Supplementary Material

Photochemical Organonitrate Formation in Wet Aerosol

Yong Bin Lim, Hwajin Kim, Jin Young Kim and Barbara J. Turpin

Table S1. Experimental Conditions

No	Atomized Solution Date	UV or Dark	RH_i (%)	RH_f (%)	T_i (K)	T_f (K)	$[NO/NO_x]_i$ (ppb)	$[NO/NO_x]_f$ (ppb)	$[O_3]_i$ (ppb)	$[O_3]_f$ (ppb)	ALW_i (%)	ALW_f (%)
1	AS + H_2O_2 + Gly 3/5/2015	UV	3.0	3.0	293	303	24.0/28.0	5.5/25.5	0	24.9	1.2	1.2
2	AS + H_2O_2 + Gly 3/31/2015	UV	3.0	3.0	294	309	8.2/9.4	4.4/15.6	6.9	7.7	1.2	1.2
3	AS + H_2O_2 + Gly 11/26/2015	UV	3.0	3.0	292	306	2.4/2.9	0/1.1	9.6	34.0	1.2	1.2
4	AS + H_2O_2 + Gly 3/23/2015	UV	70.8	38.9	294	304	5.1/6.4	0.4/4.6	7.4	11.3	45.8	19.4
5	AS + H_2O_2 + Gly 4/1/2015	UV	82.2	42.0	295	310	7.2/10.5	2.7/7.4	6.9	15.4	59.2	2.2
6	AS + Gly 5/27/2015	UV*	69.4	34.8	298	310	54.7/55.5	23.3/38.7	13.0	18.0	44.3	1.7
7	AS + H_2O_2 3/30/2015	UV	83.7	39.1	295	310	8.5/11.7	3.2/7.1	7.6	12.1	63.3	N/A
8	AS + H_2O_2 + Gly 4/27/2015	Dark	3.0	3.0	297	297	17.2/19.1	17.2/19.1	6.4	5.9	1.2	1.2
9	AS + H_2O_2 + Gly 4/28/2015	Dark	77.7	56.2	298	298	38.9/39.9	27.8/33.2	6.2	7.8	53.7	32.0
10	AS + H_2O_2 + Gly 5/7/2015	Dark	71.7	64.9	298	298	15.8/16.9	15.6/17.1	5.6	6.3	46.7	39.8
11	SA + H_2O_2 + Gly 3/9/2015	UV	7.1	3.0	293	304	80.9/83.5	41.6/77.7	0	7.7	32.4	26.5
12	SA + H_2O_2 + Gly 3/25/2015	UV	82.0	44.8	294	307	21.6/23.9	15.2/19.7	6.2	8.5	74.2	53.1
13	SA + H_2O_2 + Gly 5/6/2015	Dark	5	5	298	298	15.8/16.9	15.6/17.1	5.6	6.3	26.9	26.9
14	SA + H_2O_2 + Gly 4/29/2015	Dark	77.6	77.1	298	298	15.8/18.0	15.7/17.5	6.1	6.3	70.9	70.6

Note, AS = ammonium sulfate, SA = sulfuric acid, Gly = glyoxal, i = initial, f = final, ALW = fraction of aerosol liquid water in a wet aerosol, UV* = 1-hour irradiation, and N/A = no aqueous phase

Table S2. Elemental compositions of organic-inorganic compounds analyzed by UPLC-HR-Q-TOF-MS in the positive mode

