Supplement of

Functionality-based formation of secondary organic aerosol from \textit{m}-xylene photooxidation

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Figure S1. Schematic representation of the experimental setup. DMA for differential mobility analyzer; ID-CIMS for ion drift – chemical ionization mass spectrometry; APM for aerosol particle mass analyzer, TD-ID-CIMS for thermal desorption – ion drift – chemical ionization mass spectrometry; SMPS for scanning mobility particle sizer; and CRD for cavity ring-down spectroscopy. Monodispersed seed particles consisting of ammonium bisulfate, ammonium sulfate, and sodium chloride were exposed to oxidation products between m-xylene by OH and in the absence/presence of NH$_3$ vapors inside a 1 m$^3$ reaction chamber. RH was regulated between 10% and 70%, and $T$ was maintained at 298 K. The gaseous concentrations of the oxidation products and particle properties, such as density, chemical composition, growth, and single scattering albedo, were simultaneously quantified by ID-CIMS, APM, TD-ID-CIMS, SMPS, and CRD-Nephelometer, respectively.
Figure S2. (a) The initial oxidation steps for OH oxidation of m-xylene leading to the formation of m-xylene-OH adducts, dimethylphenol, OH-m-xylene-O₂ peroxo radicals, and methylbenzaldehyde. (b) Multi-generation products from m-xylene-OH photooxidation. The letters of P1, P2, and P3 denote the products of first, second, and third generation of reactions with OH, respectively. The compounds in each box are lumped in kinetic simulation with the rate constant with OH (k), wall loss rate constant (k_{w}), and uptake rate constant (k_{p}) listed in Table S1. The numbers denote the mass to charge ratio (m/z).
**Figure S3.** Temporal evolutions of additional P2 (a) and P3 (b) concentrations from m-xylene oxidation. The number denotes m/z value of the compound on ID-CIMS. The experiments were carried out on (NH₄)₂SO₄ seed particles with 19 ppb NH₃ and at 298 K and RH = 90%. Initiation of photooxidation by ultraviolet light occurred at t = 0.
Figure S4. Pathways for oligomerization. The mechanisms leading to formation of particle-phase oligomers from α-dicarbonyls, γ-dicarbonyls, tricarbonyls, and epoxide detected by TD-ID-CIMS.
Figure S5. Pathway for BrC formation. The mechanisms leading to formation of particle-phase nitrogen-containing organics (NCO) from α-dicarbonyls, γ-dicarbonyls, tricarbonyls, and epoxide.
Table S1. Parameters for kinetic model simulation of gas-phase concentrations. Reaction rate constants are taken from MCM V3.3.1 (Jenkin et al., 2003). The relations between products from each generation are provided in Figure S1b. $k_n = k_n[OH]$ denotes the pseudo-first order rate constant of each oxidation step. $l_n = kW_n + k_p$ is the overall loss rate of each species.

|     | $k_1 (\times 10^{-12} \text{ cm molecule}^{-1} \text{ s}^{-1})$ | $k_{w1}(\times 10^{-4} \text{ s}^{-1})$ |
|-----|---------------------------------------------------------------|--------------------------------------|
| P1  |                                                               |                                      |
| 1a  | 4.0                                                           | 6.84                                 |
| 1b  | 0.94                                                          | 3.6                                  |

|     | $k_2 (\times 10^{-12} \text{ cm molecule}^{-1} \text{ s}^{-1})$ | $k_{w2}(\times 10^{-4} \text{ s}^{-1})$ | $k_{p2}(\times 10^{-4} \text{ s}^{-1})$ |
|-----|---------------------------------------------------------------|--------------------------------------|--------------------------------------|
| P2  |                                                               |                                      |                                      |
| 2a  | 38.2                                                          | 1.8                                  |                                      |
| 2b  | 25.5                                                          | 13.1                                 | 16.3                                 |
| 2c  | 25.5                                                          | 11.9                                 | 3.3                                  |
| 2d  | 6.7                                                           | 12.9                                 | 3.5                                  |
| 2e  | 12.9                                                          | 5.9                                  | 0.92                                 |

