Supplementary Materials

for

Role of ozone in SOA formation from alkane photooxidation

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1. Particle wall loss corrections

Two limiting assumptions can be made for the interactions between particles on the wall and suspended vapor: 1) particles deposited on the wall are assumed to interact with the suspended vapors as if they had remained suspended and 2) particles deposited on the wall are assumed to cease interaction with the suspended vapors. The first assumption gives the upper bound limit on SOA mass concentration. To invoke this assumption, one applies the time-dependent organic to sulfate ratio measured by AMS to the seed volume concentration measured by DMA. We do not usually use this assumption considering the fact that the presence of organics enhances the collection efficiency of sulfates in AMS. The second assumption is applied in the present study. In this case, particles deposited on the wall remain the same size and do not undergo continued organic growth. In order to calculate the total particle mass lost on the wall as a function of time, the size-dependent particle wall loss rate parameter (β) needs to be determined. Wall loss calibration experiments were carried out by atomizing 1.0 M and 0.015 M ammonium sulfate solution ($(NH_4)_2SO_4$) into the chamber and monitoring the decay of particle number distribution using a DMA. The size dependent wall loss rate paramter (β) can be obtained by fitting equation S1 to the data for pure wall loss:

$$n_{i,s} = n_{i,0} \times \exp(-\beta t) \qquad \text{(Equ S1)}$$

where $n_{i,s}$ is the suspended particle number distribution in size bin i at time t, and $n_{i,0}$ is the initial particle number distribution in size bin i. The β values so derived were then applied to the C_{12} alkane chamber experiments. For each size bin i at each time step j, particle number distribution deposited to the wall ($n_{w,i,j}$) is calculated as:

$$n_{w,i,j} = n_{s,i,j} \times [1 - \exp(-\beta \Delta t)] \qquad \text{(Equ S2)}$$

where $n_{s,i,j}$ is the suspended particle number distribution in size bin i at time step j, and Δt is the difference between time step j and time step $j + 1$. The deposited particle size distribution ($n_{w,i,j}$) is added to the suspended particle size distribution ($n_{s,i,j}$) to give the total particle distribution ($n_{tot,i,j}$):

$$n_{tot,i,j} = n_{w,i,j} + n_{s,i,j} \qquad \text{(Equ S3)}$$

The total number concentration in size bin i at time step j ($N_{tot,i,j}$) can be calculated by converting the size distribution based on $d(lnD_p)$ to $d(D_p)$:

$$N_{tot,i,j} = n_{tot,i,j} / D_{p,i}\, ln10 \times (D_{p,i+} - D_{p,i-}) \qquad \text{(Equ S4)}$$

where $D_{p,i}$ is the median particle diameter for size bin i, $D_{p,i+}$ is the upper limit of particle diameter for size bin i, and $D_{p,i-}$ is the lower limit of particle diameter for size bin i. Assuming spherical particles, the total volume concentration at time step j ($V_{tot,j}$) is:

$$V_{tot,j} = \sum_{i}^{m} \frac{\pi}{6} D_{p,i}^{3} \times N_{tot,i,j} \qquad \text{(Equ S5)}$$

The total organic mass growth ($\Delta M_{o,j}$) at time step j is:

$$\Delta M_{o,j} = \rho \, (V_{tot,j} - V_{seed}) \qquad \text{(Equ S6)}$$

where ρ, the density for a specific C_{12} alkane SOA under high- or low- NO_x conditions, is obtained from seed free nucleation experiments.

2. HR-ToF-AMS data processing protocols

All AMS data were processed with "Squirrel", the Tof-AMS Unit Resolution Anylysis Toolkit (http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index. html), in Igor Pro Version 6.22A (Wavemetrics, Lake Oswego, OR). The ToF-AMS High Resolution Analysis software tool PIKA (Peak Integration by Key Analysis) was employed for high-resolution analysis (Decarlo et al., 2006). The interference of chamber air on the particulate spectrum was corrected by adjusting parameters in the fragmentation table based on the "filter run" (AMS is colleting chamber air with a particle filter in-line) before each alkane photooxidation experiment (Chhabra et al., 2010; Craven et al., 2012). Briefly, the ion CO_2^+ signal from ambient CO_2, which is estimated to be 370 ppm in the chamber, is removed to determine the organic contribution of CO_2^+ to m/z 44. The ion CO^+ (m/z 28), which is considered to be a common fragment of organic species, can be overwhelmed by ion N_2^+ signal derived from ambient N_2. In this study, we used the particle-phase ratio of CO^+/CO_2^+ to be unity as the default value to calculate the contribution of CO^+ to the total organic signal. We also checked W-mode, which has higher resolution than V-mode, to separate the CO^+ signal from N_2^+ signal. The $C_2H_4^+$ ion signal was removed because of its interference with the N_2^+ signal. The signals from H_2O^+, OH^+, and O^+ can be biased by water from both gas and particle phase. We use fragmentation table parameters in Aiken et al. (2008) to estimate the organic contributions (H_2O^+ = 22.5%, OH^+ = 5.625, and O^+ = 0.9%).

