Supporting Information (SI)

Simulation of SOA Formation from the Photooxidation of Monoalkylbenzenes in the Presence of Aqueous Aerosols Containing Electrolytes under Various NOₓ Levels

Chufan Zhou, Myoseon Jang, and Zecen Yu
Department of Environmental Engineering Sciences, University of Florida, P.O. Box 116450, Gainesville, FL 32611, USA

Correspondence to: Myoseon Jang (mjang@ufl.edu)

Number of tables: 3
Number of figures: 8
Section S1. Lumping structure

The oxygenated products are lumped into \( n \) bins (\( n=8 \)) based on their volatility (mmHg): \( 10^{-8}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, \) and 1. The vapor pressure of the products was estimated by employing a group contribution method (Stein and Brown, 1994; Zhao et al., 1999), which has been applied by the development of the UNIPAR model (Im et al., 2014; Beardsley and Jang, 2016). Each volatility group was further classified into \( m \) bins (\( m=8 \)) based on the aerosol-phase chemical reactivity: very fast (VF), fast (F), medium (M), slow (S), partitioning only (P), and multi-alcohol (MA), as shown in a previous paper (Beardsley and Jang, 2016). GLY, MGLY, and isoprene products only (IEPOX) are separately treated in UNIPAR and represented as Reactive (R) group because of their significant contributions to SOA formation (Jang and Kamens, 2001; Jang et al., 2002). The detailed products distributions were shown in the Tables S1-S3.

The mass-based stoichiometric coefficient \( \alpha_i \) of species, \( i \), was constructed, as shown in Eq. S1, to calculate the gas-phase concentration (\( \mu \text{g m}^{-3} \) of air) of each lumping species, \( i \).

\[
\text{HCs + oxidants} \rightarrow \alpha_1S_1 + \alpha_2S_2 + \cdots + \alpha_8S_8 \\
+ \alpha_9S_9 + \alpha_{10}S_{10} + \cdots + \alpha_{16}S_{16} \\
\vdots \quad \vdots \quad \vdots \\
+ \alpha_{41}S_{41} + \alpha_{42}S_{42} + \cdots + \alpha_{48}S_{48} \\
+ \alpha_{49}S_{49} + \alpha_{50}S_{50} + \alpha_{51}S_{51} \\
= \sum_{i=1}^{51} \alpha_i S_i, \tag{S1}
\]

where HCs represents the mass concentration (\( \mu \text{g m}^{-3} \) of air) of the studied HCs, oxidants represent the atmospheric oxidants (e.g., OH radical, \( O_3 \), and \( NO_3 \)), \( \alpha_i \) represents the mass-base stoichiometric coefficient of species \( i \), and \( S_i \) represents the lumped species \( i \) produced by oxidation.

Based on the mass contribution of the oxygenated products to each lumping species, the atomic oxygen-to-carbon ratio (O:C) and the molecular weight (MW) for each lumping species are obtained by summing up the mass-weighted O:C and MW of each product in the corresponding lumping species.
Section S2. Estimation of the atomic oxygen-to-carbon ratio \( (O: C_i) \) and molecular weight \( (MW_i) \) for each lumping species

Due to the increase in complexity from parameterizing \( O: C_i \) and \( MW_i \) as a function of HC/NO\(_x\), we assume that the \( O: C_i \) and \( MW_i \) are linearly related to the NO\(_x\) level, which is ranging from HC/NO\(_x\)=2 (high NO\(_x\) level (H-NO\(_x\))) to HC/NO\(_x\)=14 (the low NO\(_x\) level (L-NO\(_x\))). The calculation of the \( O: C_i \) is exemplified in the following part in this Section.