Aerosols (Conditions)	m/z^+	Elemental Composition	Compound	Error (ppm)
AS (Solution)	69.0509	C3H5N2	Imidazole*	89.4
	116.9984	C2H6O4Na1	Glyoxal	-149.0
	133.0271	C2H2N6Na1	Imidazole	28.4
	248.0215	C4H3N9O3Na1	Imine	-14.5
	363.0174	C4H12N4O14Na1	Imine	-18.8
AS (Dry)	89.0307 (z = 2)	C10H10O3	Organic Compound	-2.8
	133.0920 (z = 2)	C16H26O3	Organic Compound	-11.6
	161.0986	C11H13O1	Organic Compound	15.6
	203.0880	C9H15O5	Organic Compound	-16.7
	283.1749	C11H24N4O3	Organic Compound	3.0
	365.1519	C12H26N2O9Na1	Imine	-3.2
	381.2726	C19H38N2O4Na1	Imine	0.6
AS (Humid)	107.9721 (z = 2)	C4H1O9Na1	Unidentified Peak	-30.2
	133.0865	C6H13O3	Organic Compound	4.4
	161.1082	C8H14N2Na1	Imidazole	9.6
	203.1023	C7H12N6Na1	Imidazole	3.6
	261.1322	C7H14N10Na1	Imidazole	5.1
	283.1749	C7H20N10O1	Imine	12.4
	363.0483	C15H4N10O1Na1	Imine	5.8
	381.2626	C20H38O5Na1	Organic Compound	3.8
	399.2664	C12H32N10Na1	Imidazole	-9.9
	441.9170	C13N1O17	Imine	2.1
	526.9000	C12N4O19	Imine	-9.3
SA (Solution)	93.0210	C2H5O4	Organic Compound	29.7
	117.0562	C5H9O3	Organic Compound	13.5
	149.0307	C6H6O3	Organic Compound	65.7
	172.9890	C4H6O6Na1	Organic Compound	-96.3
	252.9581	C7H2O9Na1	Organic Compound	-4.0
	277.1795	C15H26O3Na1	Organic Compound	7.5
	303.2102	C16H31O5	Organic Compound	-21.1
SA (Dry)	135.0011	C5H4O3	Organic Compound	-30.9
	261.1178	C15H17O4	Organic Compound	21.7
	305.1588	C14H25O7	Organic Compound	-2.2
	331.1749	C16H27O7	Organic Compound	-0.7
	349.1742	C14H30O8	Organic Compound	-26.0
	393.2035	C16H34O9	Organic Compound	-15.3
SA (Humid)	89.0297 (z = 2)	C10H10O3	Organic Compound	-14.0
	107.9653 (z = 2)	C4H1O9Na1	Organic Peroxide	-93.2
	133.0918 (z = 2)	C16H26O3	Organic Compound	-13.1
	161.0954	C11H13O1	Organic Compound	-4.3
	203.1078	C9H15O5	Organic Compound	-16.7
	239.1504	C10H23O6	Organic Compound	6.2
	261.1323	C10H22O6Na1	Organic Compound	5.5
	283.1720	C12H27O7	Organic Compound	-11.1
	305.1557	C12H26O7Na1	Organic Compound	-4.5
	327.1983	C14H31O8	Organic Compound	-9.3
	435.8400	C3H2N1O18S3	Organonitrogen-sulfate	-6.5

