Supplement of Atmos. Chem. Phys., 15, 12867–12877, 2015
http://www.atmos-chem-phys.net/15/12867/2015/
doi:10.5194/acp-15-12867-2015-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and implications for aqueous OH

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Supplementary Material

Laboratory Evidence of Organic Peroxide and Peroxyhemiacetal Formation in the Aqueous Phase and Implications for Aqueous OH

The supplementary material contains:

Table S1. Reactions and rate/equilibrium constants used in the full kinetic model of unified glyoxal/methylglyoxal + OH

	Reactions	Rate constants (M^{1-n} s^{-1})	Ref
1	$H_2O_2 \rightarrow 2OH$	1.1e-4×Trans[a]	T, e
2	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	2.7e7	T
3	$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$	3.7	T
4	$2\ HO_2 \rightarrow H_2O_2 + O_2$	8.3e5	T
5	$OH + HO_2 \rightarrow H_2O + O_2$	7.1e9	T
6	$HO_2 + O_2^- + H^+ \rightarrow H_2O_2 + O_2$	1e8	T
7	$2OH \rightarrow H_2O_2$	5.5e9	T
8	$OH + O_2^- \rightarrow OH^- + O_2$	1e10	T
9	$O_{2g} \leftrightarrow O_2$	K_{eq} = 1.3e-3 k_r = 5.3e2	T, W
10	$CO_{2g} \leftrightarrow CO_2$	K_{eq} = 3.4e-2 k_r = 5.3e2	T, W
11	$CO_2 \leftrightarrow H^+ + HCO_3^-$	K_{eq} = 4.3e-7 k_r = 5.6e4	T
12	$HCO_3^- \rightarrow H^+ + CO_3^{-2}$	K_{eq} = 4.69e-11 k_r = 5.0e10	T
13	$CO_2^- + O_2 \rightarrow O_2^- + CO_2$	2.4e9	T
14	$HCO_3^- + OH \rightarrow CO_3^- + H_2O$	1e7	T
15	$CO_3^- + O_2^- \rightarrow CO_3^{-2} + O_2$	6.5e8	T
16	$CO_3^- + HCO_2^- \rightarrow HCO_3^- + CO_2^-$	1.5e5	T
17	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	8e5	T
18	GCOLAC + OH → GCOLAC* + H2O	6.0e8	T
19	GCOLAC* + O_2 → GCOLACOO*	1e6	G, L’
20	GCOLACOO* → GLYAC + HO_2	5e1	C
21	2GCOLACOO* → 2GCOLACO* + O_2	3e8*0.95	L’, e
22	2GCOLACOO* → GLYAC + OXLAC + O_2	3e8*0.05	L’, e
23	GCOLACO* → HCO_2H + CO_2	I	Gi, e
24	GCOLACO* → GLYAC*	1e7	Gi, e
25	GCOLAC ↔ H^+ + $GCOLAC^-$	K_{eq} = 1.48e-4 k_r = 2.0e10	T
26	$GCOLAC^-$ + OH → $GCOLAC^{*-}$ + H_2O	6.0e8	T
27	$GCOLAC^{*-}$ + O_2 → $GCOLACOO^{*-}$	1e6	G, L’
28	$GCOLACOO^{*-}$ → $GLYAC^-$ + HO_2	5e1	C
29	$2GCOLACROO^{*-}$ → $2GCOLACO^{*-}$ + O_2	3e8×0.95	L’, e
30	2 $GCOLACROO^{*-}$ → $GLYAC^-$ + $OXLAC^-$ + O_2	3e8×0.05	L’, e
31	$GCOLACO^{*-}$ → HCO_2H + CO_2^-	I	Gi, e
32	$GCOLACO^{*-}$ → $GLYAC^{*-}$	1e7	Gi, e
33	GLY + OH → GLY* + H_2O	1.1e9	T
34	GLY* + O_2 → GLYOO*	1e6	G, L’
35	GLYOO* → GLYAC + HO_2	5e1	C
36	2GLYOO* → 2*CHOHOH + 2CO_2 + O_2 + 2H_2O	3e8	L’
37	*CHOHOH + O_2 → HCO_2H + HO_2	5e6	G, L’
38	GLYAC + OH → GLYAC* + H_2O	3.62e8	T
39	GLYAC* + O_2 → GLYACOO*	1e6	G, L’
40	GLYACOO* → OXLAC + HO_2	5e1	C
41	2GLYACOO* → 2CO_2 + 2COOH	3e8	L’
42	*COOH + O_2 → CO_2 + HO_2	5e6	G, L’