Based on the simulations from the near-explicit gas kinetic model under the same metrological condition (6/19/2015), four sets of \( O: C_i \) are carried out under four conditions: \( O: C_{i\text{fresh\-H-NO}_x} (f_A=-7.6), O: C_{i\text{highly aged\-H-NO}_x} (f_A=-5.2), O: C_{i\text{fresh\-L-NO}_x} (f_A=-3.7) \), and \( O: C_{i\text{highly aged\-L-NO}_x} (f_A=-2.9) \), where the \( f_A \) is the aging factor, which is defined as shown in Eq. 1 in the manuscript. Thus, the fresh set of \( O: C_i (O: C_{i\text{fresh}}) \) under given NO\(_x\) conditions can be approached by the similar weighted average method (Section 3.2.2 in the manuscript) by combining the two sets of \( O: C_{i\text{fresh\-H-NO}_x} \) and \( O: C_{i\text{fresh\-L-NO}_x} \), as is shown in Eq. S2.

The fractional weighting factor \( (f_{NO_x}'): 0-1 \) is estimated by scaling the given HC/NO\(_x\) within the upper boundary (HC/NO\(_x\)=14) and the lower (HC/NO\(_x\)=2) boundary. Similarly, the highly aged set of \( O: C_i (O: C_{i\text{highly aged}}) \) can be obtained by combining \( O: C_{i\text{highly aged\-H-NO}_x} \) and \( O: C_{i\text{highly aged\-L-NO}_x} \) using \( f_{NO_x}' \), as shown in Eq. S3.

\[
O: C_{i\text{fresh}} = (1 - f_{NO_x}') \cdot O: C_{i\text{fresh\-H-NO}_x} + f_{NO_x}' \cdot O: C_{i\text{fresh\-L-NO}_x} \tag{S2}
\]

\[
O: C_{i\text{highly aged}} = (1 - f_{NO_x}') \cdot O: C_{i\text{highly aged\-H-NO}_x} + f_{NO_x}' \cdot O: C_{i\text{highly aged\-L-NO}_x} \tag{S3}
\]

Since the change of the \( O: C_i \) of the lumping species, \( i \), is due to the evolution of the gas-phase products, which is governed by the \( \alpha_i \), the dynamic \( O: C_i \) set can be simply estimated by comprising the \( O: C_{i\text{fresh}} \) and \( O: C_{i\text{highly aged}} \) using the fractional aging factor, \( f_A' \), as shown in Eq. S4 (same method in Eq. 2 in the manuscript).

\[
\text{dynamic } O: C_i = (1 - f_A') \cdot O: C_{i\text{fresh}} + (f_A') \cdot O: C_{i\text{highly aged}} \tag{S4}
\]

The calculation of the dynamic \( MW_i \) set follows the exact same method used for the dynamic \( O: C_i \) set. The dynamic \( O: C_i \) set and dynamic \( MW_i \) set are directly applied to estimate the activity coefficient of the organics in the inorganic (in) phase, as shown in Eq. 4 in the manuscript.
Section S3. Calculation of the activity coefficient in aqueous solutions containing electrolytes

As is described in Section 3.2 in the manuscript, 16 organic compounds (O:C ranging from 0.13 to 0.8) with various functional groups and molecular size (MW) were chosen to estimate the activity coefficient ($\gamma_{in,i}$) of the organics in the inorganic phase. The inorganic phase compositions (FS) and ambient humidity (RH) are ranged from 0.33 to 1 and 0.1 to 0.8, respectively, to cover our experimental conditions. The Aerosol Inorganic-Organic Mixtures Functional Groups Activity Coefficients (AIOMFAC) (Zuend et al., 2011) was run for the highest concentration of the 16 selected organic compounds, where $\gamma_{in,i}$ was as close to unity as possible in the inorganic SO$_4^{2-}$-NH$_4^+$-H$_2$O system. Thus, the resulting $\gamma_{in,i}$ was fit to the ln(RH), FS, O:C, and MW to generate the regression equation (Eq. 4 in the manuscript) for the relatively nonpolar compound (O:C < 0.8), as shown in Fig. S7. The resulting R$^2$ is 0.5742. For the $\gamma_{in,i}$ of the relatively polar compounds (O:C > 0.8), Eq. S5, which was generated by Beardsley and Jang (2016) for isoprene products, was applied.