*Kampf et al., 2012

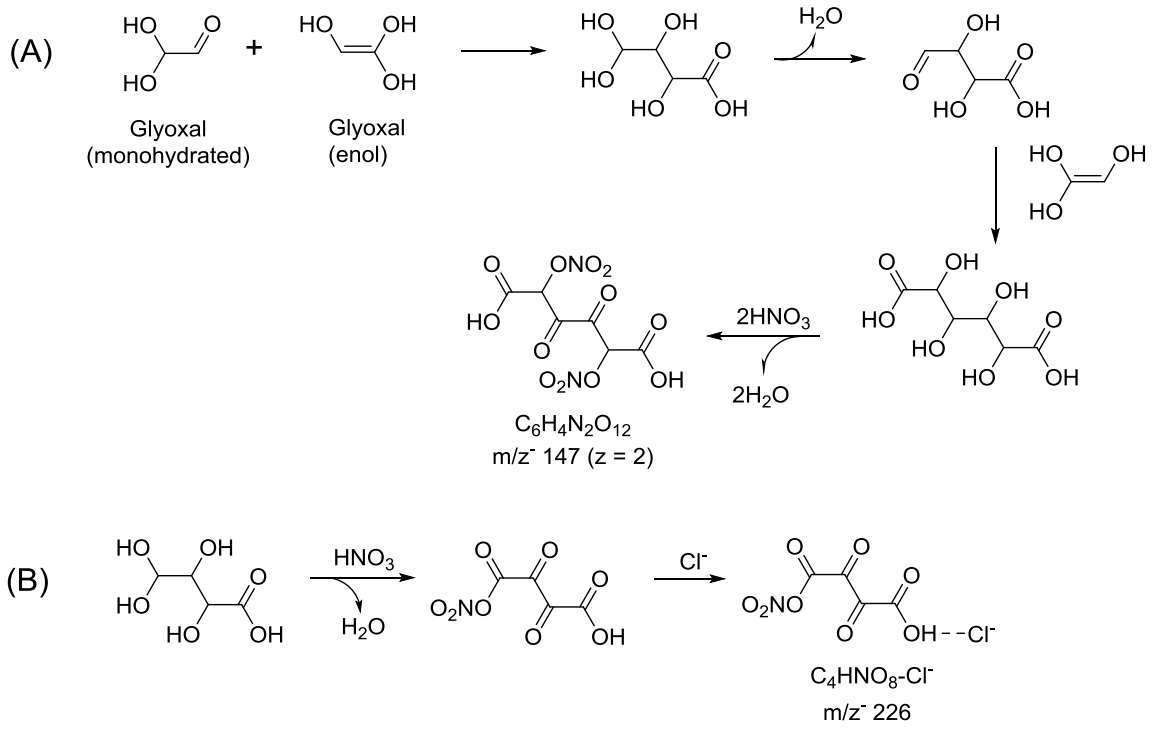
Table S3. Added reactions to the full kinetic model (Lim and Turpin, 2015 Supplementary Material)

	Reactions	Rate constants (M^{1-n} s^{-1})	Ref
1	$GLY_g \leftrightarrow GLY$	K_{eq} = 2e7 k_r = 1e5	(1, 2)
2	$GLYAC_g \leftrightarrow GLYAC$	K_{eq} = 9.12e3 k_r = 1e5	(2, 3)
3	$OXLAC_g \leftrightarrow OXLAC$	K_{eq} = 3.26e6 k_r = 1e5	(2, 3)
4	$HCO_2H_g \leftrightarrow HCO_2H$	K_{eq} = 3.55e3 k_r = 4.6e5	(2, 3)
5	$HCHO_g \leftrightarrow HCHO$	K_{eq} = 3.3e3 k_r = 4.6e5	(2, 3)
6	$GCOLAC_g \leftrightarrow GCOLAC$	K_{eq} = 1.18e4 k_r = 1e5	(2, 3)
7	$H_2O_{2g} \leftrightarrow H_2O_2$	K_{eq} = 1e5 k_r = 1e6	(2, 3)
	Gas-Phase Reactions	**Rate constants ([molecules/cm^3]$^{1-n}$ s^{-1})**	**Ref**
8	$GLY_g + OH_g \rightarrow$	9.7e-12	(4)
9	$HCO_2H_g + OH_g \rightarrow$	4.5e-13	(4)
10	$HCHO_g + OH_g \rightarrow$	8.5e-12	(4)
11	$GLYAC_g + OH_g \rightarrow$	6.2e-11	(5)
12	$OXLAC_g + OH_g \rightarrow$	2e-13	(5)
13	$GCOLAC_g + OH_g \rightarrow$	2.96e-13	(5)
14	$H_2O_2 \rightarrow 2OH$	3.77e-6	(3)

GLY = glyoxal; GLYAC = glyoxylic acid, OXLAC = oxalic acid; HCO_2H = formic acid; GCOLAC = glycolic acid; HCHO = formaldehyde; H_2O_2 = hydrogen peroxide

