g} \cdot \text{m}^{-3}$) for each
 259 reaction scenario suggesting that oxidation of first generation products are the
 260 rate-determining step (Kroll and Seinfeld, 2008; Ng et al., 2006) for SOA formation
 261 consistent with Ng et al. (2007). Modified SOA growth curves for each injection scenario
 262 (Fig. 4) illustrate IAY differences between scenarios. Hydrocarbon consumption when
 263 aerosol mass reaches $2 \mu\text{g} \cdot \text{m}^{-3}$ is used to offset the X-axis and the Y-axis offset is $2 \mu\text{g} \cdot \text{m}^{-3}$.
 264 SOA growth curves (Fig. 4) are categorized into two groups: with initial H₂O₂ injection (RS2,
 265 RS4 and RS5) and without H₂O₂ (RS1 and RS3). The scenarios including H₂O₂ have higher
 266 IAY (>0.24) and OAY (>0.11) compared with the schemes without H₂O₂ (IAY <0.22 ,
 267 OAY <0.08) ((Table S3).

268 **RS1:** RS1 is the classic chamber photooxidation experiments with only hydrocarbon and low
 269 initial NO. OAYs obtained in this work are similar to previous studies (Song, et al., 2005;
 270 Tang, et al., in preparation, a).

271 **RS2, RS4&RS5 (w/ H₂O₂):** RS2 initially injects H₂O₂ and NO with measured IAY and OAY
 272 higher than RS1 or OAY from H₂O₂ only experiments (Song, et al., 2005; Tang, et al., in

273 preparation, b). Song et al. (2007b) performed a *m*-xylene photooxidation experiment (S21B)
274 where ~20 ppb of NO was injected in the middle of an H₂O₂ oxidation experiment and
275 observed higher OAY (0.27) than RS2 in this work (1795B, OAY = 0.11) even though the
276 same total amount of NO was injected. This indicates that the induction period resulting from
277 initial NO injection (RS2) lowers OAY. It is also observed in RS2 (Table S3) that higher
278 initial NO (HC/NO = 13.0±2.4 ppbC/ppb vs. HC/NO = 38.2± 10.3 ppbC/ppb) may lead to
279 higher IAY (IAY = 0.35±0.04 vs. IAY = 0.32 ± 0.07).

280 Increases in IAY over RS2 is found when NO is injected step-wise or continuously in RS4.
281 This is consistent with Martín-Reviejo and Wirtz (2005) where continuously injected
282 HONO/NO_x experiments (benzene photooxidation) also yielded higher SOA yields than
283 NO-free H₂O₂ experiments. Similar SOA growth is observed in the current study when NO₂
284 (vs. NO) was injected stepwise (RS5) as the NO₂/NO ratio in the chamber was rapidly
285 re-established with little impact on the overall reactivity of the system. Higher OAYs in RS4
286 and RS5 are associated with shorter induction periods than the bulk NO_x injection of RS2.

287 Changes to OAY and IAY (RS4&RS5 vs. RS2) are observed for experiments commencing
288 with similar initial NO_x levels and induction periods. Generally, IAYs are greater for RS4
289 than RS2 and monotonically increase for decreasing NO injection rates (NO_x injection rates <
290 15 ppb·hr⁻¹) (1885A<1868A<1867A<1863A). However, lower IAYs are observed when the
291 stepwise NO concentration is raised to ~15 ppb·hr⁻¹ (1778A). Similarly, increasing IAY and
292 OAY is observed for RS5 compared to RS2 for stepwise small NO₂ injections (1849A and
293 1872A, NO₂ 5 ppb·hr⁻¹) with IAY decreasing relative to RS2 when NO₂ is injected at 10
294 ppb·hr⁻¹ (1885B). Inhibition of SOA formation at higher NO_x injection rates is consistent with
295 observations in Song et al. (2007b) (NO injection of 50 ppb midway through *m*-xylene
296 photooxidation experiment). Initial hydrocarbon concentration is also found to affect the
297 impact of continuous NO_x injection on SOA formation (Table S3). The IAY increases relative
298 to RS2 discussed above are not observed in RS4 (1858A) or RS5 (1859A and 1801A)
299 experiments with higher initial hydrocarbon concentration (similar NO_x as before). The
300 induction period for the high initial hydrocarbon experiments is shorter due to the higher
301 initial HC/NO ratio (Song, et al., 2005).

302 **RS3:** HONO (along with ~10% NO plus NO₂ impurity, Becker et al., 1996) were continually
303 injected in RS3 to investigate the NO effect while increasing the ·OH radical source. The
304 HONO injection rate determines SOA growth rate: compared with RS1, small amounts of
305 HONO injected (1774B, ~20 ppb·hr⁻¹) raises IAY and OAY, while large HONO injection
306 (1748B, ~60 ppb·hr⁻¹) suppresses IAY and OAY. The impacts of HONO on SOA formation
307 parallels observations made for RS4 and RS5 providing further evidence that NO has a
308 two-edged effect on SOA growth.

309 No vertical trends (Ng, et al., 2006) or sharp turns (Song, et al., 2007b) are observed in the
310 SOA growth curves during continuous or step wise injections indicating that HONO (RS3),
311 NO (RS4) and NO₂ (RS5) did not instantaneously react with intermediate photooxidation
312 products (e.g. phenol) to immediately form SOA. Therefore, we hypothesize that radical
313 kinetics are changing with injection scenario thereby influencing SOA yield.

314 Additional seeded experiments were conducted in the dual UC Riverside/CE-CERT chamber
315 to assess the impact of wall-loss of semi-volatile species. *m*-Xylene and NO_x were injected
316 and mixed thoroughly between the chambers. Next, dry (NH₄)₂SO₄ seeds (~10,000 cm⁻³ with
317 diameter of 30-50 nm) were injected to one side of the bag. No measurable differences were
318 observed in SOA formation (amount or timing) between the non-seeded and seeded
319 experiments indicating that wall loss of semivolatile compounds did not significantly impact
320 measured SOA formation from *m*-xylene photooxidation.

321 3.4 Relating NO-radical chemistry to SOA formation

322 3.4.1 NO impacts on radical kinetics

323 NO increases are typical in the atmosphere in the morning and late afternoon (Guicherit, 1975;
324 Williams et al., 1988). Conventional (RS1) chamber experiments commence with high NO,
325 which is rapidly converted to NO₂ resulting in very low residual NO concentrations during
326 SOA formation. Step-wise or continuous NO_x injection scenarios are used in this work to
327 simulate the NO increase in the daytime urban atmosphere.

328 **RS1:** HO₂· and RO₂· sharply increases at the start of an experiment and then dramatically
329 decreases when NO is depleted to sub-ppb levels in classic chamber photooxidation
330 experiments (RS1) (Fig. 5).

331 **RS2:** Experiments with initial H₂O₂ injection (RS2) have higher HO₂· and RO₂· peak
332 concentrations for longer periods of time (order of tens of minutes) than RS1. (Fig. 5 RS2).