$$\gamma_{in,i} = e^{0.050 \cdot \ln(100 \cdot RH) - 0.011 \cdot \text{org:sul} - 0.252 \cdot \text{O:C}_i + 0.007 \cdot \text{MW}_i - 0.229},$$  \hspace{1cm} (S5)

where org:sul represents the bulk organic-to-sulfate mass ratio.
Section S4. Measurement of aerosol acidity using the C-RUV technique

In the presence of organic matter (OM), the acidity (proton concentration: [H⁺], mol L⁻¹ of aerosol) reduction in acidic aerosols could be considered by two forces: (1) the neutralization with atmospheric ammonia and (2) the formation of alkyl substituted sulfates, which includes monoalkyl sulfates and dialkyl sulfates (diOS). Due to the strong acidity of monoalkyl sulfates, we only attributed the reductions in aerosol acidity and hygroscopicity to the formation of diOS. Using the inorganic concentrations measured by the PILS-IC, where organosulfate was reversed to sulfate ion due to high-temperatures (> 80 °C) water vapor, the proton concentration, which results only from ammonia neutralization, can be predicted through the inorganic thermodynamic model EAIM-II (Clegg and Seinfeld, 2006). The proton concentration, which was associated with both ammonia neutralization and diOS formation, was measured by colorimetry integrated with the reflectance UV-visible spectrometer (C-RUV) technique (Jang et al., 2008; Li et al., 2016; Li and Jang, 2012), which utilized a UV-visible spectrometer in absorbance mode to detect the color change on a sample-collected dyed filter. Thus, the difference between the two measured [H⁺] values is due to the formation of diOS. The reduction in sulfate concentration, which equalizes the PILS-IC measured [H⁺] to the C-RUV measured [H⁺], is the measured diOS concentration ([diOS]_{exp}). The C-RUV method has been previously applied to toluene and 1,3,5-trimethylbenzene SOAs (Im et al. (2014) and isoprene SOA (Beardsley and Jang (2016)).
Section S5. Derivation of the model equations used to predict the organic mass

The gas-organic phase partitioning coefficient ($K_{or,i}$, m$^3$ μg$^{-1}$) and the gas-inorganic phase partitioning coefficient ($K_{in,i}$, m$^3$ μg$^{-1}$) of each species are obtained from Eq. 3 in the manuscript. The concentrations ($C_{g,i}$, $C_{or,i}$, and $C_{in,i}$: μg m$^{-3}$ of air) of each lumping species in the gas ($g$), organic aerosol ($or$), and inorganic ($in$) phases can be derived from the Eqs. S6, S7, and S8, respectively. The partitioning and aerosol-phase reactions in the multiphase system ($g$, $or$, and $in$ phase) can be kinetically represented as shown in Fig. S8.

\[ C_{g,i} = \frac{C_{T,i}}{1 + K_{or,i} OM_T + K_{in,i} M_{in}} \]  \hspace{1cm} (S6)

\[ C_{or,i} = \frac{C_{T,i} K_{or,i} OM_T}{1 + K_{or,i} OM_T + K_{in,i} M_{in}} \] \hspace{1cm} (S7)

\[ C_{in,i} = \frac{C_{T,i} K_{in,i} M_{in}}{1 + K_{or,i} OM_T + K_{in,i} M_{in}} \] \hspace{1cm} (S8)

where the subscript $i$ represents the lumping species, $i$. $C_{T,i}$ is the total organics concentration in multiple phases (i.e., $C_{T,i} = C_{g,i} + C_{or,i} + C_{in,i}$). $OM_T$ and $M_{in}$ are the mass concentration (μg m$^{-3}$ of air) of the total organic matter and the total inorganic aerosol, respectively.