Reference

1. Ervens B & Volkamer R (2010) Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. *Atmos. Chem. Phys.* 10(17):8219-8244.
2. Warneck P (1999) The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. *PCCP* 1(24):5471-5483.
3. Lim HJ, Carlton AG, & Turpin BJ (2005) Isoprene forms secondary organic aerosol through cloud processing: Model simulations. *Environ. Sci. Technol.* 39(12):4441-4446.
4. Atkinson R & Arey J (2003) Atmospheric degradation of volatile organic compounds. *Chem. Rev.* 103(12):4605-4638.
5. Kwok ESC & Atkinson R (1995) Estimation of Hydroxyl Radical Reaction-Rate Constants for Gas-Phase Organic-Compounds Using a Structure-Reactivity Relationship - an Update. *Atmos. Environ.* 29(14):1685-1695.



Scheme S1. Proposed formation of two organonitrates, m/z⁻ 147 (A) and m/z⁻ 226 (B)

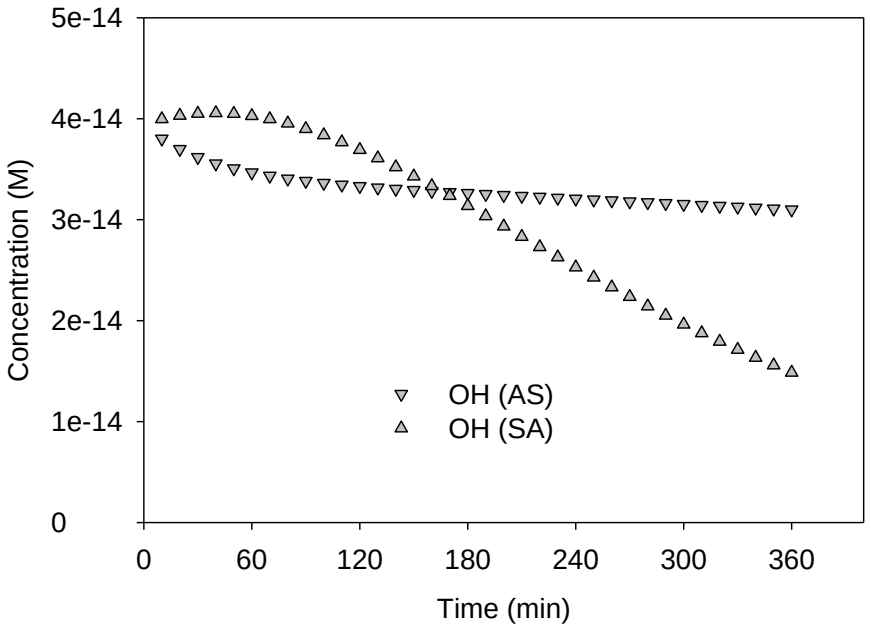


Fig. S1. The simulated concentrations of OH in ammonium sulfate aerosols (AS) and sulfuric acid aerosols (SA)