333 **RS4&RS5:** The RS4 HO₂· and RO₂· peak concentrations is extended relative to RS2 by a
334 couple hours, which is more similar to the urban atmosphere HO₂· and RO₂· trends (Dusanter
335 et al., 2009; Handisides et al., 2003; Ren et al., 2003). HO₂· and RO₂· drop further in RS4 than
336 RS2 after their peak radical concentrations due to the lack of hydrocarbon available for
337 further reaction (Fig. 5). The longer peak radical concentrations in RS4 indicates that the
338 continual presence of low NO concentrations maintains RO₂· and HO₂· concentration at
339 elevated levels (while sufficient hydrocarbons are available to react) due to RS4 maintaining
340 higher ·OH concentrations. RS5 has a similar RO₂· and HO₂· profile to RS4 (Fig. 8). It is
341 generally observed (Fig. 5) that RO₂· and HO₂· level depends on ·OH concentration since

steep decays in their concentration correspond to changing $\cdot\text{OH}$ levels. Fig. 5 supports the hypothesis (Section 3.3) that NO promotion of $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ radical results from increasing the rate of $\cdot\text{OH}$ - aromatic reaction. It should also be noted that $\text{HO}_2\cdot$ formation from H_2O_2 and $\cdot\text{OH}$ reaction can happen together with photolytic $\text{HO}_2\cdot$ production. The ratio of $\text{HO}_2\cdot$ from $\text{H}_2\text{O}_2 + \cdot\text{OH}$ to the photolytic cycle can be described by $1.62 \cdot [\text{H}_2\text{O}_2] / 2.31 \cdot [m\text{-xylene}]$ (Keyser, 1980; Calvert, et al., 2002). $\text{HO}_2\cdot$ levels are similar in RS2, RS4 and RS5 as initial $[\text{H}_2\text{O}_2]$ and $[m\text{-xylene}]$ are similar in these reaction schemes. Therefore, $\text{HO}_2\cdot$ increase by $\text{H}_2\text{O}_2 + \cdot\text{OH}$ reaction in RS2, RS4, and RS5 may enhance SOA formation from the increasing $\cdot\text{OH}$ driven by continuous NO injection.

Slight and temporary peroxy radical decreases are observed immediately after each step wise NO_x injection (RS4 and RS5). The decreases are positively correlated with NO injection rate and are smaller in RS5. This is due to instantly higher NO/HC after NO_x injection. The decreases are smaller during the initial period when sufficient hydrocarbon is available to minimize the peroxy radical decrease. The temporary decreases are avoided continuous NO injections are performed (Fig. 5 RS4-2:1867A). Additionally, NO/HC (or initial hydrocarbon) impacts on radical concentration are observed (Fig. 5 RS5-2:1801A and 1858A) with higher initial hydrocarbon leading to higher average $\text{RO}_2\cdot$ and $[\text{RO}_2\cdot][\text{HO}_2\cdot]$ but not average $\text{HO}_2\cdot$.

High NO_x injection effect: The consistently high NO_x injection rate ($>7.5 \text{ ppb}\cdot\text{hr}^{-1}$) in RS4 (Fig. 5 RS4-3:1778A and 1885A) and RS5 (1885B) leads to “higher” NO (e.g. 0.5-2ppb in 1778A) constraining peroxy radicals to low concentrations and therefore lowering SOA yields. This observation is consistent with the suggestion by Ng et al. (2007) that NO suppresses nonvolatile hydroperoxides formation from the $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ -reaction resulting in a lower SOA yield. However, if the high NO injection occurs after maximum peroxy radical concentrations (Fig. 5, RS4-4), the NO_x inhibition effect on SOA formation is not observed.

3.4.2 Linking SOA formation to average radical parameters

Average radical concentrations (Table S3) were calculated using the SAPRC-11 model with $\cdot\text{OH}$ adjusted by the measured *m*-xylene decay (Carter and Heo, 2013). Average $\cdot\text{OH}$ and $\text{RO}_2\cdot$ concentration ranges within the chamber ($2.22\text{-}10.61 \times 10^6 \text{ molecules}\cdot\text{cm}^{-3}$ and $4.97\text{-}29.58 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}$) are within typical daytime urban atmospheric levels ($1.2\text{-}20 \times 10^6 \text{ molecules}\cdot\text{cm}^{-3}$ and $5\text{-}15 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}$) while average $\text{HO}_2\cdot$ concentrations ($11.9\text{-}560 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}$) are at or above the reported maximum level of the urban atmosphere ($0.4\text{-}10 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}$) (Dusanter et al., 2009; Emmerson et al., 2005; Emmerson et al., 2007; Lee et al., 2006; Ren et al., 2003). While H_2O_2 injections may be expected to enhance $\text{HO}_2\cdot$ concentrations, NO/ $\text{HO}_2\cdot$ ratios for RS2, RS4, and RS5 (0.11-1.18, Table S4) after nucleation remain similar to classic (RS1) experiments (Section 3.2,

Fig. 3a). The average $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ ratio in RS1 is $1.91\text{--}11 \times 10^{-3}$ and approaches atmospheric conditions (Kanaya et al., 2012) as initial NO/HC increases. Experiments in RS2, RS4 and RS5 have higher $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ ratios compared with classic H_2O_2 only experiments (Fig. 6, Table S5) due to NO_x injection but lower ratios compared with RS1 as a result of higher $\text{HO}_2\cdot$ concentration originating from H_2O_2 injection. Higher NO_x injection rates within this work are used to increase the $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ ratio among experiments with H_2O_2 injection.

OAY and radical parameters: High correlation is observed between OAY and $[\cdot\text{OH}]/[\text{HO}_2\cdot]$, $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ (Table 2), which is mostly driven by H_2O_2 injection. Average $\cdot\text{OH}$, $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ concentrations in RS2, RS4 and RS5 are higher than those of RS1 (Table S3). An extra $\cdot\text{OH}$ source from H_2O_2 decomposition for RS2, RS4 and RS5 leads to higher $\text{R}\cdot$ and therefore $\text{RO}_2\cdot$. Once most of NO is converted (sub-ppb level), $\text{HO}_2\cdot$ is no longer suppressed leading to higher SOA formation from reaction of $\text{RO}_2\cdot$ with $\text{HO}_2\cdot$.

IAY and radical parameters: It is also found that IAY is well correlated with $[\cdot\text{OH}]$ and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$. There is no significant $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ difference between RS2 and RS1 indicating H_2O_2 injection enhances $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ on a comparable scale. It also indicates that the high correlation between IAY and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ is caused by the NO_x injection. $\cdot\text{OH}$ concentrations in RS1 are similar for the range of H_2O_2 only experiments (RS8 in Table S5) and the RS2 experiments further demonstrating the importance of NO to $\cdot\text{OH}$ concentration particularly for the reaction schemes that include H_2O_2 . It confirms that NO influence on SOA formation is related to $\cdot\text{OH}$ concentration consistent with previous studies (Nakao et al., 2011a; Ng et al., 2007). Also, a high correlation (0.822, p-value=0) between $\cdot\text{OH}$ and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ implies that NO influences $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ through $\cdot\text{OH}$. The positive relationship between IAY and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ is consistent with high $[\text{RO}_2\cdot]$ in the high initial hydrocarbon experiments having lower yields.