The formation of organic matter ($\Delta OM_{AR}$) through aerosol-phase reactions are described by two processes: (1) the oligomerization in $or$ phase and (2) the oligomerization in $in$ phase (i.e., acid-catalyzed reaction). The two reactions are described based on the second-order kinetic self-dimerization as shown in Eqs. S9 and S10.

\[ \frac{dC_{or,i}}{dt} = -k_{or,i} C_{or,i}^2 \left( \frac{MW_i OM_T}{\rho_{or} 10^3} \right), \] \hspace{1cm} (S9)

\[ \frac{dC_{in,i}}{dt} = -k_{AC,i} C_{in,i}^2 \left( \frac{MW_i M_{in}}{\rho_{in} 10^3} \right), \] \hspace{1cm} (S10)

where $C'_{or,i}$ and $C'_{in,i}$ are the aerosol-base organic concentration (mol L$^{-1}$) in $in$ phase and $or$ phase, respectively. $k_{or,i}$ and $k_{AC,i}$ are the second order reaction rate constant (L mol$^{-1}$ s$^{-1}$) for oligomerization in the $or$ phase and the $in$ phase, respectively. The conversion of the aerosol-base concentration ($C'_{or,i}$ and $C'_{in,i}$) (mol L$^{-1}$) to air-base concentration ($C_{or,i}$ and $C_{in,i}$) (μg m$^{-3}$) is fulfilled by the bracketed terms $\frac{MW_i OM_T}{\rho_{or} 10^3}$ and $\frac{MW_i M_{in}}{\rho_{in} 10^3}$, respectively. $MW_i$ is the molecular weight of species, $i$. $OM_T$ is the total organic matter (OM) concentration (μg m$^{-3}$). $\rho_{or}$ and $\rho_{in}$ are the densities (g cm$^{-3}$) of the $or$ phase aerosol and $in$ phase aerosol.
Based on the mass balance, $ΔOM_{AR}$ is same as the consumed total concentrations of lumping species (sum up of $C_{T,i}$ of each lumping species, $i$) as shown in the following equation.

$$ΔOM_{AR} = −∑_i ΔC_{T,i} = −∑_i \int dC_{T,i},$$  \hspace{2cm} (S11)

Thus, the following equations can be applied to kinetically express partitioning and in-particle chemistry processes of the lumping species.

$$\frac{dC_{g,i}}{dt} = k_{11}C_{or,i} − k_{12}C_{g,i} + k_{21}C_{in,i} − k_{22}C_{g,i},$$  \hspace{2cm} (S12)

$$\frac{dC_{or,i}}{dt} = −k_{11}C_{or,i} + k_{12}C_{g,i} − k_{31}C_{or,i} + k_{32}C_{in,i} − k_{0,i}C_{or,i}^2 \left(\frac{MW_iOM_T}{\rho_{or}10^3}\right),$$  \hspace{2cm} (S13)

$$\frac{dC_{in,i}}{dt} = −k_{21}C_{in,i} + k_{22}C_{in,i} + k_{31}C_{or,i} − k_{32}C_{in,i} − k_{AC,i}C_{in,i}^2 \left(\frac{MW_iM_{in}}{\rho_{in}10^3}\right),$$  \hspace{2cm} (S14)

where $k_{nm}$ is the first-order reaction rate constants ($S^{-1}$) ($n = 1, 2, 3; m = 1, 2$) in which each couple of them denotes the equilibrium among $C_{g,i}, C_{or,i}$ and $C_{in,i}$ as shown in Fig. S8.

From Eqs. S12–S14, $\frac{dC_{T,i}}{dt}$ can be rewritten as following,

$$\frac{dC_{T,i}}{dt} = \frac{dC_{g,i}}{dt} + \frac{dC_{or,i}}{dt} + \frac{dC_{in,i}}{dt} = −k_{0,i}C_{or,i}^2 \left(\frac{MW_iOM_T}{\rho_{or}10^3}\right) − k_{AC,i}C_{in,i}^2 \left(\frac{MW_iM_{in}}{\rho_{in}10^3}\right),$$  \hspace{2cm} (S15)

Eq. S15 can be rearranged with respect to $C_{T,i}$ by plugging Eqs. S7 and S8 as following.