Table S1. O_x, NO_x, and HO_x reactions incorporated in the photochemical model

Reaction	Reactants	Products	Rate Constants ($cm^3\ molec^{-1}\ s^{-1}$)	References
1	$NO_2 + hv$	$NO + O$	See Table S3	a
2	$O + O_2 + M$	$O_3 + M$	See Table S2	a
3	$O_3 + NO$	$NO_2 + O_2$	3.0E-12 × EXP (-1500/TEMP)	a
4	$O_3 + NO_2$	$NO_3 + O_2$	1.2E-13 × EXP (-2450/TEMP)	a
5	$NO_3 + hv$	$NO_2 + O$	See Table S3	a
6	$NO_3 + hv$	$NO + O_2$	See Table S3	a
7	$NO + NO_3$	$2NO_2$	1.5E-11 × EXP (170/TEMP)	a
8	$NO_2 + NO_3$	$NO + NO_2 + O_2$	4.5E-14 × EXP (-1258/TEMP)	a
9	$NO_2 + NO_3 + M$	$N_2O_5 + M$	See Table S2	a
10	N_2O_5	$NO_2 + NO_3$	See notes [b]	a
11	$N_2O_5 + hv$	$NO_2 + NO_3$	See Table S3	a
12	$O_3 + hv$	$O + O_2$	See Table S3	a
13	$O_3 + hv$	$O(^1D) + O_2$	See Table S3	a
14	$O(^1D) + N_2$	$O + N_2$	2.2E-11 × EXP (110/TEMP)	a
15	$O(^1D) + O_2$	$O + O_2$	3.3E-11 × EXP (55/TEMP)	a
16	$O(^1D) + H_2O$	$2\ OH$	1.6E-10 × EXP (60/TEMP)	a
17	$O + O_3$	$2\ O_2$	8.0E-12 × EXP (-2060/TEMP)	a
18	$O + NO + M$	$NO_2 + M$	See Table S2	a
19	$O + NO_2$	$NO + O_2$	5.6E-12 × EXP (180/TEMP)	a
20	$O + NO_2 + M$	$NO_3 + M$	See Table S2	a
21	$O + NO_3$	$NO_2 + O_2$	1.0E-11	a
22	$HO_2 + HO_2$	$H_2O_2 + O_2$	3.0E-13 × EXP (460/TEMP)	a
23	$HO_2 + HO_2 + M$	$H_2O_2 + O_2 + M$	2.1E-33 × EXP (920/TEMP) × [M]	a
24	$H_2O_2 + hv$	$2OH$	See Table S3	a
25	$HO_2 + O_3$	$OH + 2O_2$	1.0E-14 × EXP (-490/TEMP)	a
26	$HO_2 + NO$	$OH + NO_2$	3.3E-12 × EXP (270/TEMP)	a
27	$OH + OH + M$	$H_2O_2 + M$	See Table S2	a
28	$OH + OH$	$O + H_2O$	1.8E-12	a
29	$OH + HO_2$	$H_2O + O_2$	4.8E-11 × EXP (250/TEMP)	a
30	$OH + O_3$	$HO_2 + O_2$	1.7E-12 × EXP (-940/TEMP)	a
31	$OH + NO + M$	$HONO + M$	See Table S2	a
32	$OH + NO_2 + M$	$HNO_3 + M$	See Table S2	a
33	$HONO + hv$	$OH + NO$	See Table S3	a