$\Delta M_0'$ and radical parameter: Average radical concentrations for the $175 \mu\text{g}\cdot\text{m}^{-3}$ hydrocarbon consumption after $M_0 > 2 \mu\text{g}\cdot\text{m}^{-3}$ are analyzed to explore relationships between SOA growth rate and radical concentrations after the induction period. $\Delta M_0'$ ($M_0 - M_0'$) is the particle concentration increase after $M_0' = 2 \mu\text{g}\cdot\text{m}^{-3}$ until $\Delta\text{HC} - \Delta\text{HC}' = 175 \mu\text{g}\cdot\text{m}^{-3}$. $\Delta\text{HC}'$ (Section 3.1) uses $M_0' = 2 \mu\text{g}\cdot\text{m}^{-3}$ as a threshold. $\Delta M_0'$ at $\Delta\text{HC} - \Delta\text{HC}' = 175 \mu\text{g}\cdot\text{m}^{-3}$ (Fig. 4) is used as an indicator for average SOA growth rate after the induction period. Average radical parameters (e.g. $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ and $[\cdot\text{OH}]$) are calculated by dividing integrated radical parameters from the induction period threshold ($M_0' = 2 \mu\text{g}\cdot\text{m}^{-3}$) to $\Delta\text{HC} - \Delta\text{HC}' = 175 \mu\text{g}\cdot\text{m}^{-3}$. Fig. 7 shows a relationship between $\Delta M_0'$ and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ colored by $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ and sized with NO_x injection rate. A general increasing $\Delta M_0'$ trend with $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ is found (Fig. 7) with a high correlation factor (0.724, p-value=0) suggesting that a higher $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ ratio leads to higher SOA formation. It is also found (Fig. 7) that $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ is positively correlated to $\Delta M_0'$ for both points below (high NO_x injection rate; SOA suppression regime)

414 or above (low NO_x injection rate; SOA enhancement regime) the points describing the RS2
415 experiments. This is explained by high ·OH concentrations facilitating production of the
416 HO₂· and RO₂· radicals through the reaction cycles shown in Fig. 8. Further, [RO₂·]/[HO₂·] is
417 negatively correlated to ΔM₀' (Fig. S6) when only RS2, RS4 and RS5 are considered. The
418 negative correlation is attributed to increasing RO₂· (lower [HO₂·]/[RO₂·]) leading to a higher
419 fraction of NO reacting with RO₂· instead of HO₂·; this results in higher molecular
420 fragmentation thereby lowering aerosol yields. Kroll et al. (2006) suggests that SOA growth
421 rate increases as [NO]/[HO₂·] decreases. Correlations in this work are also observed among
422 [NO]/[HO₂·]; however, the correlation is weaker than the radical parameter mentioned above
423 (Table 2). The lower [NO]/[HO₂·] correlation results from differences in NO_x injection
424 methods used in this work. For example, similar amounts of hydrocarbon and NO_x are
425 injected into RS4 (1867A) and RS2 (1867B) using different injection scenarios leading to
426 similar [NO]/[HO₂·] but differing yields, which provides further evidence that the NO_x effect
427 on SOA yields depends on how NO_x is injected.

428 **RS3:** Radical concentrations are not predicted in RS3 since HONO injection is not readily
429 quantifiable. Generally, HONO serves as a source of ·OH to accelerate the initial ·OH attack
430 on the precursor aromatic during photooxidation. It is expected that more RO₂· is formed from
431 the increased OH radical concentration. However, the coexistence of “high” NO
432 concentrations results from HONO synthesis (Becker et al., 1996). Therefore, large quantities
433 of HONO injection are observed to inhibit SOA formation in this work. Smaller HONO
434 injections did not show this inhibition.

435 Organic nitrate from either NO or NO₂ reaction with RO₂· (Atkinson, 2000; Koch et al., 2007)
436 are not significantly correlated with yields. Similar fractions of peroxy radical are consumed
437 by NO_x in all experiments (9.34%-12.24%) to form organic nitrate based on SAPRC-11
438 (Table S3, RO₂XC/RO₂).

439 4. Discussion

440 4.1 Implication of modified SOA growth curve on relationships between SOA formation and 441 NO_x

442 The modified SOA growth curve (using NO₂/NO=70 threshold) for classic *m*-xylene
443 photooxidation experiments fall into three regions (Fig. 1). Regions 1, 2, and 3 are
444 experiments with moderate SOA formation, those where NO promotes SOA, and those where
445 NO suppresses SOA, respectively.

446 An *m*-xylene photooxidation mechanism is illustrated in Fig. S7 (Carter et al., 2012; Carter
447 and Heo, 2012; Nehr et al., 2012; Zhao et al., 2005). Lower energy intermediate radical
448 products are used to describe the aromatic-OH adduct pathway ($\cdot\text{OH}$ adduct between two
449 methyl groups). NO_2 reaction with the *m*-xylene adduct (dashed line, Fig. S7) is not
450 considered since NO_x levels in all experiments are below ppm level (Atkinson & Arey, 2007).
451 Three reaction pathways in addition to the induction period are used to explain the NO effect
452 on SOA formation (Fig. 8a). All experiments in Fig. 1 experience an induction period for
453 SOA formation due to chemical kinetics and gas-particle partitioning (Martín-Reviejo and
454 Wirtz, 2005). During the induction period, NO reacts with the bicyclic peroxy radical to form
455 alkoxy radicals and hence $\text{HO}_2\cdot$, α -dicarbonyls and monounsaturated dicarbonyls. These
456 products from *m*-xylene include glyoxal, methylglyoxal, unsaturated 1,4-dicarbonyls and
457 methyl unsaturated 1,4-dicarbonyls (Andino et al., 1996; Atkinson and Arey, 2007; Carter
458 and Heo, 2013; Forstner et al., 1997; Nehr et al., 2012), which are more volatile compared
459 with ring-retaining reaction products (Kroll et al., 2005; Volkamer et al., 2007). These
460 dicarbonyls yield $\text{HO}_2\cdot$ and $\cdot\text{OH}$ (Talukdar et al., 2011) leading to an increase in $\text{RO}_2\cdot$.
461 Dicarbonyl yields are not influenced by NO_x concentration ($\text{NO}_x < 100$ ppb) (Nishino et al.,
462 2010). Experiments in Region 2 consume more *m*-xylene and form larger amounts of
463 dicarbonyls during the induction period than those in Region 1 (Fig. S4), potentially
464 contributing to the higher SOA growth rate observed for Region 2 experiments after the
465 induction period. Aerosol formation during the induction period may be attributed to
466 production of semi-volatile products (e.g. benzoquinone and *m*-tolualdehyde) formed in the
467 presence of NO by P2P and to H-atom abstraction (Fig. S7) (Chan et al., 2007; Kroll et al.,
468 2007; Kroll and Seinfeld, 2005).

469 Several aerosol growth pathways are observed as the reaction proceeds (Fig. 8a). Initially,
470 when NO_2/NO is low, the NO competes with $\text{HO}_2\cdot$ inhibiting particle formation. As NO_2/NO
471 increases, an intermediate phase is achieved where the presence of NO enhances SOA
472 formation through rapid recycling of $\cdot\text{OH}$ (Pathway II). Finally, NO depletes (NO_2/NO rises)
473 to levels where existing $\text{HO}_2\cdot$ prefers to react with $\text{RO}_2\cdot$ to form additional SOA. The relative
474 contribution of each pathway varies based on instantaneous HC/NO loadings. The
475 contributions for each region (Fig. 1) relative to the length of the induction period are
476 schematically shown in Fig. 8b. The HC/NO range for aerosol promotion is observed to be
477 200-450 ppbC:ppb (Fig. 9, green dash line). Instantaneous HC/NO is above, near, and below
478 the promotion range when NO_2/NO reaches 70 for Regions 1, 2 and 3, respectively.

479 **Pathway I:** NO competes with $\text{HO}_2\cdot$ for $\text{RO}_2\cdot$ in this step (P1 vs P3, P1P vs P2P in Fig. S7).
480 NO leads to more fragmentation by P3 (Song et al., 2005) and less phenol-like compounds by
481 P2P. Initial HC/ NO_x ratio determines the time spent following Pathway I in classic
482 photooxidation experiments.