43	$GLYAC \leftrightarrow H^+ + GLYAC^-$	K_{eq} = 3.47e-4 K_r = 2.0e10	T
44	$GLYAC^- + OH \rightarrow GLYAC^{*-} + H_2O$	1.28e7	T
45	$GLYAC^- + OH \rightarrow GLYAC^* + OH^-$	2.9e9	T
46	$GLYAC^{*-} + O_2 \rightarrow GLYACOO^{*-}$	1e6	G, L’
47	$GLYACOO^{*-} \rightarrow OXLAC^- + HO_2$	1e2	C, L’
48	$2GLYACOO^{*-} \rightarrow 2CO_2^- + 2^*COOH$	3e8	L’
49	$MGLY + OH \rightarrow MGLY^* + H_2O$	7.0e8×0.92	T
50	$MGLY + OH \rightarrow {}^*MGLY + H_2O$	7.0e8×0.08	T
51	$MGLY^* + O_2 \rightarrow MGLYOO^*$	1e6	G, L’
52	$MGLYOO^* \rightarrow PYRAC + HO_2$	5e1	C
53	$2MGLYOO^* \rightarrow 2CO_2 + 2CH_3CO_2H + O_2$	3e8	L’
54	$^*MGLY + O_2 \rightarrow {}^*OOMGLY$	1e6	G, L’
55	$2^*OOMGLY \rightarrow 2^*OMGLY + O_2$	3e8×0.95	L’, e
56	$2^*OOMGLY \rightarrow HOMGLY + OMGLY + O_2$	3e8×0.05	L’, e
57	$^*OMGLY \rightarrow HCHO + GLY^*$	I	Gi, e
58	$^*OMGLY \rightarrow {}^*HOMGLY$	1e7	Gi, e
59	$HOMGLY + OH \rightarrow {}^*HOMGLY + H_2O$	4.10e7	M
60	$^*HOMGLY + O_2 \rightarrow {}^*OOHOMGLY$	1e6	G, L’
61	$^*OOHOMGLY \rightarrow OMGLY + HO_2$	5e1	C
62	$OMGLY + OH \rightarrow {}^*OMGLY + H_2O$	6.17e9	M
63	$^*OMGLY + O_2 \rightarrow {}^*OOOMGLY$	5e1	C
64	$GLY^* + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
65	$2GLY^* \rightarrow C4D$	1.3e9	G, L’
66	$GLY^* + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
67	$GLYAC^* + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
68	$GLYAC^* + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
69	$2GLYAC^* \rightarrow C4D$	1.3e9	G, L’
70	$GLYAC^* + GLY^* \rightarrow C4D$	1.3e9	G, L’
71	$GLYAC^{*-} + GLY^* \rightarrow C4D$	1.3e9	G, L’
72	$GLYAC^{*-} + GLYAC^* \rightarrow C4D$	1.3e9	G, L’
73	$2GLYAC^{*-} \rightarrow C4D$	1.3e9	G, L’
74	$GLYAC^{*-} + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
75	$GLYAC^{*-} + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
76	$GLYCOL^{*1} + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
77	$GLYCOL^{*1} + GLY^* \rightarrow C4D$	1.3e9	G, L’
78	$GLYCOL^{*1} + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
79	$GLYCOL^{*1} + GLYAC^* \rightarrow C4D$	1.3e9	G, L’
80	$GLYCOL^{*1} + GLYAC^{*-} \rightarrow C4D$	1.3e9	G, L’
81	$GLYCOL^{*2} + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
82	$GLYCOL^{*2} + GLY^* \rightarrow C4D$	1.3e9	G, L’
83	$GLYCOL^{*2} + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
84	$GLYCOL^{*2} + GLYAC^* \rightarrow C4D$	1.3e9	G, L’
85	$GCOLAC^* + {}^*CHOHOH \rightarrow C3D$	1.3e9	G, L’
86	$GCOLAC^* + GLY^* \rightarrow C4D$	1.3e9	G, L’
87	$GCOLAC^* + {}^*COOH \rightarrow C3D$	1.3e9	G, L’
88	$GCOLAC^* + GLYAC^* \rightarrow C4D$	1.3e9	G, L’
89	$GCOLAC^* + GLYAC^{*-} \rightarrow C4D$	1.3e9	G, L’
90	$GCOLAC^* + GLYCOL^{*1} \rightarrow C4D$	1.3e9	G, L’
91	$GCOLAC^* + GLYCOL^{*2} \rightarrow C4D$	1.3e9	G, L’

92	GCOLAC* + GCOLAC* → C4D	1.3e9	G, L’
93	$GCOLAC^{*-}$ + *CHOHOH → C3D	1.3e9	G, L’
94	$GCOLAC^{*-}$ + GLY* → C4D	1.3e9	G, L’
95	$GCOLAC^{*-}$ + *COOH → C3D	1.3e9	G, L’
96	$GCOLAC^{*-}$ + GLYAC* → C4D	1.3e9	G, L’
97	$GCOLAC^{*-}$ + $GLYAC^{*-}$ → C4D	1.3e9	G, L’
98	$GCOLAC^{*-}$ + $GLYAC^{*-}$ → C4D	1.3e9	G, L’
99	$GCOLAC^{*-}$ + $GLYCOL^{*1}$ → C4D	1.3e9	G, L’
100	$GCOLAC^{*-}$ + $GLYCOL^{*2}$ → C4D	1.3e9	G, L’
101	$GCOLAC^{*-}$ + GCOLAC* → C4D	1.3e9	G, L’
102	2 $GCOLAC^{*-}$ → C4D	1.3e9	G, L’
103	2MGLY* → C6D	1.3e9	G, L’
104	MGLY* + *CHOHOH → C4D	1.3e9	G, L’
105	MGLY* + GLY* → C5D	1.3e9	G, L’
106	MGLY* + *COOH → C4D	1.3e9	G, L’
107	MGLY* + GLYAC* → C5D	1.3e9	G, L’
108	MGLY* + $GLYAC^{*-}$ → C5D	1.3e9	G, L’
109	MGLY* + $GLYCOL^{*1}$ → C5D	1.3e9	G, L’
110	MGLY* + $GLYCOL^{*2}$ → C5D	1.3e9	G, L’
111	MGLY* + GCOLAC* → C5D	1.3e9	G, L’
112	MGLY* + $GCOLAC^{*-}$ → C5D	1.3e9	G, L’
113	MGLY* + CH_3CO^* → C5D	1.3e9	G, L’
114	MGLY* + *HOPYRAC → C6D	1.3e9	G, L’
115	2*HOPYRAC → C6D	1.3e9	G, L’
116	MGLY* + $*HOPYRAC^-$ → C6D	1.3e9	G, L’
117	$*HOPYRAC^-$ + $*HOPYRAC^-$ → C6D	1.3e9	G, L’
118	*HOPYRAC + $*HOPYRAC^-$ → C6D	1.3e9	G, L’
119	CH_3CO^* + *HOPYRAC → C6D	1.3e9	G, L’
120	CH_3CO^* + $*HOPYRAC^-$ → C6D	1.3e9	G, L’
121	2LA* → C6D	1.3e9	G, L’
122	LA* + MGLY* → C6D	1.3e9	G, L’
123	LA* + *CHOHOH → C4D	1.3e9	G, L’
124	LA* + GLY* → C5D	1.3e9	G, L’
125	LA* + *COOH → C4D	1.3e9	G, L’
126	LA* + GLYAC* → C5D	1.3e9	G, L’
127	LA* + $GLYAC^{*-}$ → C5D	1.3e9	G, L’
128	LA* + $GLYCOL^{*1}$ → C5D	1.3e9	G, L’
129	LA* + $GLYCOL^{*2}$ → C5D	1.3e9	G, L’
130	LA* + GCOLAC* → C5D	1.3e9	G, L’
131	LA* + $GCOLAC^{*-}$ → C5D	1.3e9	G, L’
132	LA* + CH_3CO^* → C5D	1.3e9	G, L’
133	$2CH_3CO^*$ → C4D	1.3e9	G, L’
134	LA* + *HOPYRAC → C6D	1.3e9	G, L’
135	LA* + $*HOPYRAC^-$ → C6D	1.3e9	G, L’
136	OXLAC + OH → COOH + CO_2 + H_2O	1.4e6	T
137	OXLAC ↔ H^+ + $OXLAC^-$	K_{eq} = 5.67e-2 k_r = 5.0e10	T
138	$OXLAC^-$ + OH → COOH + CO_2^- + H_2O	2.0e7	T, L’
139	$OXLAC^-$ ↔ H^+ + $OXLAC^{-2}$	K_{eq} = 5.42e-5 k_r = 5e10	T
140	$OXLAC^{-2}$ + OH → *COOH + CO_2^- + OH^-	4.0e7	T, L’