|     | $k_3 (\times 10^{-12} \text{ cm molecule}^{-1} \text{ s}^{-1})$ | $k_{w3}(\times 10^{-4} \text{ s}^{-1})$ | $k_{p3}(\times 10^{-4} \text{ s}^{-1})$ |
|-----|---------------------------------------------------------------|--------------------------------------|--------------------------------------|
| P3  |                                                               |                                      |                                      |
| 3a  | 205                                                           | 7.5                                  | 6.8                                  |
| 3b  | 360                                                           | 5.0                                  | 3.3                                  |
| 3c  | 360                                                           | 2.4                                  | 2.5                                  |
| 3e  | 12.9                                                          | 6.3                                  | 0.92                                 |

\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_1')(k_3' + l_2' - k_1')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_2' + l_1' - k_1')(k_2' + l_2' - k_1')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_2' + l_1' - k_1')(k_2' + l_2' - k_1')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_3')(k_3' + l_2' - k_3')} \]

\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_1')(k_3' + l_2' - k_3')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_1')(k_3' + l_2' - k_3')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_2' + l_1' - k_1')(k_2' + l_2' - k_1')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_2' + l_1' - k_1')(k_2' + l_2' - k_1')} \]

\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_3')(k_3' + l_2' - k_3')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_3')(k_3' + l_2' - k_3')} \]
\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_3')(k_3' + l_2' - k_3')} \]

\[ \frac{k_1'k_2'[A]_0}{(k_3' + l_2' - k_3')(k_3' + l_2' - k_3')} \]
Table S2. Mass peak assignments for oligomeric products detected by TD-ID-CIMS.

| m/z | MW  | Formula     |
|-----|-----|-------------|
|     |     | **Methylglyoxal** |           |
| Dimers |     |             |           |
| 145  | 144 | C₆H₆O₄      |           |
| 163  | 162 | C₆H₁₀O₅     |           |
| 181  | 180 | C₆H₁₂O₆     |           |
| Trimers |     |             |           |
| 217  | 216 | C₉H₁₀O₆     |           |
| 235  | 234 | C₉H₁₄O₇     |           |
| 253  | 252 | C₉H₁₆O₈     |           |
|     |     | **Glyoxal** |           |
| Dimers |     |             |           |
| 117  | 116 | C₄H₄O₄      |           |
| 135  | 162 | C₄H₆O₅      |           |
| 153  | 180 | C₄H₈O₆      |           |
| Trimers |     |             |           |
| 175  | 174 | C₆H₆O₆      |           |
| 193  | 192 | C₆H₈O₇      |           |
| 211  | 210 | C₆H₁₀O₈     |           |
|     |     | **γ-dicarbonyls** |         |
| Monomers |     |             |           |
| 85   | 84  | C₄H₄O₂      |           |
| 99   | 98  | C₅H₆O₂      |           |
| Dimers |     |             |           |
| 143  | 142 | C₆H₆O₄      |           |
| 157  | 156 | C₇H₈O₄      |           |
| 169  | 168 | C₈H₈O₄      |           |
| 197  | 196 | C₁₀H₁₂O₄    |           |
| Epoxide |     |             |           |
| 141  | 140 | C₇H₆O₃      |           |
| 155  | 154 | C₈H₁₀O₃     |           |
Table S3. Mass peak assignments for nitrogen-containing organics (NCO) from α-dicarbonyls n-heterocycles and γ-carbonyls n-chains detected by TD-ID-CIMS.