483 **Pathway II:** Pathway II domination depends on instantaneous HC/NO ratio. HC/NO around
484 200 ppbC:ppb serves as a boundary value for Pathway II domination. As shown in Fig. 8a
485 (dashed line) the concentration of $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ could increase for low NO concentrations
486 provided there is sufficient hydrocarbon available. $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ reaction rate peaks for
487 HC/NO ratios of ~200-450 ppbC:ppb (Fig. 9). It is proposed that peroxy radical formation is
488 not significantly affected by NO concentration above the upper limit of this range while NO
489 suppresses peroxy radical formation below that range. Red to blue trends (decreasing HC
490 consumption during induction period) in Regions 1 and 2 (Fig. 1) shows higher SOA growth
491 rates for decreasing HC:NO ratios for experiments with similar NO levels. This implies
492 increased SOA formation as lowering HC/NO promotes further oxidation by the $\text{RO}_2\cdot$ plus
493 $\text{HO}_2\cdot$ pathway (Fig. 8a). $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ concentration increasing for lower HC/NO is further
494 supported by the larger observed SOA growth rates during stepwise or continuous NO_x
495 injection (Section 3.3, RS4 and RS5). Experiments with similar initial HC/ NO_x are located in
496 different regions (Fig. 1) because of differences between hydrocarbon decay and NO
497 conversion rates (Stroud et al., 2004).

498 **NO “free” phase:** The NO “free” phase commences when HC/NO increases to >450
499 ppbC:ppb where $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ reaction dominates.

500 Most classic photooxidation experiments with initial NO will progress through the three
501 phases leading to the slope changes observed in the SOA growth curves (Fig. 1). The rates of
502 change of NO_2/NO and HC/NO determine the length of each phase (Fig. 8b and Fig. 9).
503 However, the HC/NO and NO_2/NO threshold for experiments will differ under atmospheric
504 conditions. Therefore, ambient atmospheric conditions must be simulated to study the
505 atmospheric NO effect on SOA formation.

506 H_2O_2 with initial NO (RS2) and step wise or continuous NO_x injection (RS4 and RS5) are
507 methods that improve the atmospheric relevance of chamber experiments (Section 3.4).
508 Linear SOA growth curve trends are found in these modified NO injection scenario
509 experiments (after the induction period) indicating that the experiment is remaining within a
510 single dominant SOA pathway rather than progressing through each pathway (Fig. 8b) as
511 occurs during traditional (RS1) photooxidation experiments.

512 4.2 NO impacts on SOA formation

513 Overall, NO exerts a two-edge impact on SOA formation defined instantaneously by radical
514 concentrations. The two-edge NO effect explains observations in 3.1 that curves in Region 2
515 (Fig. 1) with medium initial NO have higher SOA growth rates than those in Region 1 and
516 Region 3. It is the NO levels in Region 2 that increases $\cdot\text{OH}$ concentration without
517 significantly suppressing SOA formation. The f_2 value used in Section 3.2 only considers the

NO and HO₂· competition while ignoring ·OH concentration. Further, previous *m*-xylene photooxidation experiments with CO (RS6) or propene (RS7) (Song et al., 2007a) show lower SOA yield and growth rate compared those without CO or propene because ·OH concentration is suppressed (Table S5).

The NO effect on SOA formation from *m*-xylene also depends on instantaneous HC/NO. Fig. 8a illustrates the relationship between NO and peroxy radicals on SOA formation pathways. Although organic peroxides (ROOR) from self or cross reaction of RO₂· is a potential SOA source (Ziemann, 2002), RO₂· reaction with NO₂ and RO₂· self and cross reaction are not included in Fig. 8a due to their low reactivity in this study (Atkinson and Arey, 2007; Ng et al., 2007; Ziemann and Atkinson, 2012). The NO inhibition effect dominates when initial NO concentration (e.g HC/NO_x<3 ppbC:ppb) or pulse NO injection (e.g.1778A) is high. NO competes with HO₂· for RO₂· depressing hydroxperoxide (ROOH) formation, which is a major SOA component (Bonn et al., 2004). More volatile compounds are formed when NO reacts with RO₂· (Johnson et al., 2005; Kroll et al., 2006; Presto et al., 2005). NO suppression gradually ceases when NO is sufficiently converted to NO₂ (below sub-ppb level (Kroll and Seinfeld, 2008)). In this study, NO₂/NO>70 is identified as a threshold for adequate NO conversion to form SOA from classic *m*-xylene photooxidation chamber experiments with initial HC/NO_x higher than 3 ppbC:ppb. However, typical 12 hour daytime average concentration ratio of NO₂/NO in atmosphere is only 10 (Seinfeld and Pandis, 2006). In this study, higher SOA formation and instantaneous NO₂/NO ranging from 4.1-10.2 was achieved during stepwise NO injection. This indicates SOA yields from classic *m*-xylene photooxidation experiments may underestimate SOA formation for typical atmospheric conditions.

It is further demonstrated that increasing SOA formation rates not only depend on the NO concentration but also on the HC/NO ratio. As revealed by Fig. 8a, the reaction of RO₂· and HO₂· is suppressed directly (pathway I) and enhanced indirectly (pathway II) by NO. The net effect of NO on the rate of RO₂· and HO₂· formation are described by eq. 4-1 and eq. 4-2. Further, eq. 4-3 and eq. 4-4 describe the condition for RO₂· and HO₂· to increase, respectively. The NO concentration must therefore be in the range given by eq. 4-5 to promote HO₂· and RO₂· reaction. It is observed that higher available RO· and RO₂· widens the NO concentration range that increases SOA formation.

$$\frac{d[RO_2 \cdot]}{dt} = k_5[O_2][R \cdot] - k_1[RO_2 \cdot][NO] \quad (4-1)$$

$$\frac{d[HO_2 \cdot]}{dt} = k_6[O_2][RO \cdot] - k_2[HO_2 \cdot][NO] \quad (4-2)$$

$$[NO] < k_5[O_2][R \cdot]/k_1[RO_2 \cdot] = M \quad (4-3)$$

$$[NO] < k_6[O_2][RO\cdot]/k_2[HO_2\cdot] = N \quad (4-4)$$

$$A < [NO] < [M, N] \quad (4-5)$$

By assuming $[RO_2\cdot]$ and $[HO_2\cdot]$ are on the order of 10^{-2} ppb, NO should be 4×10^6 times and 2×10^8 times lower than $[R\cdot]$ and $[RO\cdot]$, respectively. The maximum $[R\cdot]$ and $[RO\cdot]$ can be estimated (eq.4-7 and eq.4-9) by assuming $[RH] = 50$ ppb, $[\cdot OH] = 0.1$ ppt, $[NO_2] = 30$ ppb, $[RO_2\cdot] = 50$ ppt and $[NO] = 1$ ppb. $[R\cdot]$ and $[RO\cdot]$ are estimated as 2.7×10^{-7} ppb and 2.8×10^{-7} ppb, respectively, suggesting that NO should be below 1.1 ppb under atmospheric conditions to promote $HO_2\cdot$ and $RO_2\cdot$ reaction.

$$\frac{d[R\cdot]}{dt} = k_4[RH][HO\cdot] - k_5[O_2][R\cdot] \quad (4-6)$$

$$[R\cdot]_{max} = k_4[RH][HO\cdot]/k_5[O_2] \quad (4-7)$$

$$\frac{d[RO\cdot]}{dt} = k_1[RO_2\cdot][NO] - k_6[O_2][RO\cdot] - k_7[NO_2][RO\cdot] \quad (4-8)$$

$$[RO\cdot]_{max} = k_1[RO_2\cdot][NO]/(k_6[O_2] + k_7[NO_2]) \quad (4-9)$$

564

The NO promotion will disappear (Fig. 2a) when NO concentration becomes less than 300ppt as occurs in traditional chamber experiments. However, NO increases in the morning and late afternoon (Guicherit, 1975; Williams et al., 1988) make it possible to enhance SOA formation in an urban atmosphere, especially when HC/NO is above 200 ppbC:ppb.

