Supporting information

Physical State and Acidity Inorganic Sulfate Can Regulate the Production of Secondary Organic Material from Isoprene Photooxidation Products

by

Mikinori Kuwata[†,§], Yingjun Liu[†], Karena McKinney[†], and Scot T. Martin[†,*]

† School of Engineering and Applied Sciences & Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA 02138

§ Now at Division of Earth Sciences, Nanyang Technological University, Singapore, and Earth Observatory of Singapore

E-mail: scot_martin@harvard.edu

http://www.seas.harvard.edu/environmental-chemistry

Submitted: December 4, 2014

Physical Chemistry and Chemical Physics

*To Whom Correspondence Should be Addressed

AMS data analysis

High-resolution data were used to update the fragmentation table for both sulfate and ammonium to evaluate mass concentrations more precisely. The accurate evaluation of inorganic signals was also important for updating the fragmentation table of organic ions because their contribution was calculated by subtracting inorganic signals from total signal intensity. In the case of the organic signals, the fragmentation table was updated for *m*/*z* 18, 28, 30, 39, 40, 46, 48, 64, 65, 80, 81, and 98 (TableS1). The correction for water peaks at *m*/*z* 18 was estimated as described ref 1. Briefly, the intensity from water peaks related to organic compounds was estimated by subtracting contributions of sulfate ions from total signal. The experiments were conducted for dry conditions, meaning that the contributions from water in the gas and particle phases were negligible. The obtained water signals originated from organic compounds were correlated with the signal intensity of *m*/*z* 44. The relative ionization efficiency of water was taken as 2.0 and that of organic molecules was taken as 1.4.

Particle-time-of-flight (PToF) data were employed to evaluate the contributions of organic ions at *m*/*z* 28 (CO^+ and $C_2H_4^+$) to the mass spectra. The air beam signal at *m*/*z* 28 (N_2^+) was subtracted from the data. Particle-phase signals were fit by lognormal functions to obtain signal intensities, which were compared with those for *m*/*z* 44. The obtained ratio was employed to update the fragmentation table.

Table S1. Update to the AMS fragmentation table. N/A denotes not unavailable. 'Minor' indicates that the contribution of the ion was relatively small among the isobaric ions.

m/*z*	Default	This study	Corresponding organic ions
18	0.225 frag_organic[44]	1.4 frag_organic[44]	H_3O^+
28	frag_organic[44]	2.6 frag_organic[44]	CO^+, $C_2H_4^+$
30	0.022 frag_organic[29]	30	CH_2O^+, $C_2H_6^+$ (minor)
39	N/A	39	$C_3H_3^+$
40	N/A	40,-frag_air[40]	$C_3H_4^+$
46	N/A	46	$CH_2O_2^+$, $C_2H_6O^+$ (minor)
48	0.5 frag_organic[62]	48,-frag_sulphate[48]	C_4^+
64	0.5 frag_organic[50],0.5 frag_organic[78]	64,-frag_sulphate[64]	$C_5H_4^+$
65	0.5 frag_organic[51],0.5 frag_organic[79]	65,-frag_sulphate[65]	$C_5H_5^+$
80	0.75 frag_organic[94]	80,-frag_sulphate[80]	$C_5H_4O^+$, $C_6H_8^+$ (minor)
81	0.5 frag_organic[67],0.5 frag_organic[95]	81,-frag_sulphate[81]	$C_5H_5O^+$, $C_6H_9^+$ (minor)
98	0.5 frag_organic[84],0.5 frag_organic[112]	98,-frag_sulphate[98]	$C_5H_6O_2^+$, $C_6H_{10}O^+$ (minor)

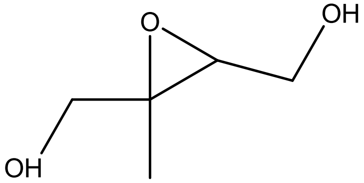
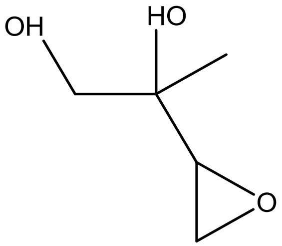
Table S2. Examples of laboratory experiments on SOM formation from isoprene employing sulfate particles.