$$\frac{dC_{T,i}}{dt} = \left(k_{0,i} \frac{\rho_{or}10^3OM_TK_{or,i}^2}{MW_i(1 + K_{or,i}OM_T + K_{in,i}M_{in})^2} + k_{AC,i} \frac{\rho_{in}10^3M_{in}K_{in,i}^2}{MW_i(1 + K_{or,i}OM_T + K_{in,i}M_{in})^2}\right)C_{T,i}^2,$$  \hspace{2cm} (S16)

Based on the assumption that $OM_T, M_{in}, k_{0,i}$, and $k_{AC,i}$ are constants during each computational time step, Eq. S16 can be solved as following by being integrated as a second-order differential equation.

$$ΔOM_{AR} = −∑_i ΔC_{T,i} = −∑_i \int_{t_0}^{t} (k_{0,i}\beta_{1,i} + k_{AC,i}\beta_{2,i})C_{T,i}dt,$$  \hspace{2cm} (S17)

where $\beta_{1,i} = \frac{\rho_{or}10^3OM_TK_{or,i}^2}{MW_i(1 + K_{or,i}OM_T + K_{in,i}M_{in})^2}$ and $\beta_{2,i} = \frac{\rho_{in}10^3M_{in}K_{in,i}^2}{MW_i(1 + K_{or,i}OM_T + K_{in,i}M_{in})^2}$ are the simplified terms associating with oligomerization in the $OR$ phase and the $IN$ phase, respectively. Hence, the analytical solution corresponding to $ΔOM_{AR}$ can be achieved as shown in the following equation.

$$ΔOM_{AR} = −∑_i ΔC_{T,i} = −∑_i \frac{C_{T,i}^2\Delta t(k_{0,i}\beta_{1,i} + k_{AC,i}\beta_{2,i})}{C_{T,i}^2\Delta t(k_{0,i}\beta_{1,i} + k_{AC,i}\beta_{2,i}) + 1},$$  \hspace{2cm} (S18)
Beardsley, R. L., and Jang, M.: Simulating the SOA formation of isoprene from partitioning and aerosol phase reactions in the presence of inorganics, Atmospheric Chemistry and Physics, 16, 5993-6009, 10.5194/acp-16-5993-2016, 2016.


Im, Y., Jang, M., and Beardsley, R. L.: Simulation of aromatic SOA formation using the lumping model integrated with explicit gas-phase kinetic mechanisms and aerosol-phase reactions, Atmospheric Chemistry and Physics, 14, 4013-4027, 10.5194/acp-14-4013-2014, 2014.


Zhao, L. W., Li, P., and Yalkowsky, S. H.: Predicting the entropy of boiling for organic compounds, J Chem Inf Comp Sci, 39, 1112-1116, Doi 10.1021/Ci990054w, 1999.

Table S1. Major oxygenated products distribution in gas phase for toluene oxidation under four conditions (i.e., high NO\textsubscript{x} fresh, low NO\textsubscript{x} fresh, high NO\textsubscript{x} aged, and low NO\textsubscript{x} aged). High NO\textsubscript{x}: HC/NO\textsubscript{x}=2; low NO\textsubscript{x}: HC/NO\textsubscript{x}=14.

<table>
<thead>
<tr>
<th>α\textsubscript{m,n}</th>
<th>Toluene: Vapor Pressure (mmHg) [n]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 1 (10\textsuperscript{-8})</td>
</tr>
<tr>
<td>R</td>
<td></td>
</tr>
<tr>
<td>VF</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>0.53/0.56</td>
</tr>
<tr>
<td>S</td>
<td>0.97/0.80</td>
</tr>
<tr>
<td>P</td>
<td>0.89/0.97</td>
</tr>
<tr>
<td>MA</td>
<td>0.28/0.65</td>
</tr>
</tbody>
</table>

The number in the cells denotes the mass fraction of the product to the lumping species under conditions of high NO\textsubscript{x} fresh, low NO\textsubscript{x} fresh, high NO\textsubscript{x} aged, and low NO\textsubscript{x} aged, respectively (from left to right, top to bottom). No number indicates the organic compound is the major contributor (mass fraction > 0.9) regardless of the NO\textsubscript{x} condition. Some of the trivial products were not listed.
Table S2. Major oxygenated products distribution in gas phase for ethylbenzene oxidation under four conditions (i.e., high NOₓ fresh, low NOₓ fresh, high NOₓ aged, and low NOₓ aged). High NOₓ: HC/NOₓ=2; low NOₓ: HC/NOₓ=14.