Dry conditions were used in this work to specifically concentrate on the NO impact on SOA formation. An increase trend of SOA formation with increasing RH from aromatic photooxidation has been reported in previous studies (Zhou et al., 2011; Kamens et al., 2011; Parikh et al., 2011). Healy, et al. (2009) suggests that increasing humidity contributes to higher $\cdot OH$ concentrations leading to greater oxidation of the aromatic precursor. Based on the current work, increasing $\cdot OH$ concentrations would be expected to promote SOA formation. The impact of $\cdot OH$ concentration due to increased humidity is likely to be much smaller than the influence of NO_x documented in this work.

5. Conclusion

Instantaneous NO effects on SOA formation from *m*-xylene under different atmospheric activities are observed from data mining 10 years of aromatic hydrocarbon chamber

581 experiments conducted in the UCR/CE-CERT chamber. A two-edged NO effect on SOA
582 formation is found in this study indicating that NO could promote SOA formation from
583 $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ at low concentration ($<5\text{ppb}$) with sufficient hydrocarbon ($\text{HC/NO} >400$)
584 present. Traditional chamber experiments with HC and NO_x only injected at the start of the
585 experiment progresses through multiple pathways and may not be as atmospherically relevant
586 when considered as a whole. This study suggests that continuous NO injection into
587 environmental chamber experiments could improve such chamber simulations. Better NO
588 injection scenarios avoiding NO suppression on SOA while raising $[\cdot\text{OH}]/[\text{HO}_2\cdot]$ ratio should
589 be explored in future studies in order to improve urban atmosphere characterization with
590 coexistence of NO, NO_2 , VOC and SOA. Moreover, the modified SOA growth curve is
591 identified as a valuable tool to compare the instantaneous SOA growth rate of different
592 experiments. While this modified approach is challenging and in its infancy, the trend of
593 incorporating instantaneous NO_2/NO into SOA formation analysis is expected to continue
594 since it provides more detailed SOA growth information at the sub-ppb NO levels generally
595 ignored by previous models. Further experiments and analyses are needed to more precisely
596 define the boundary condition for NO promotion of SOA formation from other hydrocarbon
597 precursors.

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602 **Reference**

- 603 Andino, J.M., Smith, J.N., Flagan, R.C., Goddard, W.A., Seinfeld, J.H. 1996. Mechanism of
604 atmospheric photooxidation of aromatics: A theoretical study. *The Journal of Physical*
605 *Chemistry*, 100(26), 10967-10980.
- 606 Atkinson, R. 2000. Atmospheric chemistry of VOCs and NO_x . *Atmospheric Environment*, 34(12-14),
607 2063-2101.
- 608 Atkinson, R. 1989. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with
609 organic compounds. *Journal of Physical and Chemical Reference Data*, Monograph 1, 1–246
- 610 Atkinson, R., Arey, J. 2007. Mechanisms of the gas-phase reactions of aromatic hydrocarbons and
611 PAHs with OH and NO_3 radicals. *Polycyclic Aromatic Compounds*, 27(1), 15-40.
- 612 Becker, K.H., Kleffmann, J., Kurtenbach, R., Wiesen, P. 1996. Solubility of nitrous acid (HONO) in
613 sulfuric acid solutions. *The Journal of Physical Chemistry*, 100(36), 14984-14990.
- 614 Binkowski, F.S., Roselle, S.J. 2003. Models - 3 Community Multiscale Air Quality (CMAQ) model
615 aerosol component 1. Model description. *Journal of Geophysical Research: Atmospheres*,
616 108(D6).

617 Bonn, B., von Kuhlmann, R., Lawrence, M.G. 2004. High contribution of biogenic hydroperoxides to
 618 secondary organic aerosol formation. *Geophysical Research Letters*, 31, L10108.
 619 Borrás, E., Tortajada-Genaro, L.A. 2012. Secondary organic aerosol formation from the
 620 photo-oxidation of benzene. *Atmospheric Environment*, 47, 154-163.
 621 Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., Yarwood, G.
 622 2002. *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*. Oxford University
 623 Press New York.
 624 Cao, G., Jang, M. 2008. Secondary organic aerosol formation from toluene photooxidation under
 625 various NO_x conditions and particle acidity. *Atmos. Chem. Phys. Discuss*, 8, 14467-14495.
 626 Carter, W.P. 2010. Development of the SAPRC-07 chemical mechanism. *Atmospheric Environment*,
 627 44(40), 5324-5335.
 628 Carter, W.P., Cocker III, D.R., Fitz, D.R., Malkina, I.L., Bumiller, K., Sauer, C.G., Pisano, J.T.,
 629 Bufalino, C., Song, C. 2005. A new environmental chamber for evaluation of gas-phase
 630 chemical mechanisms and secondary aerosol formation. *Atmospheric Environment*, 39(40),
 631 7768-7788.
 632 Carter, W.P., Heo, G. 2013. Development of revised SAPRC aromatics mechanisms. *Atmospheric*
 633 *Environment*, 77, 404-414.
 634 Carter, W.P., Heo, G., Cocker III, D.R., Nakao, S. 2012. SOA Formation: Chamber Study and Model
 635 Development. Final report to CARB, Contract 08-326, May 21. Available at:
 636 <http://www.cert.ucr.edu/~carter/absts.htm#pmchrpt>
 637 Carter, W.P.L., Heo, G. 2012. Development of Revised SAPRC Aromatics Mechanisms. Report to the
 638 California Air Resources Board Contracts 07-730, April 12. Available at:
 639 <http://www.cert.ucr.edu/~carter/SAPRC/saprc11.pdf>
 640 Chan, A., Chan, M., Surratt, J., Chhabra, P., Loza, C., Crounse, J., Yee, L., Flagan, R., Wennberg, P.,
 641 Seinfeld, J. 2010. Role of aldehyde chemistry and NO_x concentrations in secondary organic
 642 aerosol formation. *Atmos. Chem. Phys*, 10(15), 7169-7188.
 643 Chan, A., Kroll, J., Ng, N., Seinfeld, J. 2007. Kinetic modeling of secondary organic aerosol formation:
 644 effects of particle-and gas-phase reactions of semivolatile products. *Atmospheric Chemistry*
 645 *and Physics*, 7(15), 4135-4147.
 646 Cocker III, D.R., Flagan, R.C., Seinfeld, J.H. 2001a. State-of-the-art chamber facility for studying
 647 atmospheric aerosol chemistry. *Environmental science & technology*, 35(12), 2594-2601.
 648 Cocker III, D.R., Mader, B.T., Kalberer, M., Flagan, R.C., Seinfeld, J.H. 2001b. The effect of water on
 649 gas-particle partitioning of secondary organic aerosol: II. *m*-xylene and
 650 1,3,5-trimethylbenzene photooxidation systems. *Atmospheric Environment*, 35(35),
 651 6073-6085.
 652 Cusack, M., Pérez, N., Pey, J., Wiedensohler, A., Alastuey, A., Querol, X. 2013. Variability of
 653 sub-micrometer particle number size distributions and concentrations in the Western
 654 Mediterranean regional background. *Tellus B*, 65, 19243
 655 Dusanter, S., Vimal, D., Stevens, P., Volkamer, R., Molina, L.T., Baker, A., Meinardi, S., Blake, D.,
 656 Sheehy, P., Merten, A. 2009. Measurements of OH and HO₂ concentrations during the
 657 MCMA-2006 field campaign-Part 2: Model comparison and radical budget. *Atmospheric*
 658 *Chemistry and Physics*, 9(18), 6655-6675.
 659 Emanuelsson, E., Hallquist, M., Kristensen, K., Glasius, M., Bohn, B., Fuchs, H., Kammer, B.,
 660 Kiendler-Scharr, A., Nehr, S., Rubach, F. 2013. Formation of anthropogenic secondary organic