141	$LA + OH \rightarrow LA^* + H_2O$	4.3e8	H
142	$LA^* + O_2 \rightarrow LAOO^*$	1e6	G, L’
143	$LAROO^* \rightarrow PYRAC + HO_2$	5e1	C
144	$LA \leftrightarrow LA^- + H^+$	K_{eq} = 1.38e-4 k_r = 5.0e10	E&C
145	$LA^- + OH \rightarrow LA^{*-} + H_2O$	3e8	B
146	$LA^{*-} + O_2 \rightarrow LAOO^{*-}$	1e6	G, L’
147	$LAOO^{*-} \rightarrow PYRAC^- + HO_2$	5e1	C
148	$PYRAC + OH \rightarrow PYRAC^* + H_2O$	6.0e7×0.85	T
149	$PYRAC + OH \rightarrow CH_3CO^* + CO_2 + H_2O$	6.0e7×0.15	T
150	$CH_3CO^* + O_2 \rightarrow CH_3C(O)OO^*$	1e6	G, L’
151	$CH3C(O)OO^* \rightarrow CH_3CO_2H + HO_2$	5e1	C
152	$2CH3C(O)OO^* \rightarrow 2CH_3C(O)O^* + O_2$	3e8	L’
153	$CH_3C(O)O^* \rightarrow CO_2 + HCHO$	1e7	Gi
154	$PYRAC^* + O_2 \rightarrow PYRACOO^*$	1e6	G, L’
144	$2PYRACOO^* \rightarrow 2PYRACO^* + O_2$	3e8×0.95	L’, e
145	$2PYRACOO^* \rightarrow HOPYRAC + OPYRAC + O_2$	3e8×0.15	L’, e
146	$PYRACO^* \rightarrow HCHO + GLYAC^*$	I	Gi, e
147	$PYRACO^* \rightarrow {}^*HOPYRAC$	1e7	Gi, e
148	$HOPYRAC + OH \rightarrow {}^*HOPYRAC + H_2O$	3.6e8	H
149	$^*HOPYRAC + O_2 \rightarrow {}^*OOHOPYRAC$	1e6	G, L’
150	$^*OOHOPYRAC \rightarrow OPYRAC + HO_2$	5e1	C
151	$OPYRAC + OH \rightarrow {}^*OPYRAC + H_2O$	5e7	e
152	$^*OPYRAC + O_2 \rightarrow {}^*OO(O)PYRAC$	1e6	G, L’
153	$^*OO(O)PYRAC \rightarrow MOXLAC + HO_2$	5e1	C
154	$PYRAC \leftrightarrow PYRAC^- + H^+$	K_{eq} = 3.2e-3 k_r = 2e10	T
155	$PYRAC^- + OH \rightarrow PYRAC^{*-} + H_2O$	6.0e7×0.95	T
156	$PYRAC^- + OH \rightarrow CH3CO^* + CO_2 + OH^-$	6.0e7×0.05	T
157	$PYRAC^{*-} + O_2 \rightarrow PYRACOO^{*-}$	5e1	C
158	$2PYRACOO^{*-} \rightarrow 2PYRACO^{*-} + O_2$	3e8×0.95	L’, e
159	$2PYRACOO^{*-} \rightarrow HOPYRAC^- + OPYRAC^- + O_2$	3e8×0.05	L’, e
160	$PYRACO^{*-} \rightarrow HCHO + GLYAC^{*-} + O_2$	I	Gi, e
161	$PYRACO^{*-} \rightarrow {}^*HOPYRAC^-$	1e7	Gi, e
162	$HOPYRAC \leftrightarrow HOPYRAC^- + H^+$	K_{eq} = 3.2e-3 k_r = 2e10	e
163	$OPYRAC \leftrightarrow OPYRAC^- + H^+$	K_{eq} = 3.2e-3 k_r = 2e10	e
164	$HOPYRAC^- + OH \rightarrow {}^*HOPYRAC^- + H_2O$	2.6e9	H
165	$^*HOPYRAC^- + O_2 \rightarrow {}^*OOHOPYRAC^-$	1e6	G, L’
166	$^*OOHOPYRAC^- \rightarrow OPYRAC^- + HO_2$	5e1	C
167	$OPYRAC^- + OH \rightarrow {}^*OPYRAC^- + H_2O$	5e7	M
168	$^*OPYRAC^- + O2 \rightarrow {}^*OO(O)PYRAC^-$	1e6	G, L’
169	$^*OO(O)PYRAC^- \rightarrow MOXLAC^- + HO_2$	5e1	C
170	$MOXLAC + OH \rightarrow GLYAC^* + CO_2 + H_2O$	5.7e7	Gl
171	$MOXLAC^- + OH \rightarrow GLYAC^{*-} + CO_2 + H_2O$	7.85e7	e
172	$MOXLAC^{-2} + OH \rightarrow GLYAC^{*-} + CO_2 + OH^-$	1.0e8	H
173	$MOXLAC \leftrightarrow MOXLAC^- + H^+$	K_{eq} = 3.16e-3 k_r = 5e10	H
174	$MOXLAC^- \leftrightarrow MOXLAC^{-2} + H^+$	K_{eq} = 1.5e-2	V