Reference	Particle Acidity	RH (%)
Reactive uptake of isoprene photooxidation products		
This study	X = 0-1.0 (multistep)	< 5%
Chamber experiments using sulfate particles		
Harvard Environmental Chamber [2]	X = 1.0	40%, 60%
Jang et al. (2002) [3]	X = 0.41, 1.0	45-50%
Czoschke et al. (2003) [4]	X = 0.40, 1.0	< 10%
Kroll et al. (2005) [5]	X = 1.0	43, 44, 47, 49%
Surratt et al. (2006) [6]	X = 0.50, 1.0	<5%
Surratt et al. (2007) [7]	X = 0, 0.37, 1.0	30%
Ng et al. (2008) [8]	X = 1.0; $MgSO_4$+H_2SO_4 (3:5)	<10%
Kleindienst et al. (2009) [9]	X = 1.0	3, 31%
Rollins et al. (2009) [10]	X=1.0	57%
Surratt et al. (2010) [11]	X = 1.0; $MgSO_4$+H_2SO_4	<12%
Jaoui et al. (2010) [12]	X = 1.0 (addition of SO_2 to gas phase)	30%
Chhabra et al. (2010) [13]	X = 1.0	< 10%
Zhang et al. (2011) [14]	X = 1.0	15-38% 45-88% 16-42% 45-80%

Table S3. Examples of mode diameter and ammonium sulfate volume fraction for particles of different *X* and +1 or +2 charge. The corresponding number-diameter distributions are shown in Figure S1. The table shows the particle properties after coating sulfuric acid onto ammonium sulfate particles (i.e., just prior to inflow into reactor 2). The +1 and +2 particles were generated in a number ratio of 2:1.

	Mode Diameter (nm)		Volume Fraction of Ammonium Sulfate	
	+1	+2	+1	+2
X = 1.0	53.3	73.3	1	1
X = 0.7	57.3	79.1	0.80	0.80
X = 0.2	85.1	105.5	0.25	0.34

Table S4. Isoprene epoxydiol (IEPOX) isomers used in this study.

Name	Structure	Chemical Formula	Molar Mass (kg mol^{-1})
trans-β-IEPOX ((2-methyloxirane-2,3-diyl)dimethanol)		$C_5H_{10}O_3$	0.118
δ1-IEPOX (2-(oxiran-2-yl)propane-1,2-diol)		$C_5H_{10}O_3$	0.118

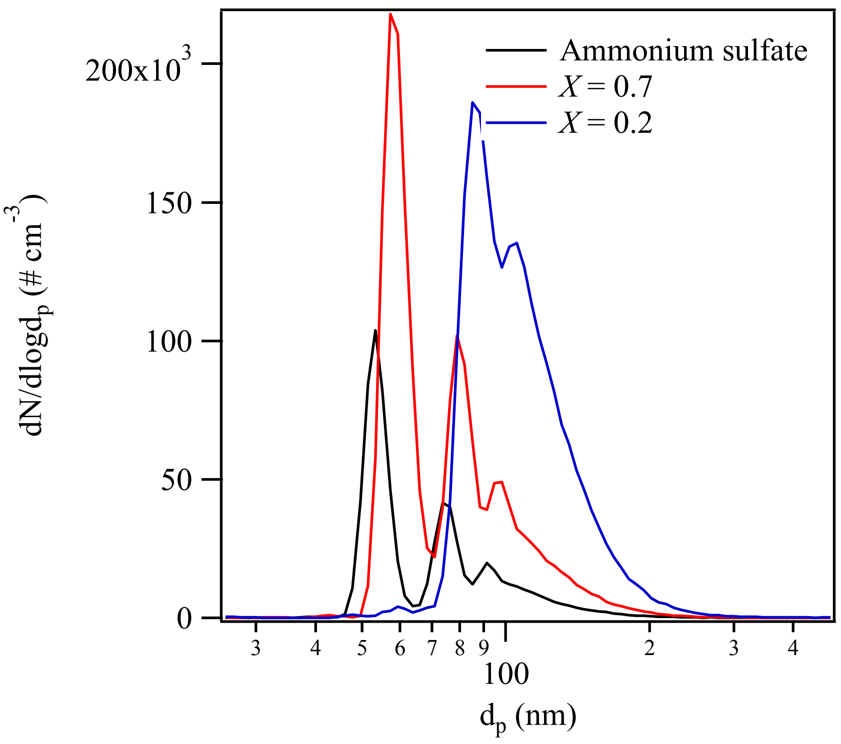


Figure S1

Number-diameter distributions of sulfate particles in outflow from particle generation system (i.e., just prior to inflow into reactor 2).