<table>
<thead>
<tr>
<th>α&lt;sub&gt;n&lt;/sub&gt;</th>
<th>Ethylbenzene: Vapor Pressure (mmHg) [n]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 1 (10⁻⁸)</td>
</tr>
<tr>
<td>R</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>VF</td>
<td><img src="image9" alt="Image" /></td>
</tr>
<tr>
<td>F</td>
<td><img src="image17" alt="Image" /></td>
</tr>
<tr>
<td>M</td>
<td><img src="image25" alt="Image" /></td>
</tr>
<tr>
<td>S</td>
<td><img src="image33" alt="Image" /></td>
</tr>
<tr>
<td>P</td>
<td><img src="image41" alt="Image" /></td>
</tr>
<tr>
<td>MA</td>
<td><img src="image49" alt="Image" /></td>
</tr>
</tbody>
</table>

The number in the cells denotes the mass fraction of the product to the lumping species under conditions of high NOₓ fresh, low NOₓ fresh, high NOₓ aged, and low NOₓ aged, respectively (from left to right, top to bottom). No number indicates the organic compound is the major contributor (mass fraction > 0.9) regardless of the NOₓ condition. Some of the trivial products were not listed.
Table S3. Major oxygenated products ocim in gas phase for n-propylbenzene under four conditions (i.e., high NOx fresh, low NOx fresh, high NOx aged, and low NOx aged). High NOx: HC/NOx=2; low NOx: HC/NOx=14.

<table>
<thead>
<tr>
<th>Reactivity [m]</th>
<th>Propylbenzene: Vapor Pressure (mmHg) [n]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 1 (10^8)</td>
</tr>
<tr>
<td>R</td>
<td></td>
</tr>
<tr>
<td>VF</td>
<td>0.00/0.87</td>
</tr>
<tr>
<td>F</td>
<td>0.00/0.88</td>
</tr>
<tr>
<td>M</td>
<td>0.59/0.00</td>
</tr>
<tr>
<td>S</td>
<td>0.00/0.89</td>
</tr>
<tr>
<td>P</td>
<td>0.00/0.28</td>
</tr>
<tr>
<td>MA</td>
<td></td>
</tr>
</tbody>
</table>