		k_r = 5e10	
175	$CH_3CO_2H + OH \rightarrow *CH_2CO_2H + H_2O$	1.36e7	T
176	$CH_3CO_2H + OH \rightarrow CO_2 + HCHO + HO_2 + H_2O$	2.40e6	T
177	$*CH_2CO_2H + O_2 \rightarrow *OOCH_2CO_2H$	1e6	G, L’
178	$2*OOCH_2CO_2H \rightarrow 2*OCH_2CO_2H + O_2$	3e8*0.95	L’, e
179	$2*OOCH_2CO_2H \rightarrow GLYAC + GCOLAC + O_2$	3e8*0.05	L’, e
180	$*OCH_2CO_2H \rightarrow 2CO_2 + 2HCHO$	I	Gi, e
181	$*OCH_2CO_2H \rightarrow GCOLAC*$	1e7	Gi, e
182	$CH_3CO_2H \leftrightarrow CH_3CO_2^- + H^+$	K_{eq} = 1.75e-5 k_r = 5.0e10	T
183	$CH_3CO_2^- + OH \rightarrow *CH_2CO_2^- + H_2O$	7.23e7	T
184	$CH_2CO_2^- + OH \rightarrow CO_2 + HCHO + HO_2 + OH^-$	1.28e7	T
185	$*CH_2CO_2^- + O_2 \rightarrow *OOCH_2CO_2^-$	1e6	G, L’
186	$2*OOCH_2CO_2n1 \rightarrow 2*OCH_2CO_2 + O_2$	3e8×0.95	L’, e
187	$2*OOCH_2CO_2^- \rightarrow GLYAC^- + GCOLAC^- + O2$	3e8×0.05	L’, e
188	$*OCH_2CO_2^- \rightarrow 2CO_2^- + 2HCHO$	I	Gi, e
189	$*OCH_2CO_2^- \rightarrow GCOLAC*^-$	1e7	Gi, e
190	$H_2O \leftrightarrow H^+ + OH^-$	K_{eq} = 1.0e-14 k_r = 1.4e11	T
191	$HO_2 \leftrightarrow H^+ + O_2^-$	K_{eq} = 1.6e-5 k_r = 5.0e10	T
192	$HCO_2H + OH \rightarrow *COOH + H_2O$	1e8	T
193	$HCO_2^- + OH \rightarrow CO_2^- + H_2O$	2.4e9	T
194	$HCO_2H \leftrightarrow H^+ + HCO_2^-$	K_{eq} = 1.77e-4 k_r = 5.0e10	T
195	$GLYAC + H_2O_2 \rightarrow HCO_2H + CO_2 + H_2O$	0.3	T
196	$PYRAC + H_2O_2 \rightarrow CH_2CO_2H + H_2O + CO_2$	0.11	T
197	$PYRAC^- + H_2O_2 \rightarrow CH_2CO_2^- + H_2O + CO_2$	0.11	T
198	$MOXLAC + H_2O_2 \rightarrow OXLAC + CO_2 + H_2O$	0.5	T
199	$MOXLAC^- + H_2O_2 \rightarrow OXLAC^- + CO_2 + H_2O$	0.5	T
200	$HCO_2H + OH \rightarrow COOH + H_2O$	1e8	T
201	$HCO_2^- + OH \rightarrow CO_2^- + H_2O$	2.4e9	T
202	$HCO_2H \leftrightarrow H^+ + HCO_2^-$	K_{eq} = 1.77e-4 k_r = 5.0e10	T
203	$2*CHOHOH \rightarrow GLY$	1.3e9	G, L’
204	$*CHOHOH + *COOH \rightarrow GLYAC$	1.3e9	G, L’
205	$2*COOH \rightarrow OXLAC$	1.3e9	G, L’
206	$C3D \leftrightarrow MA + H2O$	K_{eq} = 1e5 k_r = 1e-8	L’
207	$MA + OH \rightarrow C3D* + H_2O$	1.6e7	E
208	$TA + OH \rightarrow C4D* + H_2O$	3.1e8	M
209	$2*COOH \rightarrow OXLAC$	1.3e9	G, L’
210	$CO_2^- + *COOH \rightarrow OXLAC^-$	1.3e9	G, L’
211	$2CO_2^- \rightarrow OXLAC^{-2}$	1.3e9	G, L’
212	$PYRAC^- \rightarrow 0.45CH_3CO_2^-$ [b]	1e-4 [b]	C, e
213	$GCOLACOO* + HO_2 \rightarrow GCOLACOOH + O_2$	3e6 [c]	e
214	$GCOLACOO*^- + HO_2 \rightarrow GCOLACOOH^- + O_2$	3e6 [c]	e
215	$*OOMGLY + HO_2 \rightarrow HOOMGLY + O_2$	3e6 [c]	e
216	$PYRACOO* + HO_2 \rightarrow PYRACOOH + O_2$	3e6 [c]	e
217	$PYRACOO*^- + HO_2 \rightarrow PYRACOOH^- + O_2$	3e6 [c]	e
218	$*OOCH2COOH + HO_2 \rightarrow HOOCH2COOH + O_2$	3e6 [c]	e

219	*OOCH2COO$^-$ + HO_2 → HOOCH2COO$^-$ + O_2	3e6 [c]	e
220	GCOLACOOH + OH → products	6e8[d]	e
221	GCOLACOOH$^-$ + OH → products	6e8[d]	e
222	HOOMGLY + OH → products	7e8[d]	e
223	PYRACOOH + OH → products	6e7[d]	e
224	PYRACOOH$^-$ + OH → products	6e7[d]	e
225	HOOCH2COOH + OH → products	1.4e7[d]	e
226	MGLY ↔ DeMGLY[e]	K_{eq} = 2700 k_r = 6	M S
227	DeMGLY + OH → MGLY* + H_2O	7e8×0.92[f]	T
228	DeMGLY + OH → *MGLY + H_2O	7e8×0.08[f]	T
229	ROOH + DeMGLY ↔ PHA	K_{eq} = 6.25[g] k_r = 1.6e-4[g]	L", T'
230	ROOH → RO* + OH	k = 1.1e-4[h]	e
231	PHA + OH → products	7e8[i]	T
232	OH_g ↔ OH	K_{eq} = 30[j] k_r = 3.5e5[k]	L W
233	HO_{2g} ↔ HO_2	K_{eq} = 4e3[l] k_r = 4.2e5[m]	L W
234	$ROOH_g$[n] ↔ ROOH	Keq = 1000 [o] kr = 5.7e2[p]	L W