34	OH + HONO	$NO_2 + H_2O$	1.8E-11 × EXP (-390/TEMP)	a
35	$OH + HNO_3$	$NO_3 + H_2O$	See Notes [c]	a
36	$OH + H_2O_2$	$HO_2 + H_2O$	2.9E-11 × EXP (-161/TEMP)	a
37	$OH + NO_3$	$HO_2 + NO_2$	2.2E-11	a
38	$HO_2 + NO_3$	$OH + NO_2 + O_2$	3.5E-12	a
39	$HO_2 + NO_2 + M$	$HNO_4 + M$	See Table S2	a
40	HNO_4	$HO_2 + NO_2$	See Notes [d]	a
41	$HNO_4 + OH$	$NO_2 + H_2O + O_2$	1.3E-12 × EXP (380/TEMP)	a
42	$NO_3 + NO_3$	$2NO_2 + O_2$	8.5E-13 × EXP (-2450/TEMP)	a

[a] Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., J., K. M., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 17. JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov, 2011.

[b] For Reaction No. 10, the reaction rate constant $k\_{R10} = k\_{R9}$ / Keq, where Keq = 2.7E-27 × EXP (11000/TEMP).

[c] For Reaction No. 35, the reaction rate constant $k\_{R35} = k_1 + k_3 \times M/(1+k_3/k_2 \times M)$, where k_1 = 2.4E-14 × EXP (460/TEMP); k_2 = 2.7E-17 × EXP (2199/TEMP); and k_3 = 6.5E-34 × EXP (1335/TEMP).

[d] For Reaction No. 40, the reaction rate constant $k\_{R40} = k\_{R39}$ / Keq, where Keq = 2.1E-27 × EXP (10900/TEMP).

Table S2. Termolecular reaction rate constant calculations

Reaction	k_0^{300}	n	k_{inf}^{300}	m	F
$O + O_2 + M \rightarrow O_3 + M$	6.0E-34	2.3	—	—	0.6
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	2.0E-30	4.4	1.4E-12	0.7	0.6
$O + NO + M \rightarrow NO_2 + M$	9.0E-31	1.5	3.0E-11	0.0	0.6
$O + NO_2 + M \rightarrow NO_3 + M$	2.5E-31	1.8	2.2E-11	0.7	0.6
$OH + OH + M \rightarrow H_2O_2 + M$	6.9E-31	1.0	2.6E-11	0.0	0.6
$OH + NO + M \rightarrow HONO + M$	7.0E-31	2.6	3.6E-11	0.1	0.6
$OH + NO_2 + M \rightarrow HNO_3 + M$	2.0E-30	3.0	2.5E-11	0.0	0.6
$HO_2 + NO_2 + M \rightarrow HNO_4 + M$	2.0E-31	3.4	2.9E-12	1.1	0.6

Reaction rate constants are given in the form

$$k_0(T)=k_0^{300}\left(\frac{T}{300}\right)^{-n}\ \mathrm{cm^6 molecules^{-2} s^{-1}}$$

$$k_\infty(T)=k_\infty^{300}\left(\frac{T}{300}\right)^{-m}\ \mathrm{cm^3 molecules^{-1} s^{-1}}$$

To obtain the effective second-order rate constant at a given temperature and pressure (altitude z) the following formula is used:

$$k(T, z)=\left\{\frac{k_0(T)[M]}{1+(k_0(T)[M]/k_\infty(T))}\right\}F^{\{1+[\log_{10}(k_0(T)[M]/k_\infty(T))]^2\}^{-1}}$$

Table S3. Photolysis rate constants in Caltech Environmental Chamber

Photolysis Reactions	Value of j (s^{-1}) [a]
$NO_2 + hv \rightarrow NO + O$	4.629E-3
$NO_3 + hv \rightarrow NO_2 + O$	2.109E-3
$NO_3 + hv \rightarrow NO + O_2$	3.863E-5
$N_2O_5 + hv \rightarrow NO_2 + NO_3$	2.286E-5
$O_3 + hv \rightarrow O + O_2$	7.102E-6
$O_3 + hv \rightarrow O(^1D) + O_2$	5.078E-6
$H_2O_2 + hv \rightarrow 2OH$	4.660E-6
$HONO + hv \rightarrow OH + NO$	1.130E-3

[a] Photolysis rate constants are calculated using the irradiance spectrum measured for the chamber UV lights and absorption cross section values and quantum yields from Sander et al. (2011).