| m/z | MW  | Formula     | Compound          |
|-----|-----|-------------|-------------------|
| 83  | 82  | C₄H₆N₂      | ![Methylglyoxal_n-heterocycles_1](image) |
| 125 | 124 | C₆H₈ON₂     | ![Methylglyoxal_n-heterocycles_2](image) |
| 251 | 250 | C₆H₁₀O₅     | ![Methylglyoxal_n-heterocycles_3](image) |
| 69  | 68  | C₃H₄N₂      | ![Glyoxal_n-heterocycles_1](image)     |
| 97  | 96  | C₄H₄ON₂     | ![Glyoxal_n-heterocycles_2](image)     |
| 142 | 141 | C₆H₇O₂N     | ![γ-carbonyls_n-chains_1](image)       |
| 156 | 155 | C₇H₉O₂N     | ![γ-carbonyls_n-chains_2](image)       |
| 196 | 195 | C₄H₆O₂N₂    | ![γ-carbonyls_n-chains_3](image)       |
Table S4. Mass peak assignments for organic acids and PAQ detected by TD-ID-CIMS.

| m/z  | MW  | Formula    | Compound |
|------|------|------------|----------|
| 89   | 88   | C₃H₄O₃    |          |
| 113  | 112  | C₃H₄O₃    |          |
| 115  | 114  | C₃H₆O₃    |          |
| 125  | 124  | C₇H₈O₂    |          |
| 127  | 126  | C₅H₆O₃    |          |
| 129  | 128  | C₆H₈O₃    |          |
| 131  | 130  | C₅H₆O₄    |          |
| 137  | 136  | C₈H₈O₂    |          |
| 139  | 138  | C₈H₁₀O₂   |          |
| 151  | 150  | C₈H₆O₃    |          |
| 153  | 152  | C₈H₈O₃    |          |
| 155  | 154  | C₈H₁₀O₃   |          |
| 167  | 166  | C₈H₆O₄    |          |
| 171  | 170  | C₈H₁₀O₄   |          |
Table S5. The percent contributions of COOs from \textit{m}-xylene-OH oxidation to the particle-phase mass intensity. GL: glyoxal, MG: methylglyoxal, GL+MG: cross-reaction of glyoxal and methylglyoxal. Note that the cross-reaction products of γ-carbonyls/tricarbonyls with α-dicarbonyls are summed into the contribution of γ-carbonyls/tricarbonyls. The experiments were carried on (NH$_4$)$_2$SO$_4$ seed particle with 19 ppb of NH$_3$.

| Condensable oxidized organics | Oligomerization | NCO formation | Total |
|------------------------------|-----------------|---------------|-------|
| GL                           | 3%              | 3%            | 6%    |
| MG                           | 10%             | 12%           | 22%   |
| γ-dicarbonyls                | 7%              | 8%            | 15%   |
| epoxide                      | 2%              | 0.3%          | 2%    |
| Carboxylates                 |                 |               | 47%   |
| PAQ                          |                 |               | 8%    |
Table S6. Saturation vapor pressures ($P_s$) of dicarbonyls, organic acids, and PAQ.

| Compound                        | $P_s$ (atm, 298 K) |
|--------------------------------|--------------------|
| **Dicarbonyls**                 |                    |
| Glyoxal                         | $2.3 \times 10^{-2}$|
| Methylglyoxal                   | $1.6 \times 10^{-1}$|
| Methylbutenedial                | $3.9 \times 10^{-4}$|
| **Organic acids**               |                    |
| Toluic acid                     | $1.1 \times 10^{-5}$|
| 4-Oxo-2-pentenoic acid          | $6.6 \times 10^{-6}$|
| Acetylpyruvic acid              |                    |
| Pyruvic acid                    | $6.1 \times 10^{-4}$|
| Glyoxylic acid                  | $1.9 \times 10^{-3}$|
| **PAQ**                         |                    |
| Dihydroxy dimethyl benzene      | $1 \times 10^{-7}$  |
| Trihydroxy dimethyl benzene     | $8 \times 10^{-9}$  |
| Hydroxy dimethyl quinone        | $3 \times 10^{-7}$  |
Table S7. Measured gaseous concentrations of condensable oxidized organics from \textit{m}-xylene-OH oxidation at 10% and 70% RH.