[a]Trans = Transmittance = $10^{-18.4 \times 0.80 \times [H_2O_2]}$; * = radical (e.g., glyoxal* = glyoxal radical); *[n] = radical type n (e.g., GLYCOLAC*[1] = glycolic acid radical type 1); O* (or *O) = alkoxy radical ; OO* (or *OO) = peroxy radical; CnD = C_n dimer (e.g., C2D = C_2 dimer); X_g = X in the gas phase (e.g., O_{2g} = O_2 in the gas phase); MGLY = methylglyoxal, PYRAC = pyruvic acid, GLYAC = glyoxylic acid, GLYCOL = glycolaldehyde, GLYCOLAC = glycolic acid, LA = lactic acid, MOXLAC = mesoxalic acid, OXLAC = oxalic acid; n = n[th] order; K_{eq} = the equilibrium constant (M), k_r = the reverse rate constant for corresponding K_{eq}., Thus, the forward rate constant can be calculated by $K_{eq} \times k_r$; (g) = in the gas phase; I (= the decomposition rate constant from alkoxy radicals) = 5e6 s^{-1} for ~10μM acetic acid/methylglyoxal, 8e6 s^{-1} for ~10^2 μM acetic acid/methylglyoxal, and 2e7 s^{-1} for ~10^3μM acetic acid/ 3.2e7 s^{-1} for ~10^3μM methylglyoxal; [b] PYRAC is assumed to photolyze to produce only 45% acetic acid with 5 times slower than the literature value (Carlton et al., 2006). [c]The rate constant for ROO* + HO_2 is assumed to be similar to that for HO_2 + HO_2 (ROO* = peroxy radical). [d] The rate constant for ROOH + OH is assumed to be that of the parent organic compound + OH (e.g. GCOLAC + OH for GCOLACOOH + OH). [d] DeMGLY = dehydrated MGLY (containing an aldehyde moiety). Therefore, MGLY is a hydrated form of methylglyoxal. [f] The rate constant for DeMGLY + OH is assumed to be the same as that for MGLY + OH. [g]The rate constant for the formation of peroxyhemiacetals is assumed to be 1e-3, which is the acid catalysis rate constant on aerosol surface (Lim and Ziemann, PCCP, 2009). k_r is from unpublished data from Tran and Ziemann (2006). Therefore, K_{eq} = 1e-3/1.6e-4 = 6.25. [h]The ROOH photolysis rate is assumed to be the same as the H2O2 photolysis rate. [i]The rate constant for PHA + OH is assumed to be the same as that for MGLY + OH. [j]Henry's law constant for OH. [k]diffusion-controlled transfer coefficient for OH. However, these j and k values are changed to maintain ~1e-14 M of OH; otherwise, OH is ~1e-12 M. [l]Henry's law constant for OH_2. [m]diffusion-controlled transfer coefficient for OH_2. [n]It is assumed that $[ROOH]_g$ = 1ppb. [o]Henry's law constant for ROOH. [p]diffusion-controlled transfer coefficient for ROOH (based on the estimation by Lim et al, 2005).

Reference

T = Tan et al., 2009, 2010 and 2012
G = Guzman et al., JPCA, 2006
C = Carter et al., JPC, 1979
H = Herrmann et al., AE, 2005
E = Ervens et al., PCCP, 2003
M = Monod et al., AE, 2005, 2008

L = Lim et al.,EST, 2005
L' = Lim et al., ACP, 2010
W = Warneck, PCCP, 1999
E&C = Eyal and Canari, Ind. Eng. Chem. Res., 1995
B = Buxton et al., JPCRD, 1988
Gi = Gilbert et al., 1976 and 1981
V = Volgger et al., J. Chrom. A, 1997
e = Estimation
S = Sareen et al., PNAS, 2013
L" = Lim and Ziemann, PCCP, 2009
T' = Tran and Ziemann, unpublished data, 2006
(http://gcep.host.ualr.edu/Archives/2006/2006FinalWorkshop/2006TTran.pdf)

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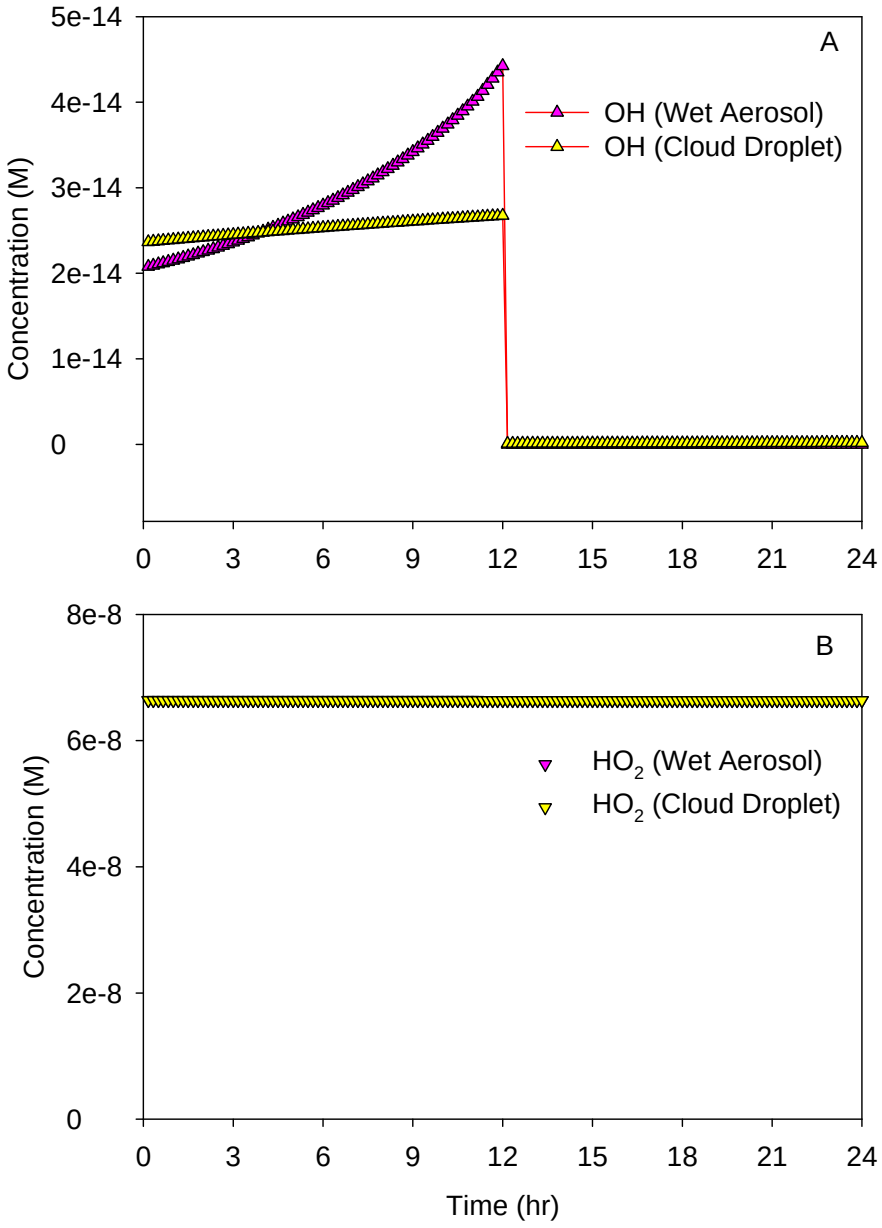


