



Supplement of

Simulating the SOA formation of isoprene from partitioning and aerosol phase reactions in the presence of inorganics

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Section S1: Gas phase simulations and lumping

Gas phase oxidation. The Master Chemical Mechanism v3.2 (Saunders et al., 1997, 2003) was employed within the Morpho Kinetc Solver (Jeffries, H.E. et al., 1998) to simulate isoprene photooxidation for the range of VOC/NO_x shown in Table S1. The simulations were run using the temperature (T), relative humidity (RH) and total ultra-violet radiation (UV) data measured on 23 April 2014 measured in the UF APHOR chamber (Figure S1). Then, the predicted gas phase concentrations of each species at the maximum HO₂/NO were used for lumping as a function of VOC/NO_x.

Table S1. Concentrations of isoprene and NO_x used in gas phase photooxidation simulations of isoprene used in lumping as a function of VOC/NO_x

ISO (ppb)	500	500	500	500	500	500	500	500	500	500	500
NOx (ppb)	25	40	50	75	100	150	200	300	400	500	625
VOC/NOx	100	62.5	50	33.33	25	16.67	12.5	8.33	6.25	5	4



Figure S1. Time profile of relative humidity, temperature, and total ultra-violet radiation measured in the UF-APHOR chambers on 23 April 2014.

MCM and Morpho were also used to provide the Δ ISO required by UNIPAR for each experimental simulation. It was determined that the MCM is reasonably representative of the actual

photooxidation by comparing the measured and predicted concentrations of isoprene, NO, NO₂ and O₃ in each experiment. Figure S2 shows the measured and modeled concentrations from the east chamber of experiment A on 27 January 2015 as an example. The major discrepancies in each simulation occur between the model and experimental values for O₃ and NO₂ as can be seen in Fig. S2. MCM predicts a higher O₃ concentration than reality and that it forms more quickly. On the other hand, while the predicted and measured peak NO₂ match reasonably well the measured NO₂ is higher than the predicted late in the experiment. This is likely due to organonitrates being detected as NO₂ by the chemiluminescence NO_x analyzer.



Figure S2. Time profile of the measured and predicted isoprene, NO, NO₂, and O₃ from 27 January, 2015 in the east UF-APHOR chamber.

Lumping. As is described in detail in Sect. 3.1, the products from MCM are lumped based on their vapor pressure and reactivity in aerosol phase reactions. Figure S3 shows the product of highest concentration in each lumping group when VOC/NO_x is 25. The empty groups are those for which isoprene has no photooxidation products.

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Figure S3. The lumping structure of UNIPAR filled with the product of highest concentration in each lumping group at a VOC/NO_x of 25. Empty bins represent lumping groups for which isoprene has no photooxidation products.

Section S2: Estimation of aerosol acidity([H⁺])

In UNIPAR, the aerosol liquid water content (LWC) and acidity ([H⁺], mol L⁻¹ aerosol) are predicted using the inorganic thermodynamic model E-AIM II (Clegg et al., 1998) as a function of the concentrations of sulfate ($C_{SO_4^{2-}}$, µmol m⁻³) and ammonium($C_{NH_4^+}$, µmol m⁻³), corrected for

the ammonia rich condition based on the results of Li and Jang (2012). Since isoprene are SHMP SOA, the interaction of organics and inorganics in the mixed phase may influence the dissociation of inorganic acids potentially leading to large deviations from the predicted [H⁺]. AIOMFAC was employed to determine whether not this influence is significant. Table S2 shows the fractional dissociation of H_2SO_4 in the presence of varying amounts of tetrol and hexane, which represent polar and non-polar organic species. Although there is a reduction in the dissociation of sulfuric acid due to the presence of both tetrol and hexane, the maximum percent difference in these simulations is less than 12%. Based on these results, it was assumed that protonation is not significantly impacted by the presence of organics, and the [H⁺] predicted by the inorganic composition is simply diluted by the concentration of organics in each time step. This assumption introduces uncertainty into the prediction of aerosol phase reactions, but there is not currently an approach with little uncertainty to predict [H⁺] of mixed inorganic/organic aerosol composed of a large number of species.