aerosol (SOA) and its influence on biogenic SOA properties. *Atmospheric Chemistry and Physics*, 13(5), 2837-2855.

Emmerson, K., Carslaw, N., Carpenter, L., Heard, D., Lee, J., Pilling, M. 2005. Urban atmospheric chemistry during the PUMA campaign 1: Comparison of modelled OH and HO₂ concentrations with measurements. *Journal of atmospheric chemistry*, 52(2), 143-164.

Emmerson, K.M., Carslaw, N., Carslaw, D., Lee, J.D., McFiggans, G., Bloss, W.J., Gravestock, T., Heard, D.E., Hopkins, J., Ingham, T. 2007. Free radical modelling studies during the UK TORCH Campaign in Summer 2003. *Atmospheric Chemistry and Physics*, 7(1), 167-181.

Forstner, H.J.L., Flagan, R.C., Seinfeld, J.H. 1997. Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: Molecular composition. *Environmental Science & Technology*, 31(5), 1345-1358.

Guicherit, R. 1975. Photochemical smog formation in the Netherlands(in Dutch). Report No. G 646, TNO Research Institute for Environmental Hygiene, 104

Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., Goldstein, A. 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics*, 9(14), 5155-5236.

Handisides, G.M., Plaß-Dülmer, C., Gilge, S., Bingemer, H., Berresheim, H. 2003. Hohenpeissenberg Photochemical Experiment (HOPE 2000): Measurements and photostationary state calculations of OH and peroxy radicals. *Atmospheric Chemistry and Physics*, 3(5), 1565-1588.

Healy, R.M., Temime, B., Kuprovskite, K., Wenger, J.C. 2009. Effect of relative humidity on gas/particle partitioning and aerosol mass yield in the photooxidation of p-xylene. *Environmental Science & Technology*, 43(6), 1884-1889.

Henze, D., Seinfeld, J., Ng, N., Kroll, J., Fu, T.M., Jacob, D., Heald, C. 2008. Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high-vs. low-yield pathways. *Atmospheric Chemistry and Physics*, 8(9), 2405-2421.

Hurley, M.D., Sokolov, O., Wallington, T.J., Takekawa, H., Karasawa, M., Klotz, B.Ö., Barnes, I., Becker, K.H. 2001. Organic aerosol formation during the atmospheric degradation of toluene. *Environmental Science & Technology*, 35(7), 1358-1366.

Izumi, K., Fukuyama, T. 1990. Photochemical aerosol formation from aromatic hydrocarbons in the presence of NO_x. *Atmospheric Environment. Part A. General Topics*, 24(6), 1433-1441.

Jenkin, M., Saunders, S., Wagner, V., Pilling, M. 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1), 181-193.

Jiang, W. 2003. Instantaneous secondary organic aerosol yields and their comparison with overall aerosol yields for aromatic and biogenic hydrocarbons. *Atmospheric Environment*, 37(38), 5439-5444.

Johnson, D., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M. 2005. Simulating the formation of secondary organic aerosol from the photooxidation of aromatic hydrocarbons. *Environmental Chemistry*, 2(1), 35-48.

Kamens, R.M., Zhang, H., Chen, E.H., Zhou, Y., Parikh, H.M., Wilson, R.L., Galloway, K.E., Rosen, E.P. 2011. Secondary organic aerosol formation from toluene in an atmospheric hydrocarbon mixture: water and particle seed effects. *Atmospheric Environment*, 45(13), 2324-2334.

Kanakidou, M., Seinfeld, J., Pandis, S., Barnes, I., Dentener, F., Facchini, M., Van Dingenen, R.,

705 Ervens, B., Nenes, A., Nielsen, C. 2005. Organic aerosol and global climate modelling: a
 706 review. *Atmospheric Chemistry and Physics*, 5(4), 1053-1123.

707 Kanaya, Y., Hofzumahaus, A., Dorn, H.-P., Brauers, T., Fuchs, H., Holland, F., Rohrer, F., Bohn, B.,
 708 Tillmann, R., Wegener, R. 2012. Comparisons of observed and modeled OH and HO₂
 709 concentrations during the ambient measurement period of the HO_x Comp field campaign.
 710 *Atmospheric Chemistry and Physics*, 12(5), 2567-2585.

711 Kautzman, K., Surratt, J., Chan, M., Chan, A., Hersey, S., Chhabra, P., Dalleska, N., Wennberg, P.,
 712 Flagan, R., Seinfeld, J. 2009. Chemical composition of gas-and aerosol-phase products from
 713 the photooxidation of naphthalene. *The Journal of Physical Chemistry A*, 114(2), 913-934.

714 Koch, R., Knispel, R., Elend, M., Siese, M., Zetzsch, C. 2007. Consecutive reactions of aromatic-OH
 715 adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, *m*- and *p*-xylene,
 716 hexamethylbenzene, phenol, *m*-cresol and aniline. *Atmospheric Chemistry and Physics*, 7(8),
 717 2057-2071.

718 Kroll, J.H., Chan, A.W.H., Ng, N.L., Flagan, R.C., Seinfeld, J.H. 2007. Reactions of semivolatile
 719 organics and their effects on secondary organic aerosol formation. *Environmental Science &*
 720 *Technology*, 41(10), 3545-3550.

721 Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., Seinfeld, J.H. 2006. Secondary organic aerosol
 722 formation from isoprene photooxidation. *Environmental science & technology*, 40(6),
 723 1869-1877.

724 Kroll, J.H., Ng, N.L., Murphy, S.M., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H. 2005. Chamber
 725 studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds.
 726 *Journal of Geophysical Research: Atmospheres* (1984–2012), 110(D23).

727 Kroll, J.H., Seinfeld, J.H. 2008. Chemistry of secondary organic aerosol: Formation and evolution of
 728 low-volatility organics in the atmosphere. *Atmospheric Environment*, 42(16), 3593-3624.

729 Kroll, J.H., Seinfeld, J.H. 2005. Representation of secondary organic aerosol laboratory chamber data
 730 for the interpretation of mechanisms of particle growth. *Environmental Science & Technology*,
 731 39(11), 4159-4165.

732 Kuwata, M., Zorn, S.R., Martin, S.T. 2011. Using elemental ratios to predict the density of organic
 733 material composed of carbon, hydrogen, and oxygen. *Environmental Science & Technology*,
 734 46(2), 787-794.