Fig. S1. The atmospheric simulated concentrations of OH (A) and HO_2 (B) in wet aerosols and cloud droplets for 24 hours (The first 12 hrs are daytime)

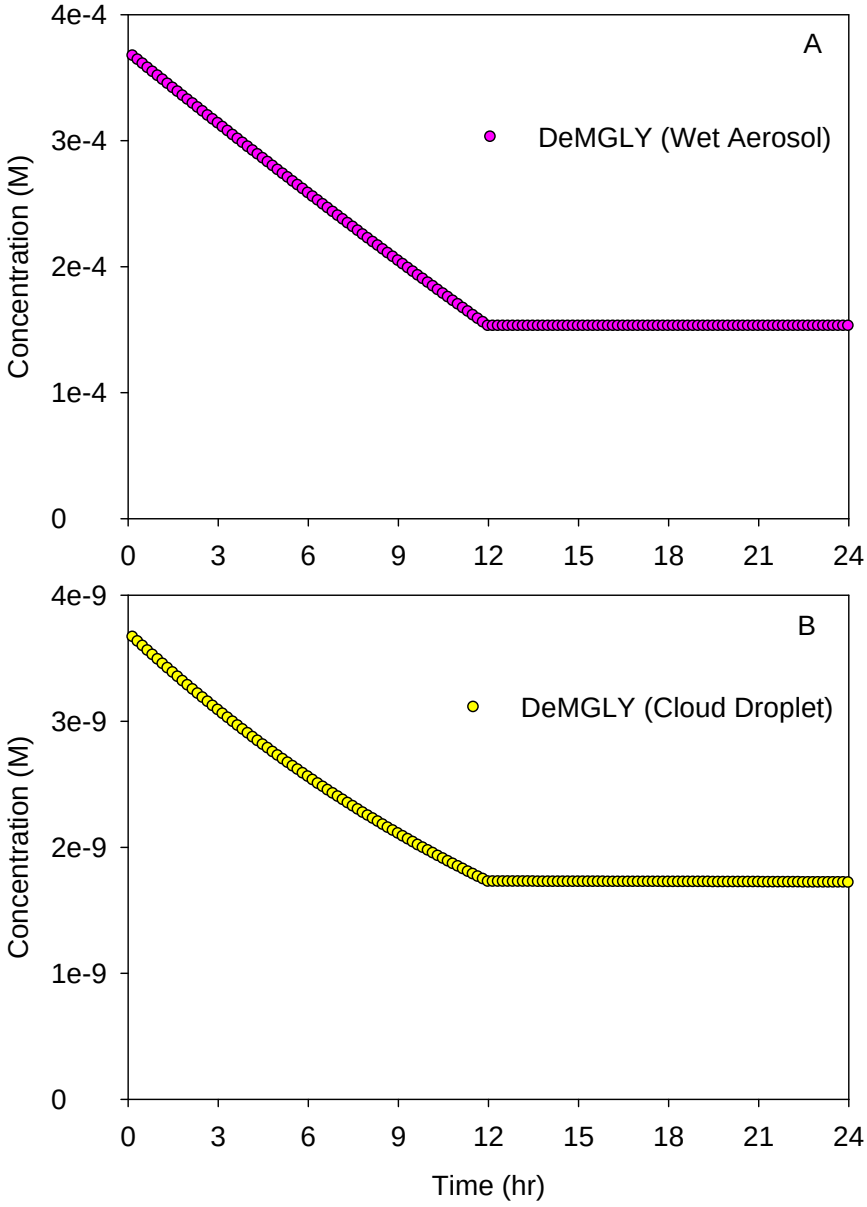


Fig. S2. The atmospheric simulated concentrations of DeMGLY (dehydrated methylglyoxal) in wet aerosols (A) and cloud droplets (B) for 24 hours (The first 12 hrs are daytime)