Table S2. Output from AIOMFAC simulations performed to determine the impact of the presence
of organics on the protonation of sulfuric acid. Tetrol and hexane were used to represent polar and
non-polar organics.

organic	RH(%)	Xorg	Хн+	X _{SO4}	X _{HSO4}	H/(H+SO4+HSO4)
tetrol	46.35	0.000	0.150	0.039	0.072	0.575
tetrol	44.04	0.194	0.120	0.005	0.110	0.510
tetrol	47.66	0.114	0.125	0.011	0.103	0.523
tetrol	20.06	0.000	0.202	0.042	0.118	0.558
tetrol	20.51	0.366	0.169	0.003	0.164	0.504
tetrol	19.71	0.204	0.216	0.012	0.192	0.514
hexane	49.98	0.000	0.143	0.038	0.067	0.577
hexane	51.98	0.210	0.125	0.018	0.090	0.538
hexane	50.97	0.089	0.114	0.026	0.063	0.563
hexane	20.06	0.000	0.202	0.042	0.118	0.558
hexane	21.05	0.204	0.203	0.008	0.187	0.510
hexane	22.56	0.382	0.185	0.022	0.141	0.531

Section S3. Derivation of the model equations used to predict the organic mass from aerosol phase reactions (OM_{AR})

In modeling isoprene SOA formation in the presence of a SHMP aerosol, the total concentration ($C_{T,i}$, µg m⁻³ of air) of each lumping species ($i_{m,n}$) is split solely between $C_{g,i}$ and $C_{mix,i}$ (Eq. S1) by a single gas-particle partitioning coefficient, $K_{mix,i}$ (m³µg⁻¹),

$$C_{T,i} = C_{g,i} + C_{mix,i}, \tag{S1}$$

$$K_{mix,i} = \frac{C_{mix,i}}{C_{g,i}M_{mix}},$$
(S2)

where M_{mix} is the mass of the total suspended matter and is the sum of the inorganic mass (M_{in}) and the total organic mass (OM_T).

 $C_{mix,i}$ and $C_{g,i}$ can be determined by combining Eq. S3 and Eq. S4 as follows,

$$C_{mix,i} = C_{T,i} \left(\frac{K_{mix,i} M_{mix}}{1 + K_{mix,i} M_{mix}} \right)$$
(S3)

$$C_{g,i} = C_{T,i} \left(\frac{1}{1 + K_{mix,i} M_{mix}} \right)$$
(S4)

Calculation of $K_{mix,i}$ (Eq. S5) follows the gas-particle absorption model (Pankow, 1994).

$$K_{mix,i} = \frac{7.501 \,\mathrm{RT}}{10^9 \,MW_{mix} \gamma_{mix,i} \,p_{L,i}^o},\tag{S5}$$

where *R* is the gas constant (8.314 J K⁻¹ mol⁻¹), *T* is the temperature (K), MW_{mix} is the average molecular weight (g mol⁻¹) of the SHMP aerosol, $\gamma_{mix,i}$ is the activity coefficient of the lumping species in the SHMP aerosol, and $p^{o}_{L,i}$ is the sub-cooled liquid vapor pressure (mmHg) of $i_{m,n}$.

Once $C_{mix,i}$ is determined for each Δt , the OM_{AR} formation of $i_{m,n}$ is estimated in UNIPAR assuming a second-order self-dimerization reaction as is shown in Eq. S6,

$$\frac{dC'_{mix,i}}{dt} = -k_{AR,i}C'_{mix,i}^{2}.$$

where $C_{mix,i}$ is the aerosol phase concentration of $i_{m,n}$ in mol L⁻¹ of medium and $k_{AR,i}$ (L mol⁻¹ s⁻¹) is the aerosol phase reaction rate of each $i_{m,n}$. $k_{AR,i}$ (Eq. S7) is calculated each time step using the semiempirical model developed by Jang et al. (2005) as a function of the reactivity, *R* (VF, F, M, S; Sect. 3.1), and pK_{BH+} of $i_{m,n}$ in the aerosol phase, [H⁺] and LWC (activity of water, a_w) from the inorganic thermodynamic model (Sect. 3.2), and the excess acidity, *X* (Im et al., 2014; Jang et al., 2006).