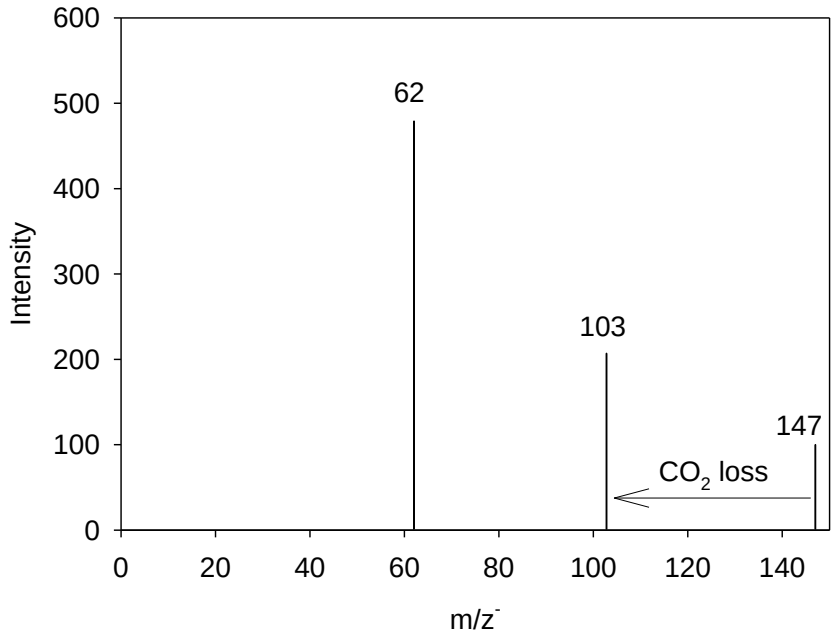


Figure S2. LC-MS/MS analysis for m/z$^-$ 147 from smog chamber AS aerosols

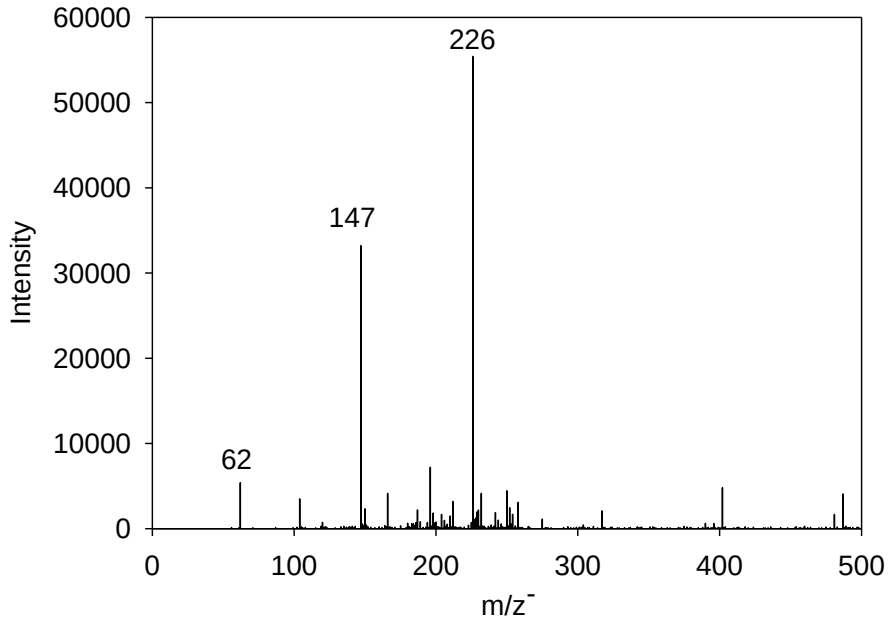


Figure S3. The mass spectrum for the mixture solution of glyoxal (7.6 mM) and nitric acid (15 mM) in the negative mode