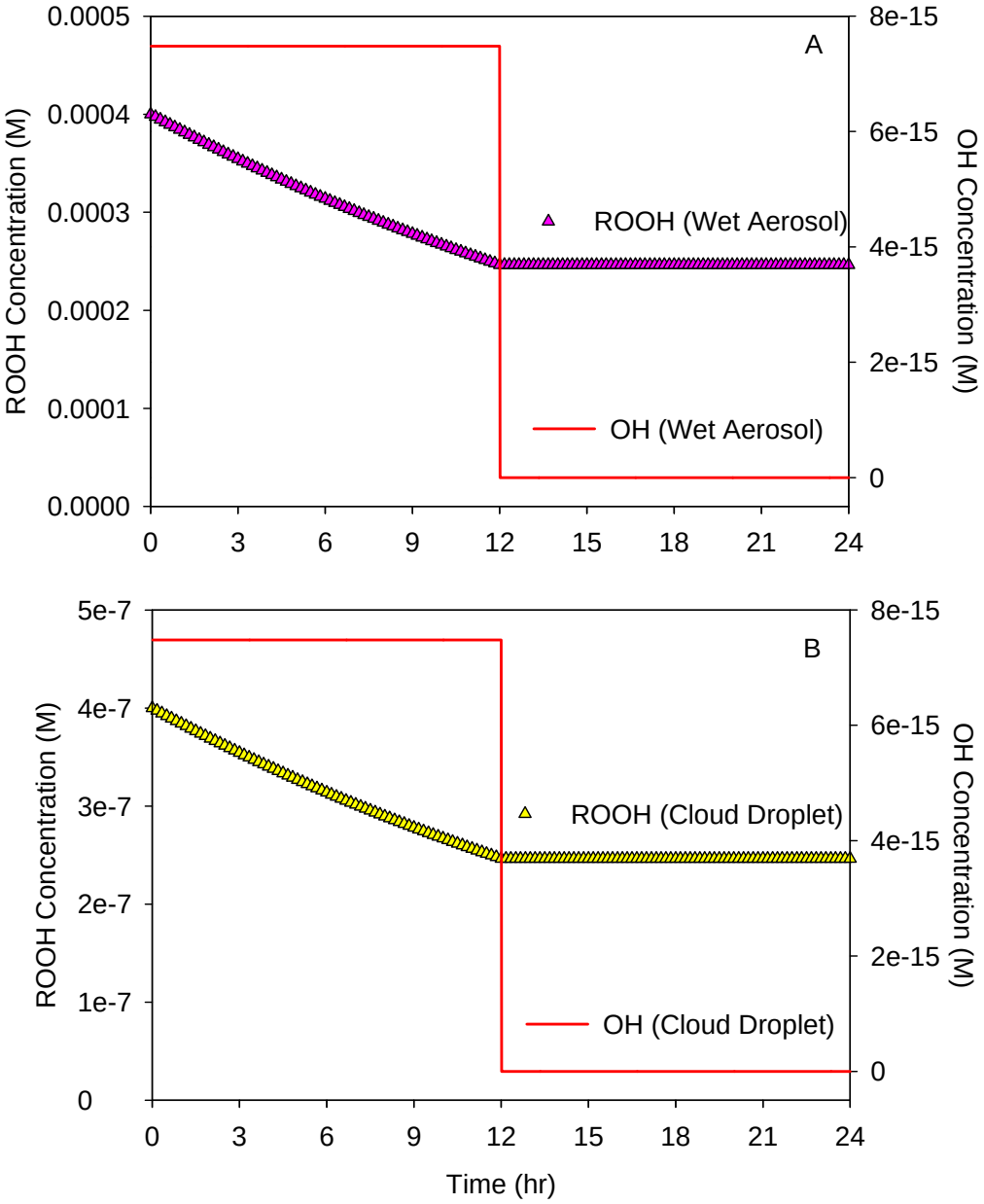


Fig. S3. The atmospheric simulated concentrations of ROOH and OH in wet aerosols (A) and cloud droplets (B) for 24 hours (The first 12 hrs are daytime)