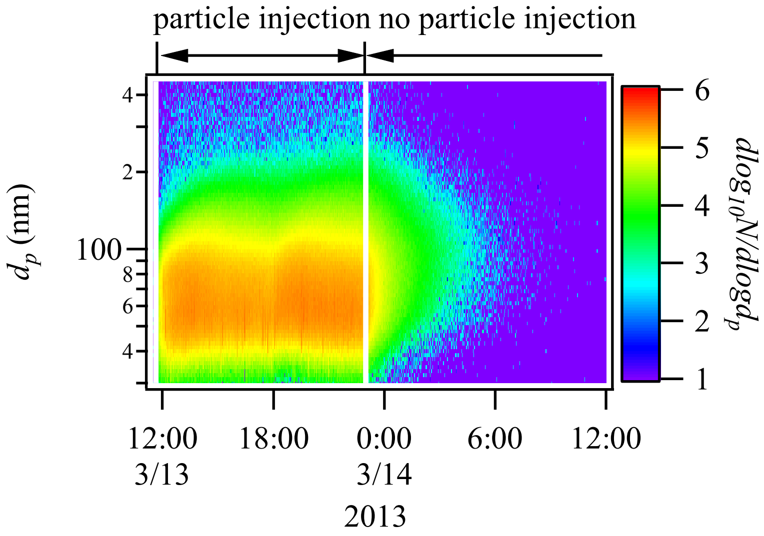


Figure S2

Evolution of particle number-diameter distribution following termination of sulfate particle injection. SOM particles were formed by reactive uptake of β-IEPOX by acidic sulfate particles ($X = 0.06$). Injection of β-IEPOX was continued after termination of particle injection.

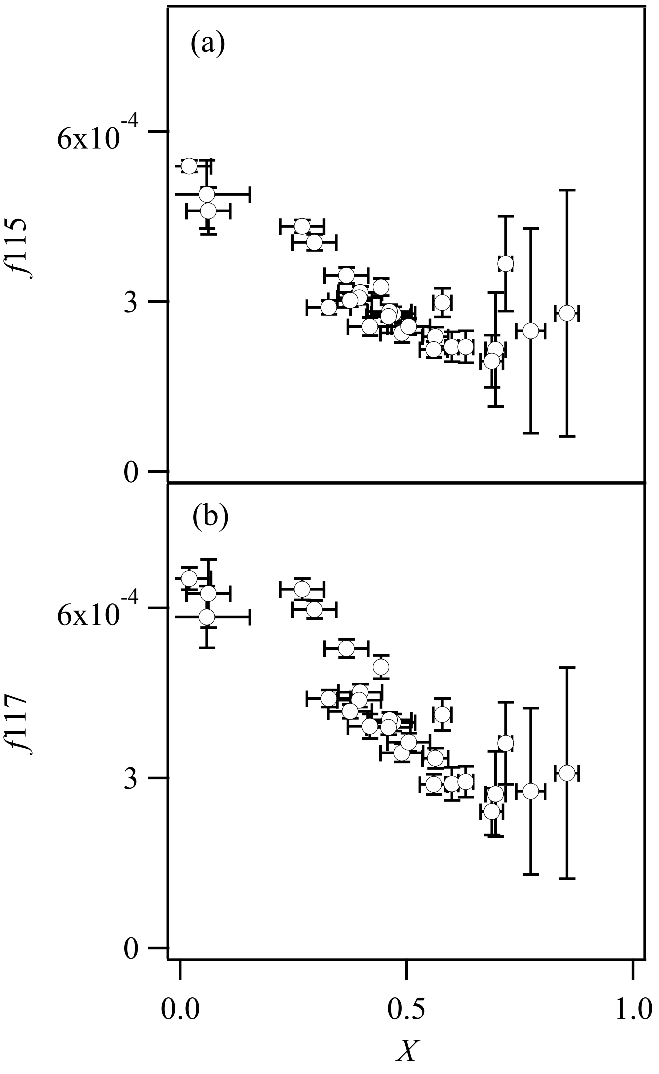


Figure S3

Fractions of (a) *m*/*z* 115 and (b) *m*/*z* 117 plotted against *X*.