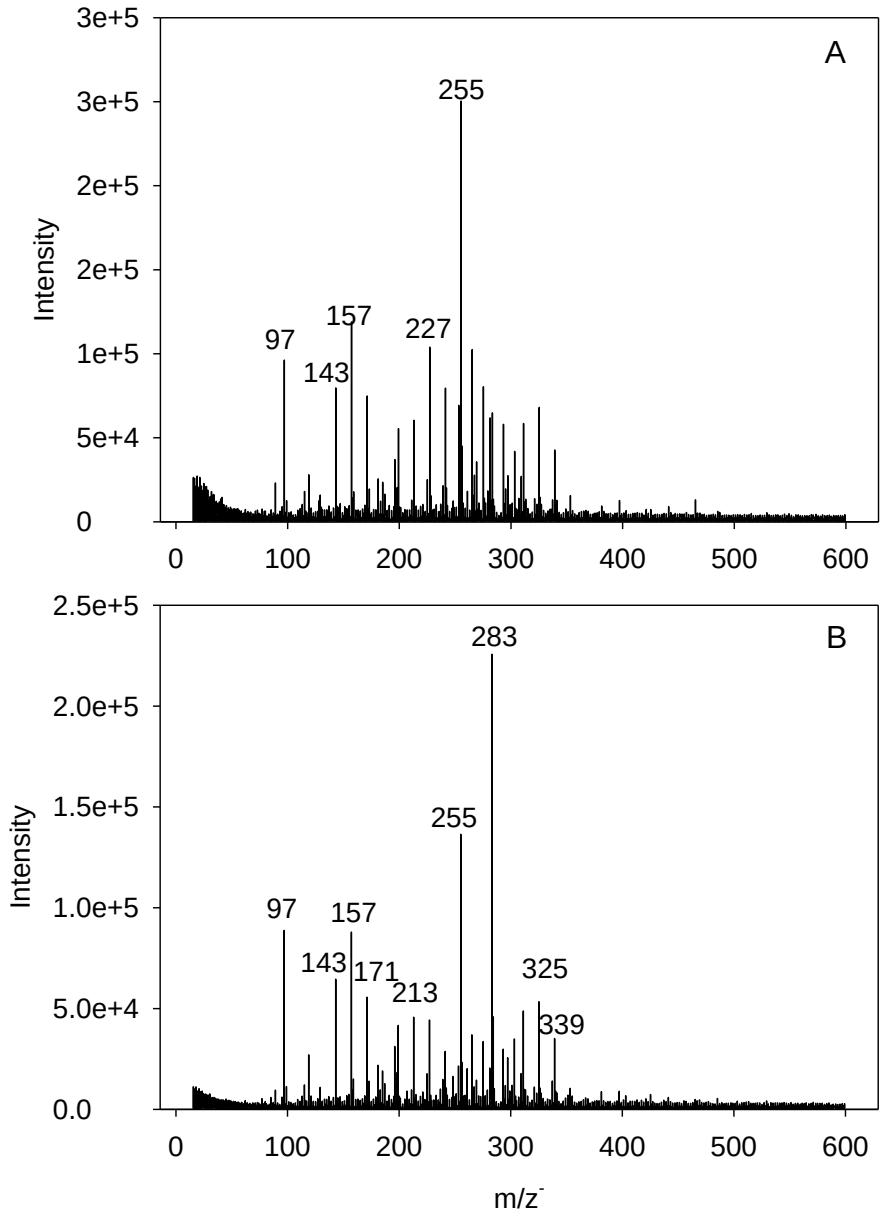


Figure S4. Negative-mode mass spectra for 3 hour dark reactions of glyoxal-H_2O_2-$(NH_4)_2SO_4$ aerosols (A) and glyoxal-H_2O_2-H_2SO_4 aerosols (B) under humid conditions (> 70 % RH)

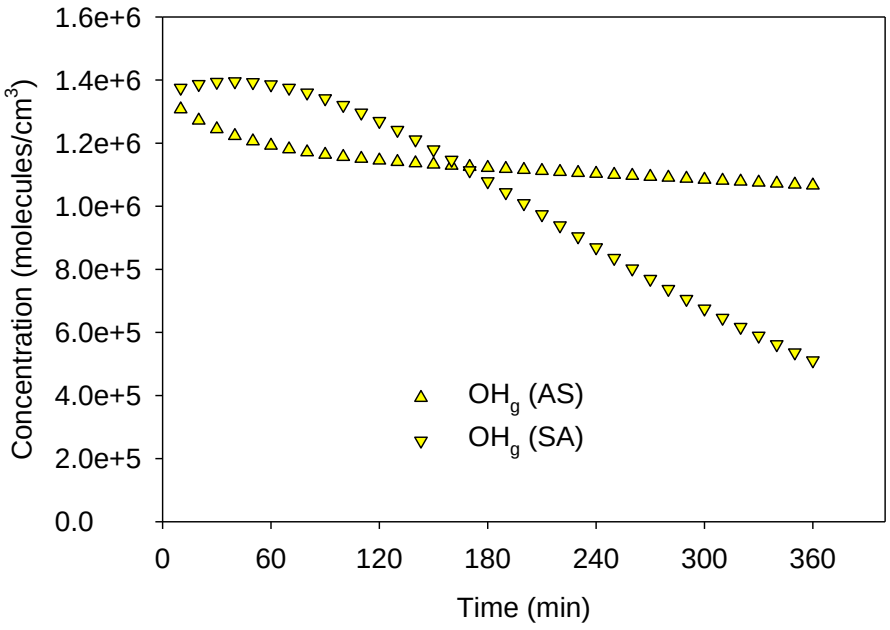


Fig. S5. The simulated gas-phase OH concentrations during photochemical reactions of AS aerosols (AS) and SA aerosols (SA)