$$k_{AR,i} = 10^{(0.0005^* pK_{BH^+} + y^*X + 1.3^*R + \log(a_w) + \log([H^+]) - 5.5)}$$
(S7)

Then by assuming that OM_{AR} is non-volatile and irreversible, $\Delta OM_{AR,i}$ can be calculated as the reduction in $C_{T,i}$ for each time step (Eq. S8),

$$\Delta OM_{AR} = -\sum_{i} \Delta C_{T,i} = -\sum_{i} \int \frac{dC_{T,i}}{dt}.$$
(S8)

Where,

$$\frac{dC_{T,i}}{dt} = \frac{dC_{g,i}}{dt} + \frac{dC_{mix,i}}{dt}$$
(S9)

$$\frac{dC_{g,i}}{dt} = k_2 C_{mix,i} - k_1 C_{g,i}$$
(S10)

$$\frac{dC_{mix,i}}{dt} = k_1 C_{g,i} - k_2 C_{mix,i} - k_{AR,i} C_{mix,i}^2 f_{mix,i}$$
(S11)

$$\frac{dC_{T,i}}{dt} = k_2 C_{mix,i} - k_1 C_{g,i} + k_1 C_{g,i} - k_2 C_{mix,i} - k_{AR,i} C_{mix,i}^2 f_{mix,i}$$
(S12)

$$\frac{dC_{T,i}}{dt} = -k_{AR,i}C_{mix,i}{}^2 f_{mix,i}$$
(S13)

 $C_{mix,i}$ is the concentration in $\mu g/m^3$ and $C_{mix,i}$ is the aerosol phase concentration of $i_{m,n}$ in mol L⁻¹ of aerosol. $f_{mix,i}$ is the conversion factor from $C_{mix,i}$ to $C_{mix,i}$

$$C_{mix,i} = C_{T,i} \left(\frac{K_{mix,i} M_{mix}}{1 + K_{mix,i} M_{mix}} \right) \text{ and } f_{mix,i} = \frac{C_{mix,i}}{C'_{mixi}} = \left(\frac{MW_i * M_{mix}}{\rho_{mix} 10^3} \right)$$
(S14)

$$\frac{dC_{T,i}}{dt} = -k_{AR,i}C_{T,i}^2 \left(\frac{K_{mix,i}M_{mix}}{1+K_{mix,i}M_{mix}}\right)^2 \left(\frac{MW_i * M_{mix}}{\rho_{mix}10^3}\right)$$
(S15)

Then, combining equations S8 and S15 and solving the second-order ODE provides the analytical solution utilized in UNIPAR (Eq. S16),

$$\Delta OM_{AR} = -\sum_{i} \frac{k_{AR,i} \beta_{3,i} C_{T,i}^2 \Delta t}{1 + k_{AR,i} \beta_{3,i} C_{T,i} \Delta t},$$
(S16)

where $\beta_{3,i}$ is equal to

$$\beta_{3,i} = \frac{K_{mix,i}^2 M_{mix} \rho_{mix} 10^3}{M W_i (1 + K_{mix,i} M_{mix})^2}.$$
(S17)

Section S4: Prediction of the activity coefficients of organic species in SHMP isoprene SOA

As is described in Sect 3.3 of the manuscript, the non-ideality of each lumping species in the SHMP aerosol is accounted for by the acitivity coefficient $\gamma_{mix,i}$. $\gamma_{mix,i}$ will vary between each species due to differences in polarity and molar volume, and over time due to changes in aerosol phase composition. In order to estimate $\gamma_{mix,i}$ for the lumped isoprene photooxidation products,



Figure S4. The $\gamma_{mix,i}$ predicted by AIOMFAC plotted against the $\gamma_{mix,i}$ predicted by the regressions in Eq. S18 and S19 along with a y=x line and the R².