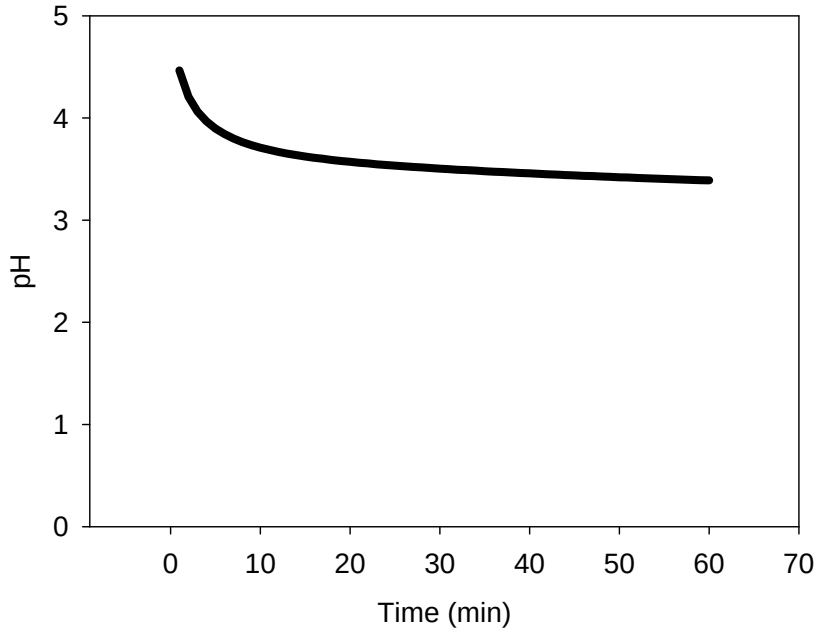


Fig. S4. pH simulation during photooxidation of methylglyoxal for 60 minutes

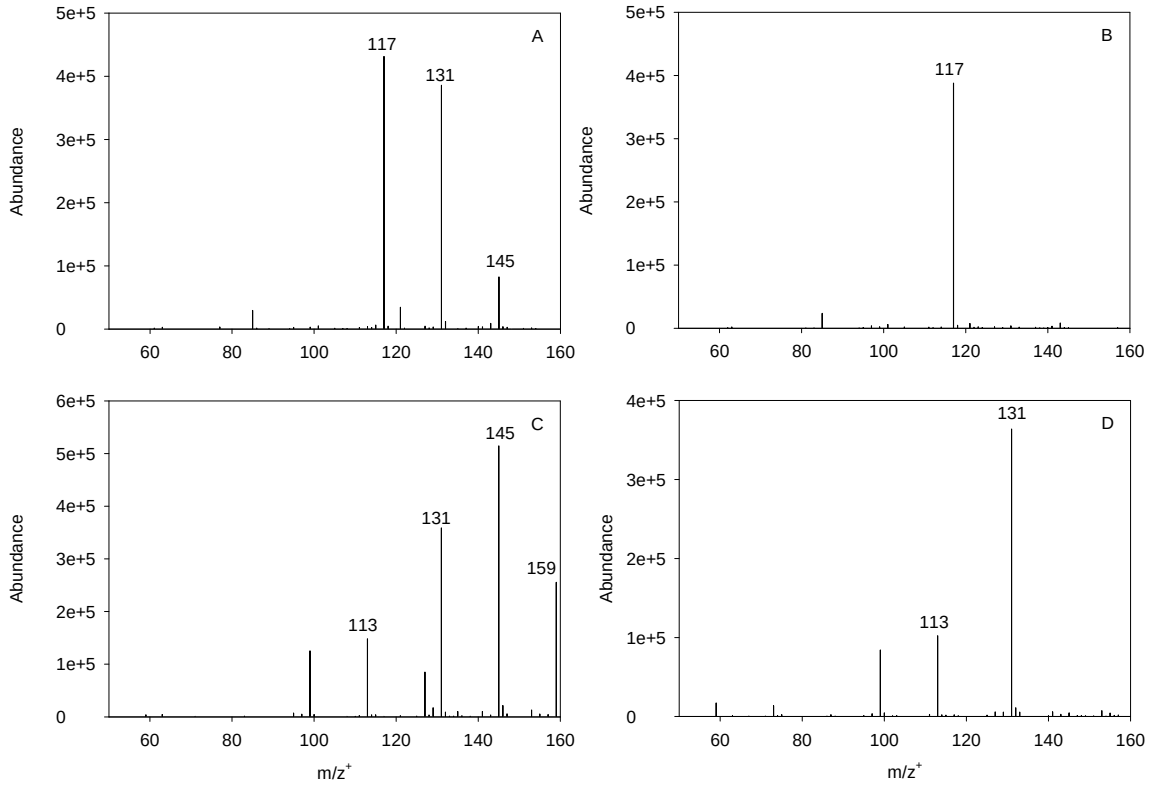
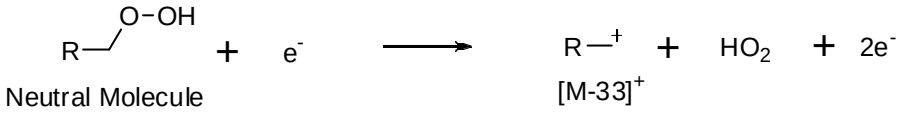


Fig. S5. The positive mode ESI-MS spectra for glyoxal in 50% MeOH/50% water (A) and 100% water (B), and methylglyoxal in 50% MeOH/50% water (C) and 100% water (D)

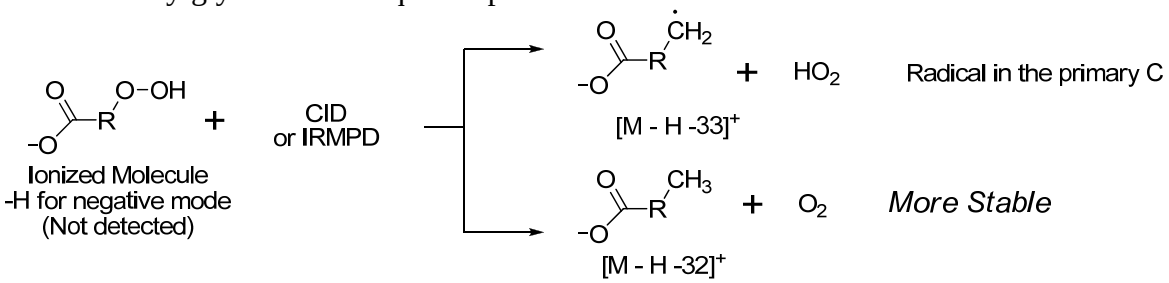
Fragmentation of organic (hydro)peroxide: *HO_2 loss vs. O_2 loss*
In the electron impact ionization method from a themal desorption particle beam mass spectrometer, HO_2 loss from an organic peroxide is well established (Tobias and Ziemann, 2000).



Scheme S1

In the electrospray ionization method from FTICR-MS/MS, however, we propose O_2 loss from an organic peroxide in both positive and negative modes.

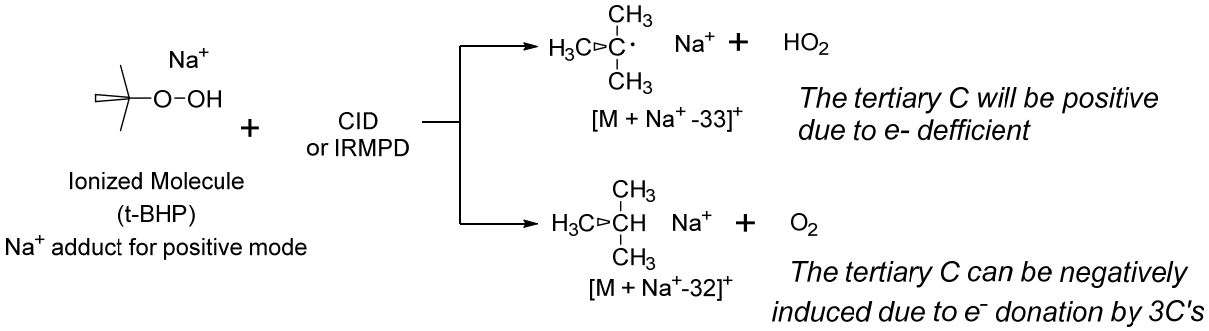
A. Negative mode for a photochemically produced organic peroxide from methylglyoxal in the aqueous phase



Scheme S2

The HO_2 loss fragment will have a radical on the primary carbon. However, the O_2 loss fragment will have no radical, yet will be still ionized molecule. Thus O_2 loss fragment is more stable than HO_2 loss fragment and will be detected in FTICR-MS/MS.

B. Positive mode for t-butyl hydroperoxide (t-BHP)



Scheme S3

The HO_2 loss fragment will have a radical on the tertiary carbon and will be positive due to electron deficiency. Na^+ will be repelled, so the HO_2 fragment will not be detected. However, the O_2 loss fragment will have no radical and be negatively induced due to electron donation by three neighboring carbons. Since Na^+ will be still attached, the O_2 fragment will be detected in FTICR-MS/MS.