735 Lee, J.D., Lewis, A.C., Monks, P.S., Jacob, M., Hamilton, J.F., Hopkins, J.R., Watson, N.M., Saxton,
 736 J.E., Ennis, C., Carpenter, L.J. 2006. Ozone photochemistry and elevated isoprene during the
 737 UK heatwave of August 2003. *Atmospheric Environment*, 40(39), 7598-7613.

738 Malloy, Q.G., Nakao, S., Qi, L., Austin, R., Stothers, C., Hagino, H., Cocker III, D.R. 2009. Real-Time
 739 Aerosol Density Determination Utilizing a Modified Scanning Mobility Particle
 740 Sizer—Aerosol Particle Mass Analyzer System. *Aerosol Science and Technology*, 43(7),
 741 673-678.

742 Martín-Reviejo, M., Wirtz, K. 2005. Is benzene a precursor for secondary organic aerosol?
 743 *Environmental Science & Technology*, 39(4), 1045-1054.

744 Na, K., Sawant, A.A., Song, C., Cocker III, D.R. 2004. Primary and secondary carbonaceous species in
 745 the atmosphere of Western Riverside County, California. *Atmospheric Environment*, 38(9),
 746 1345-1355.

747 Nakao, S., Clark, C., Tang, P., Sato, K., Cocker III, D. 2011a. Secondary organic aerosol formation
 748 from phenolic compounds in the absence of NO_x. *Atmos. Chem. Phys.*, 11,

10649-10660. Nakao, S., Liu, Y., Tang, P., Chen, C., Zhang, J., Cocker III, D. 2011b. Role of glyoxal in SOA formation from aromatic hydrocarbons: gas-phase reaction trumps reactive uptake. *Atmos. Chem. Phys. Discuss.*, 11, 30599-30625. Nehr, S., Bohn, B., Wahner, A. 2012. Prompt HO₂ formation following the reaction of OH with aromatic compounds under atmospheric conditions. *The Journal of Physical Chemistry A*, 116(24), 6015-6026.

Ng, N., Kroll, J., Chan, A., Chhabra, P., Flagan, R., Seinfeld, J. 2007. Secondary organic aerosol formation from *m*-xylene, toluene, and benzene. *Atmospheric Chemistry and Physics Discussions*, 7(2), 4085-4126.

Ng, N.L., Kroll, J.H., Keywood, M.D., Bahreini, R., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., Lee, A., Goldstein, A.H. 2006. Contribution of first-versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons. *Environmental science & technology*, 40(7), 2283-2297.

Nishino, N., Arey, J., Atkinson, R. 2010. Formation yields of glyoxal and methylglyoxal from the gas-phase OH radical-initiated reactions of toluene, xylenes, and trimethylbenzenes as a function of NO₂ concentration. *The Journal of Physical Chemistry A*, 114(37), 10140-10147.

Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C., Seinfeld, J.H. 1996. Gas/particle partitioning and secondary organic aerosol yields. *Environmental Science & Technology*, 30(8), 2580-2585.

Presto, A.A., Huff Hartz, K.E., Donahue, N.M. 2005. Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NO_x concentration. *Environmental Science & Technology*, 39(18), 7046-7054.

Qi, L., Nakao, S., Tang, P., Cocker III, D. 2010. Temperature effect on physical and chemical properties of secondary organic aerosol from *m*-xylene photooxidation. *Atmospheric Chemistry and Physics*, 10(8), 3847-3854.

Parikh, H.M., Carlton, A.G., Vizuete, W., Kamens, R.M. 2011. Modeling secondary organic aerosol using a dynamic partitioning approach incorporating particle aqueous-phase chemistry. *Atmospheric Environment*, 45(5), 1126-1137.

Rattigan, O.V., Dirk Felton, H., Bae, M.-S., Schwab, J.J., Demerjian, K.L. 2010. Multi-year hourly PM_{2.5} carbon measurements in New York: Diurnal, day of week and seasonal patterns. *Atmospheric Environment*, 44(16), 2043-2053.

Ren, X., Harder, H., Martinez, M., Leshner, R.L., Olinger, A., Shirley, T., Adams, J., Simpas, J.B., Brune, W.H. 2003. HO_x concentrations and OH reactivity observations in New York City during PMTACS-NY2001. *Atmospheric Environment*, 37(26), 3627-3637.

Seinfeld, J., Pandis, S. 2006. *Atmospheric chemistry and physics: from air pollution to climate change*. Atmospheric chemistry and physics: from air pollution to climate change.

Sillman, S. 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment*, 33(12), 1821-1846.

Song, C., Na, K., Cocker III, D.R. 2005. Impact of the hydrocarbon to NO_x ratio on secondary organic aerosol formation. *Environmental Science & Technology*, 39(9), 3143-3149.

Song, C., Na, K., Warren, B., Malloy, Q., Cocker III, D.R. 2007a. Impact of propene on secondary organic aerosol formation from *m*-xylene. *Environmental Science & Technology*, 41(20), 6990-6995.

Song, C., Na, K., Warren, B., Malloy, Q., Cocker III, D.R. 2007b. Secondary organic aerosol formation from *m*-xylene in the absence of NO_x. *Environmental Science & Technology*, 41(21),

793 7409-7416.

794 Song, C., Na, K., Warren, B., Malloy, Q., Cocker III, D.R. 2007c. Secondary organic aerosol formation
 795 from the photooxidation of *p*- and *o*-xylene. *Environmental Science & Technology*, 41(21),
 796 7403-7408.

797 Talukdar, R., Zhu, L., Feierabend, K., Burkholder, J. 2011. Rate coefficients for the reaction of
 798 methylglyoxal (CH₃COCHO) with OH and NO₃ and glyoxal (HCO)₂ with NO₃. *Atmos. Chem.*
 799 *Phys*, 11, 10837-10851.

800 Volkamer, R., San Martini, F., Molina, L.T., Salcedo, D., Jimenez, J.L., Molina, M.J. 2007. A missing
 801 sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol.
 802 *Geophysical Research Letters*, 34(19).

803 Warren, B., Song, C., Cocker III, D.R. 2008. Light intensity and light source influence on secondary
 804 organic aerosol formation for the *m*-xylene/NO_x photooxidation system. *Environmental*
 805 *Science & Technology*, 42(15), 5461-5466.

806 White, S.J., Jamie, I.M., Angove, D.E. 2014. Chemical characterisation of semi-volatile and aerosol
 807 compounds from the photooxidation of toluene and NO_x. *Atmospheric Environment*, 83,
 808 237-244.

809 Williams, M.L., Broughton, G., Bower, J., Drury, V., Lilley, K., Powell, K., Rogers, F., Stevenson, K.
 810 1988. Ambient NO_x concentrations in the UK 1976–1984—a summary. *Atmospheric*
 811 *Environment* (1967), 22(12), 2819-2840.

812 Zhao, J., Zhang, R., Misawa, K., Shibuya, K. 2005. Experimental product study of the OH-initiated
 813 oxidation of *m*-xylene. *Journal of Photochemistry and Photobiology A: Chemistry*, 176(1),
 814 199-207.

815 Zhou, Y., Zhang, H., Parikh, H.M., Chen, E.H., Rattanavaraha, W., Rosen, E.P., Wang, W., Kamens,
 816 R.M. 2011. Secondary organic aerosol formation from xylenes and mixtures of toluene and
 817 xylenes in an atmospheric urban hydrocarbon mixture: water and particle seed effects (II).
 818 *Atmospheric Environment*, 45(23), 3882-3890.