AIOMFAC was run for the highest concentration product of each lumping group in the presence of a mixed isoprene SOA-ammonium sulfate aerosol with the SOA composition based on the results of Nguyen et al. (2011). The bulk organic to sulfur mass ratio (org:sulf), concentration of i, and RH were varied to cover the range of experimental values. The resulting $\gamma_{mix,i}$ were fit to the bulk org:sulf, ln(RH), the oxygen to carbon molar ratio (O:C_i) of i and molar volume($V_{mol,i}$) of i for two ranges of O:C. The parameterizations are shown in equations S18 and S19 below.

$O:C \le 0.8$

$$\ln(\gamma_{mixi}) = 2.354 + 0.146 * \ln(RH) + 0.128 * org : sulf - 3.195 * O:C$$
(S18)

O:C > 0.8

$$\ln(\gamma_{mixi}) = -0.229 + 0.050 * \ln(RH) - 0.011 * org : sulf - 0.252 * O : C + 0.007 * V_{moli}$$
(S19)

The regressions for $\gamma_{mix,i}$ have R^2 of 0.72 and 0.46 for O:C less than or equal to 0.8 and greater than 0.8, respectively, as is shown in Figure S4. The polar compounds used in fitting Eq S18 have AIOMFAC predicted $\gamma_{mix,i}$ that range from 0.5 to 5.5, while those of O:C greater than 0.8 only range from 0.5 to 1.5. The small range of $\gamma_{mix,i}$ for Eq. S14 leads to higher residuals and a lower R^2 , but all of the values predicted by AIOMFAC and the regressions generated are close to unity minimizing the impact of error on model output.

Section S5. Concentration of isoprene SOA products as a function of VOC/NO_x

In both the simulated and experimental SOA formation of isoprene, there is an increase in SOA yield with increasing NO_x (decreasing VOC/NO_x), and the influence of NOx is stronger in the presence of acidity. The mass stoichiometric coefficients of products that contribute significantly to the simulated isoprene SOA are shown in Figure S5 below. The stochiometric coefficients are



Figure S5. The stoichiometric mass coefficients $(\alpha_{m,n})$ of selected products which contribute significantly to isoprene SOA as a function of VOC/NO_x.

calculated using simulations based on the Master Chemical Mechanism within the Morpho Kinetc Solver (Sect. S1). As can be seen, all of the products are lower in concentration with a reduction in NOx under the conditions of this study (VOC/NO_x: 10 to 100). The reduction in products that are highly reactive in aerosol phase reactions, such as glyoxal (6F, in Figure S5) explains the increased sensitivity to VOC/NO_x in the presence of acidic seed.

Section S6. Model Sensitivity and Uncertainity

In order to determine the impact of the uncertainty of the underlying modules and parameterizations applied in UNIPAR, sensitivity tests were performed in which vapor pressure $(p^{o}_{L,i})$, enthalpy of vaporization (ΔH_{vap}) , activity coefficient of i in the SHMP aerosol $(\gamma_{mix,i})$, and the aerosol phase reaction rate of i $(k_{AR,i})$ were increased and decreased by a factor chosen to exceed

the possible error of the method. After applying the factors, simulations of Exp. SA1 were performed and the resulting percent change in OM_T is shown in Figure S5.



Sensitivity of simulated OM_T to variations in selected model parameters

Figure S6. The percent change in the model predicted OM_T from experiment SA1 after each parameter was increased and decreased by a factor chosen to exceed the uncertainty of the underlying methods used for estimating each variable.

Section S7. Product structures of 3OS_p-M

In the absence of inorganic aqueous phase, 70% of the total organic mass is predicted to be from lumping group $3OS_p$ -M, which is comprised almost entirely of the organic peroxides, with the MCM products C510OOH (~40%), C57OOH (~27%), C58OOH(~15%) and HMACROOH(11%) making up approximately 93% (structures shown in Fig. S7)



Figure S7. The structures of the organic peroxides that comprise lumping group 3OS_p-M.

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