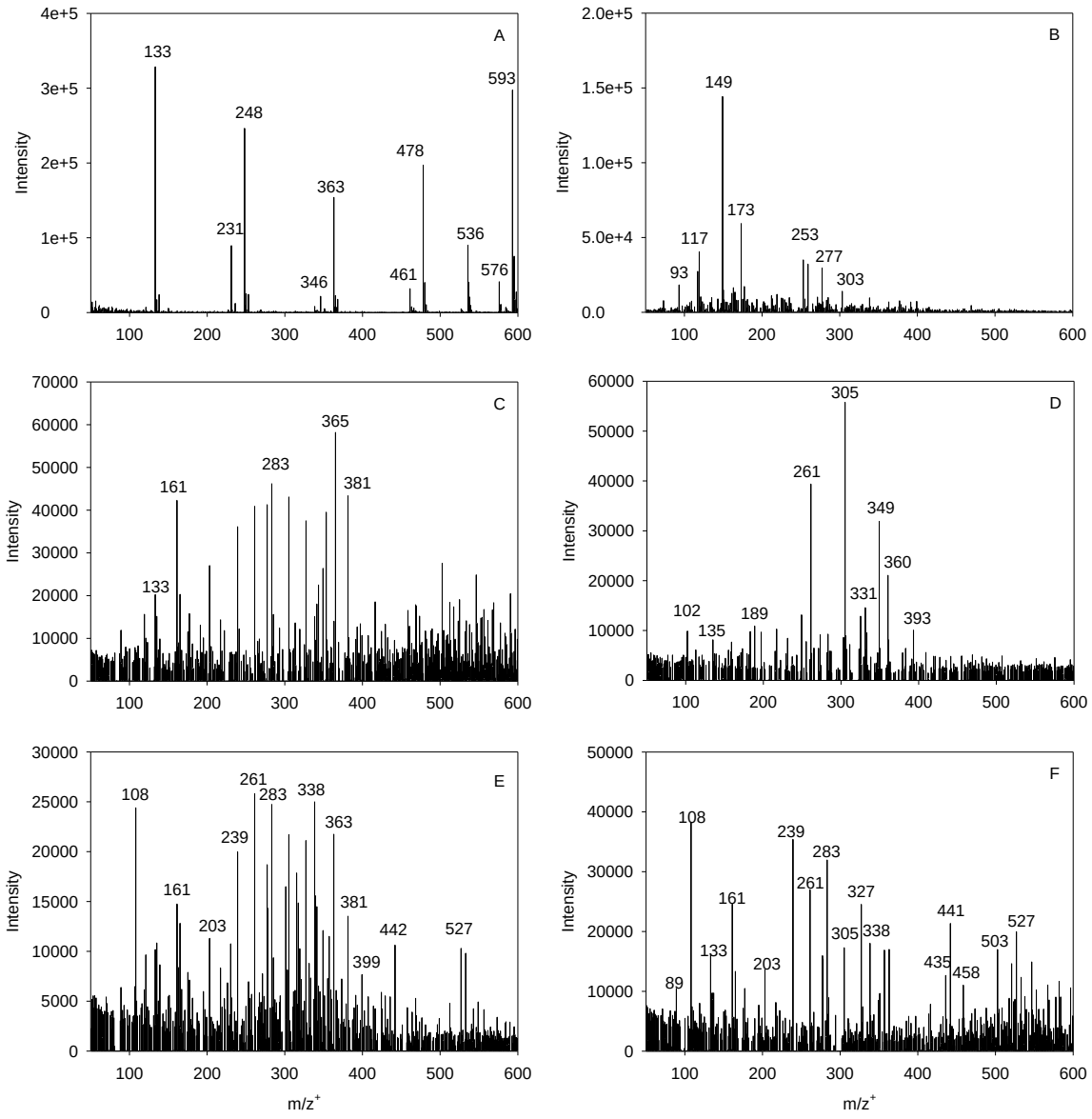


Fig. S6. Positive-mode mass spectra of dark reactions of glyoxal-H_2O_2-$(NH_4)_2SO_4$ (A, C and E) and glyoxal-H_2O_2-H_2SO_4 (B, D and F). A and B are solutions. C and D are dry aerosols and E and F are humid aerosols at time = 0 min