819 Ziemann, P.J. 2002. Evidence for low-volatility diacyl peroxides as a nucleating agent and major
 820 component of aerosol formed from reactions of O₃ with cyclohexene and homologous
 821 compounds. *The Journal of Physical Chemistry A*, 106(17), 4390-4402.

822 Ziemann, P.J., Atkinson, R. 2012. Kinetics, products, and mechanisms of secondary organic aerosol
 823 formation. *Chemical Society Reviews*, 41(19), 6582-6605.

Table 1. Experimental Conditions of Five Reaction Scenarios under Black Lights
($k_f=0.40 \text{ min}^{-1}$)

RS	Run ID	Initial Injection ppb				Continuous Injection	
		HC	NO	NO ₂	H ₂ O ₂	Compound	Amount
1	1748A	112	62.18	7.81	N/A	N/A	N/A
1	1749B	98.0	59.27	7.64	N/A	N/A	N/A
1	1774A	98.1	27.33	0.65	N/A	N/A	N/A
1	1841A	79.6	36.83	2.49	N/A	N/A	N/A
1	1843A	69.2	42.29	0	N/A	N/A	N/A
1	1843B	70.1	42.67	0	N/A	N/A	N/A
1	1872B	72.8	22.22	0	N/A	N/A	N/A
2	1749A	99.0	58.37	8.32	1000	N/A	N/A
2	1795B	71.4	17.73	1.24	1000	N/A	N/A
2	1849B	82.4	17.97	0	1000	N/A	N/A
2	1858B	125	19.96	0.52	1000	N/A	N/A
2	1859B	111	51.84	2.05	1000	N/A	N/A
2	1863B	71.5	50.74	0.1	1000	N/A	N/A
2	1867B	78.0	22.84	28.6	1000	N/A	N/A
3	1748B	112	62.44	7.74	N/A	HONO	750ul/hr ^a
3	1774B	94.4	27.1	1.22	N/A	HONO	250ul/hr ^b
4	1777A ^d	83.0	19.17	2.30	1000	NO	~5ppb/hr
4	1778A ^{c,d}	67.5	20	1.42	1000	NO	~15ppb/hr
4	1795A	68.3	19.41	0.90	1000	NO	~5ppb/hr
4	1858A	128	19.89	0.53	1000	NO	~5ppb/hr
4	1863A	72.1	20.35	0	1000	NO	~5ppb/hr
4	1867A	80.7	21.75	1.65	1000	NO	5ppb/hr*
4	1868A	70.5	18.91	0.56	1000	NO	7.5ppb/hr*
4	1885A	82.3	23.97	0	1000	NO	10ppb/hr*
5	1801A	127	20.66	1.27	1000	NO ₂	~5ppb/hr
5	1849A	79.5	17.76	0	1000	NO ₂	~5ppb/hr
5	1859A	113	18.92	1.38	1000	NO ₂	~5ppb/hr
5	1872A	72.1	21.48	0.02	1000	NO ₂	~5ppb/hr
5	1885B	83.2	23.86	0.13	1000	NO ₂	~10ppb/hr

Note: 1- Classic Scenario; 2- H₂O₂ Scenario; 3- Continuous HONO Scenario; 4-Stepwise/Continuous* NO Scenario; 5-Stepwise NO₂ Scenario; a) Injection by droplets, assuming one drop is 150 ul; b) Injection by syringe; c) ~30ppb NO is injected at the third hour; d) *m*-xylene data are measured by a different GC column compared with other experiment

Table 2. Correlation between Overall Yields, Instant Yield and Average Radical Concentration of Four Reaction Scenarios

	$\cdot\text{OH}$	$\text{HO}_2\cdot$	$\text{RO}_2\cdot$	$\text{HO}_2\cdot*\text{RO}_2\cdot$	$\text{HO}_2\cdot/\text{RO}_2\cdot$	$\cdot\text{OH}/\text{HO}_2\cdot$	$\text{NO}/\text{HO}_2\cdot$
OAY	0.506	0.548	0.529	0.528	0.517	-0.549	-0.419
p-value	0.008	0.004	0.005	0.006	0.007	0.001	0.033
IAY	0.543	0.537	0.304	0.386	0.618	-0.552	-0.386
p-value	0.004	0.005	0.131	0.051	0.001	0.003	0.051

Note: OAY: overall aerosol yield; IAY: instant yield. p-value determines the appropriateness of rejecting the null hypothesis in a hypothesis test. P-values range from 0 to 1, 0-reject null hypothesis and 1 accept null hypothesis. Alpha (α) level used is 0.05. If the p-value of a test statistic is less than alpha, the null hypothesis is rejected. Run 1778A are not included due to extreme high NO injection rate and low $[\text{RO}_2\cdot]$.

Fig. 1. Modified (X&Y offset) SOA growth curves of 56 classic *m*-xylene photooxidation experiments under black lights ($k_1=0.13 \text{ min}^{-1}$)

Fig. 2. Relationship between the SOA growth rate and NO_2 concentration (a) and HC/NO ratio (b)

Fig. 3. a) Modified SOA growth curves of 52 classic *m*-xylene photooxidation experiments colored with f_2 (fraction of $\text{RO}_2\cdot$ reacts with $\text{HO}_2\cdot$); b) Modified SOA growth curves of 52 classic *m*-xylene photooxidation experiments colored by hydrocarbon reaction rate (R_{HC})

Fig. 4. Modified SOA growth curve of five reaction scenarios

Fig. 5. Times series $\cdot\text{OH}$, $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ change of RS1:1774A; RS2:1795B; RS4: 1) 1795A, 2) 1867A, 3) 1778A, 4) 1777A); RS5: 1) 1849A, 2) 1801A

Fig. 6. Relationship between yield and radical ratio: a) Overall aerosol yield (OAY) and $\cdot\text{OH}/\text{HO}_2\cdot$; b) Instantaneous aerosol yield (IAY) and $\text{HO}_2\cdot/\text{RO}_2\cdot$.

Fig. 7. Relationship between $\Delta M_0'$ and $[\text{HO}_2\cdot]/[\text{RO}_2\cdot]$ during $\Delta\text{HC}' = [0, 175] \mu\text{g}/\text{m}^3$ colored with injected $[\cdot\text{OH}]/[\text{HO}\cdot]$ and sized with NO_x injection rate (Bigger size resembles smaller NO_x injection rate)

$k_1 = 9.23 \text{ e}^{-12} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Carter, 2010); $k_2 = 8.50 \text{ e}^{-12} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Bohn & Zetzsch, 1997);
 $k_3 = 7.63 \text{ e}^{-12} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Carter, 2010); $k_4 = 2.31 \text{ e}^{-12} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Calvert, et al., 2002);
 $k_5 = 1.80 \text{ e}^{-15} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Koch, et al., 2007); $k_6 = 8.00 \text{ e}^{-14} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Calvert, et al., 2002);
 $k_7 = 4.00 \text{ e}^{-11} \text{ cm}^3 \cdot \text{moldecule}^{-1} \cdot \text{s}^{-1}$ (Calvert, et al., 2002), the reaction rate of $\text{RO}\cdot$ with NO_2 , not showed

a)

b)

Fig. 8. a) Relationship between NO and SOA formation from $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$;
b) Progressive dominate reaction pathways and phases during classic *m*-xylene photooxidation

Fig. 9. Typical instant NO_2/NO and HC/NO change trend in three regions (Region 1: 219A; Region 2: 566A; Region 3: 249A; green dash line promotion HC/NO range)