| m/z  | Average Concentration (ppb) | Ratio ($R_c$) |
|------|-----------------------------|---------------|
|      | 10% RH                      | 70% RH        |               |
| **Dicarbonyls** |                              |               |               |
| 59   | 1.3                         | 0.51          |               |
| 73   | 3.4                         | 1.0           | 2.8 ± 0.5     |
| 99   | 4.2                         | 1.7           |               |
| **Carboxylate acids** |                              |               |               |
| 89   | 2.1                         | 0.69          |               |
| 113  | 4.1                         | 1.6           |               |
| 115  | 3.7                         | 1.4           |               |
| 117  | 2.0                         | 0.52          |               |
| 119  | 1.1                         | 0.31          |               |
| 127  | 3.3                         | 1.18          |               |
| 129  | 1.3                         | 0.36          |               |
| 137  | 0.42                        | 0.19          | 3.2 ± 0.8     |
| 139  | 2.5                         | 1.11          |               |
| 143  | 1.5                         | 0.40          |               |
| 151  | 2.7                         | 0.59          |               |
| 153  | 0.66                        | 0.35          |               |
| 159  | 1.3                         | 0.36          |               |
| 161  | 0.97                        | 0.25          |               |
| 199  | 3.3                         | 0.90          |               |
| **PAQ** |                              |               |               |
| 155  | 0.47                        | 0.23          |               |
| 171  | 0.39                        | 0.21          | 1.9 ± 0.1     |
| 187  | 0.3                         | 0.16          |               |
| **Nitrophenols** |                              |               |               |
| 154  | 1.4                         | 0.7           |               |
| 168  | 1.0                         | 0.4           | 2.6 ± 0.7     |
| 184  | 0.5                         | 0.15          |               |
| **m-Xylene** |                              |               |               |
| Initial | 1936                       | 1936          |               |
| Final  | 1330                        | 1363          |               |
Table S8. Density of identified major SOA components by TD-ID-CIMS.

| Compounds                        | m/z | Density (g cm$^{-3}$) |
|----------------------------------|-----|-----------------------|
| Methylimidazole                  | 83  | 1.03                  |
| Methylglyoxal                    | 73  | 1.05                  |
| butenedial                       | 85  | 1.06                  |
| 4-Oxo-2-pentenoic acid           | 115 | 1.2                   |
| Imidazole                        | 69  | 1.23                  |
| Pyruvic acid                     | 89  | 1.25                  |
| Benzoic acid                     | 123 | 1.27                  |
| Glyoxal                          | 59  | 1.27                  |
| Dihydroxy toluene                | 125 | 1.29                  |
| Acetylpyruvic acid               | 131 | 1.3                   |
| Glyoxylic acid                   | 75  | 1.38                  |
| Trihydroxy toluene               | 141 | 1.4                   |
| Glyoxal oligomers                | 175 | 1.71                  |
| 2-hydroxy-5-methylquinone        | 139 | 1.4                   |
| Oxalic acid                      | 91  | 1.9                   |
| Methylglyoxal oligomers          | 127 | 1.9                   |
**Table S9.** Measured uptake coefficient (γ) for COOs on ammonium sulfate seed particles in the presence of ammonia. $D_o =$ initial diameter, $D_p =$ final diameter after the exposure time of $dt$, $N =$ the particle number concentration, $S =$ average particle surface area, and $[A] =$ average concentration of species A. FR = percent contributions to the particle-phase mass intensity (Table S5).