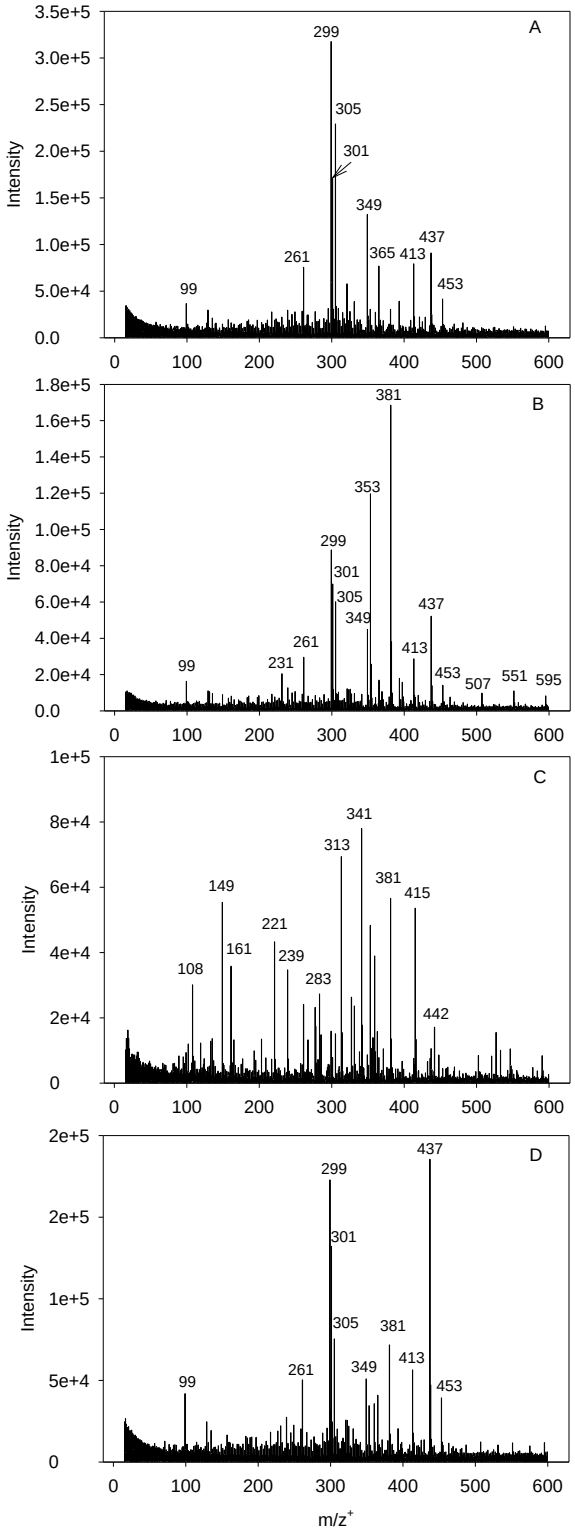


Fig. S7. Negative-mode mass spectra for 3 dark-reacted AS aerosols (A) and SA aerosols (B) in the humid chamber, and AS aerosols (C) and SA aerosols (D) in the dry chamber