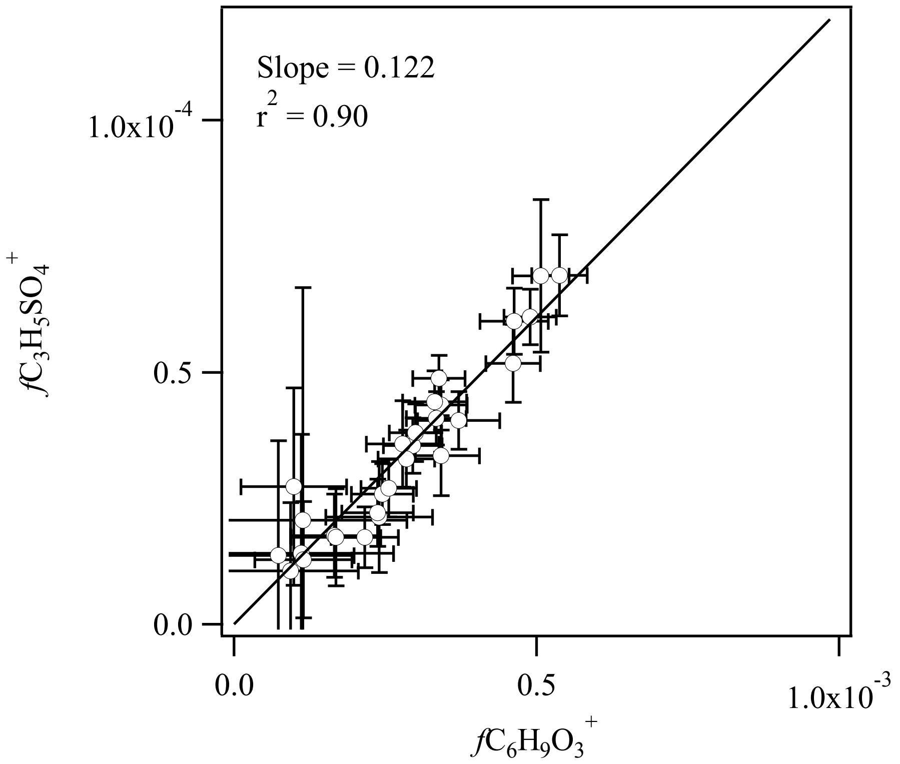


Figure S4

Correlation between organosulfate ($C_3H_5SO_4^+$) and oligomer ($C_6H_9O_3^+$) signals.

References

1. Q. Chen, Y. Liu, N. M. Donahue, J. E. Shilling and S. T. Martin, *Environ. Sci. Technol.*, 2011, **45**, 4763-4770.
2. M. Kuwata, S. R. Zorn and S. T. Martin, *Environ. Sci. Technol.*, 2012, **46**, 787-794.
3. M. S. Jang, N. M. Czoschke, S. Lee and R. M. Kamens, *Science*, 2002, **298**, 814-817.
4. N. M. Czoschke, M. Jang and R. M. Kamens, *Atmos. Environ.*, 2003, **37**, 4287-4299.
5. J. H. Kroll, N. L. Ng, S. M. Murphy, R. C. Flagan and J. H. Seinfeld, *Geophys. Res. Lett.*, 2005, **32**.
6. J. D. Surratt, S. M. Murphy, J. H. Kroll, a. L. N. Ng, L. Hildebrandt, A. Sorooshian, R. Szmigielski, R. Vermeylen, W. Maenhaut, M. Claeys, R. C. Flagan and J. H. Seinfeld, *Journal of Physical Chemistry A*, 2006, **110**, 9665-9690.
7. J. D. Surratt, M. Lewandowski, J. H. Offenberg, M. Jaoui, T. E. Kleindienst, E. O. Edney and J. H. Seinfeld, *Environ. Sci. Technol.*, 2007, **41**, 5363-5369.
8. N. L. Ng, A. J. Kwan, J. D. Surratt, A. W. H. Chan, P. S. Chhabra, A. Sorooshian, H. O. T. Pye, J. D. Crounse, P. O. Wennberg, R. C. Flagan and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2008, **8**, 4117-4140.
9. T. E. Kleindienst, M. Lewandowski, J. H. Offenberg, M. Jaoui and E. O. Edney, *Atmos. Chem. Phys.*, 2009, **9**, 6541-6558.
10. A. W. Rollins, A. Kiendler-Scharr, J. L. Fry, T. Brauers, S. S. Brown, H. P. Dorn, W. P. Dube, H. Fuchs, A. Mensah, T. F. Mentel, F. Rohrer, R. Tillmann, R. Wegener, P. J. Wooldridge and R. C. Cohen, *Atmospheric Chemistry and Physics*, 2009, **9**, 6685-6703.
11. J. D. Surratt, A. W. H. Chan, N. C. Eddingsaas, M. Chan, C. L. Loza, A. J. Kwan, S. P. Hersey, R. C. Flagan, P. O. Wennberg and J. H. Seinfeld, *PNAS*, 2010, **107**, 6640-6645.
12. M. Jaoui, E. W. Corse, M. Lewandowski, J. H. Offenberg, T. E. Kleindienst and E. O. Edney, *Atmos. Environ.*, 2010, **44**, 1798-1805.
13. P. S. Chhabra, R. C. Flagan and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2010, **10**, 4111-4131.
14. H. Zhang, J. D. Surratt, Y. H. Lin, J. Bapat and R. M. Kamens, *Atmos. Chem. Phys.*, 2011, **11**, 6411-6424.