| Species                  | $D_o$ (nm) | $D_p$ (nm) | $S$ ($10^{-5}$ cm$^2$ cm$^{-3}$) | $[A]$ (ppb) | FR  | $\gamma$ ($10^{-3}$) |
|--------------------------|-----------|-----------|-------------------------------|-------------|-----|---------------------|
| RH = 70%                 |            |           |                               |             |     |                     |
| Glyoxal                  | 100.0     | 240.8     | 1.72                          | 0.51        | 5.7%| 8.0 ± 2.2           |
| Methylglyoxal            | 100.0     | 240.8     | 1.72                          | 1.0         | 22% | 13 ± 3              |
| $\gamma$-Dicarbonyls     | 100.0     | 240.8     | 1.72                          | 1.7         | 11% | 3.0 ± 0.5           |
| Toluic acid              | 100.0     | 240.8     | 1.72                          | 0.19        | 0.5%| 1.0 ± 0.2           |
| Pyruvic acid             | 100.0     | 240.8     | 1.72                          | 0.69        | 3.6%| 2.9 ± 0.4           |
| 4-Oxo-2-pentenoic acid   | 100.0     | 240.8     | 1.72                          | 1.4         | 7.7%| 2.5 ± 0.4           |
| 3-Methyl-4-Oxo-2-pentenoic acid | 100.0 | 240.8 | 1.72 | 0.40 | 1.8% | 2.2 ± 0.5 |
| PAQ                      | 100.0     | 240.8     | 1.72                          | 0.60        | 8.0%| 5.3 ± 1.8           |
| Nitrophenol†             | 100.0     | 229.0     | 1.57                          | 1.3         | 5.6%| 1.7 ± 0.3           |
| RH = 10%                 |            |           |                               |             |     |                     |
| Glyoxal                  | 100.0     | 310.0     | 2.31                          | 1.3         | 0.9%| 0.74 ± 0.30         |
| Methylglyoxal            | 100.0     | 310.0     | 2.31                          | 3.4         | 3.9%| 1.0 ± 0.5           |
| $\gamma$-Dicarbonyls     | 100.0     | 310.0     | 2.31                          | 4.2         | 2.1%| 0.37 ± 0.12         |
| Toluic acid              | 100.0     | 310.0     | 2.31                          | 0.42        | 0.6%| 0.99 ± 0.21         |
| Pyruvic acid             | 100.0     | 310.0     | 2.31                          | 2.1         | 7.5%| 2.8 ± 0.6           |
| 4-Oxo-2-pentenoic acid   | 100.0     | 310.0     | 2.31                          | 3.7         | 12.2%| 2.3 ± 0.5          |
| 3-Methyl-4-Oxo-2-pentenoic acid | 100.0 | 310.0 | 2.31 | 1.3 | 4.1% | 2.0 ± 0.5 |
| PAQ                      | 100.0     | 310.0     | 2.31                          | 1.2         | 8.4%| 4.6 ± 1.5           |
| Nitrophenol†             | 100.0     | 303.5     | 2.20                          | 2.9         | 8.2%| 1.7 ± 0.2           |

*Measured in the presence of 100 ppb NO$_x$.  

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Table S10. Average uptake coefficients ($\gamma$) over all identified species of each type of condensable oxidized organics from m-xylene-OH oxidation at 10% and 70% RH.

| COO type         | 10% RH | 70% RH |
|------------------|--------|--------|
| **m-Xylene**     |        |        |
| Dicarbonyls      | 0.7 ± 0.3 | 8.0 ± 3.7 |
| Carboxylic acids | 2.0 ± 0.7 | 2.1 ± 0.8 |
| PAQ              | 4.6 ± 1.5 | 5.3 ± 1.8 |
| Nitrophenols     | 1.7 ± 0.2 | 1.7 ± 0.3 |
| **Toluene**      |        |        |
| Dicarbonyls      | 0.7 ± 0.2 | 7.8 ± 1.9 |
| Carboxylic acids | 1.8 ± 0.3 | 2.0 ± 0.4 |
| PAQ              | 4.2 ± 1.5 | 5.0 ± 1.5 |
| Nitrophenols     | 1.6 ± 0.3 | 1.6 ± 0.3 |