The number in the cells denotes the mass fraction of the product to the lumping species under conditions of high NOx, fresh, low NOx, fresh, high NOx, aged, and low NOx, aged, respectively (from left to right, top to bottom). No number indicates the organic compound is the major contributor (mass fraction > 0.9) regardless of the NOx condition. Some of the trivial products were not listed.
Figure S1: Time profiles of experimental measurements and simulation for three different hydrocarbons (HC): (a) toluene (Tol), (b) ethylbenzene (EB), and (c) n-propylbenzene (PB), along with $O_3$, $NO_2$, and NO concentration. The experimental conditions are available in Table 1.
Figure S2: The mass-based stoichiometric coefficients ($\alpha_i$) of each species, $i$, from ethylbenzene oxidation under low NO$_x$ level (simulation based on the sunlight of Exp. Tol9, 06/14/18) at (a) fresh condition and (b) highly aged condition, and under high NO$_x$ level at (c) fresh condition and (d) highly aged condition, where $f_A$ is the aging factor as derived in Eq. 1. The oxygenated products predicted by the explicit gas kinetic model are lumped as a function of vapor pressure (8 groups: $10^{-8}$, $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$, and 1 mmHg) and aerosol phase reactivity (6 groups), i.e., very fast (VF: tricarbonyls and $\alpha$-hydroxybicarboxyls), fast (F: 2 epoxides or aldehydes), medium (M: 1 epoxide or aldehyde), slow (S: ketones), partitioning only (P), and multialcohol (MA). MGLY (methylglyoxal) and GLY (glyoxal) were lumped separately due to the relatively high reactivity.
Figure S3: The mass-based stoichiometric coefficients ($\alpha_i$) of each species, $i$, from n-propylbenzene oxidation under low NO$_x$ level (simulation based on the sunlight of Exp. Tol9, 06/14/18) at (a) fresh condition and (b) highly aged condition, and under high NO$_x$ level at (c) fresh condition and (d) highly aged condition, where $f_A$ is the aging factor as derived in Eq. 1. The oxygenated products predicted by the explicit gas kinetic model are lumped as a function of vapor pressure (8 groups: $10^{-8}$, $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$, and 1 mmHg) and aerosol phase reactivity (6 groups), i.e., very fast (VF: tricarbonyls and $\alpha$-hydroxybicarbonyls), fast (F: 2 epoxides or aldehydes, ), medium (M: 1 epoxide or aldehyde), slow (S: ketones), partitioning only (P), and multialcohol (MA). MGLY (methylglyoxal) and GLY (glyoxal) were lumped separately due to the relatively high reactivity.
Figure S4: Simulated (a) ethylbenzene and (b) n-propylbenzene SOA yields ($Y_{SOA} = \Delta OM/\Delta HC$) as a function of relative humidity (RH: 0.1 ~ 0.9) and fractional free sulfate (FFS: 0 ~ 1), where $FFS = ([SO_4^{2-}] - 0.5[NH_4^+]) / [SO_4^{2-}]$ and is used to estimate aerosol acidity ($[H^+]$) in inorganic thermodynamic model. The RH and FFS are fixed during the simulations. The gas-phase simulations are based on the experimental condition of 06/14/2018 (Exp. Tol9 in Table 1) (initial HC concentration = 20 ppb, HC/NOx = 2, sulfate mass concentration = 20 µg/m³, and the mass ratio of the consumed HC to sulfate (ΔHC:sulf) for ethylbenzene and propylbenzene = 1.8 and 1.2).
Figure S5: Time profiles of measured and modeled SOA mass concentrations for toluene (Tol: a-e), ethylbenzene (EB: f-h), and n-propylbenzene (PB: i-k) SOA under various NO$_x$ levels in the presence/absence of inorganic seeded aerosol. The red, green, and blue colors indicate experiments with sulfuric acid seed, without inorganic seed, and with ammonium sulfate seed, respectively. SA denotes the direct-SA injection experiment. “wet” or “dry” in the figure denotes the physical state of the inorganic seed. Solid, dashed, and dotted lines denote total OM (OM$_T$), the OM from partitioning only (OM$_P$), and the OM from the aerosol-phase reactions (OM$_{AR}$), respectively. The uncertainty associated with experimentally measured OM
is 9 %, which is estimated from the uncertainties of measured OC and correction of particle wall loss. The experimental conditions are available in Table 1 in the manuscript.
Fig. S6: Prediction of model uncertainty (simulated SOA mass deviated from the baseline SOA mass) due to the variation of major model parameters. The simulations employ the experiment performed on 06/14/2018 (Exp. Tol9 in Table 1). The estimated errors associated with vapor pressure ($V_p$), enthalpy of vaporization ($\Delta H_{vap}$), activity coefficients of the organics in the inorganic phase ($\gamma_{in,i}$) and oligomerization reaction rate constants in the inorganic phase ($k_{AC,i}$) were predicted with increasing/decreasing $V_p$, $\Delta H_{vap}$, $\gamma_{in,i}$, and $k_{AC,i}$ by factors of 1.5, 1.1, 1.5, and 2, respectively.
Figure S7: The $\gamma_{in,i}$ predicted by AIOMFAC were plotted against the $\gamma_{in,i}$ predicted by the regressions in Eq. 4 in the manuscript along with the line of $y = x$. $R^2$ is shown in the figure.
Figure S8. Simplified kinetic scheme for Fig. 1 in the manuscript for the products partitioning and aerosol-phase oligomerization in the UNIPAR model.