The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxy radical

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Supplementary material

Table S1. Mechanisms for the OH oxidation of isoprene in the box model.

Fig. S1. Time series of products in the aqueous isoprene-OH reaction under the condition of 1.5 L top space in the 2.1 L reactor.

Fig.S2. Experiments 1 and 2 (green and blue) for the kinetics of aqueous OH-initiated oxidation of isoprene (ISO), methacrolein (MACR), and methyl vinyl ketone (MVK) relative to salicylic acid at 283 K. (a) ISO/SA; (b) MACR/SA; (c) MVK/SA.

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Table S1. Mechanisms for the OH oxidation of isoprene in the box model.

NO	Reaction	Initial Rate constant (M^{-1} s^{-1})	Adjusted Rate constant (M^{-1} s^{-1})
1	$H_2O_2 + h\nu \rightarrow 2 \cdot OH$	2.2×10^{-5} (s^{-1})	2.2×10^{-5} (s^{-1})
2	$H_2O_2 + \cdot OH \rightarrow HO_2 \cdot + H_2O$	2.7×10^{7}	2.7×10^{7}
3	$HO_2 \cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH$	3.7	3.7
4	$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$	8.3×10^{5}	8.3×10^{5}
5	$\text{isoprene} + \cdot OH \rightarrow R1O_2$	1.8×10^{9}	1.8×10^{9}
6	$\text{isoprene} + \cdot OH \rightarrow R2O_2$	5.4×10^{9}	5.4×10^{9}
7	$\text{isoprene} + \cdot OH \rightarrow R3O_2$	6.0×10^{8}	6.0×10^{8}
8	$\text{isoprene} + \cdot OH \rightarrow R4O_2$	6.0×10^{8}	6.0×10^{8}
9	$\text{isoprene} + \cdot OH \rightarrow R5O_2$	9.6×10^{8}	9.6×10^{8}

10	isoprene + $\cdot OH \rightarrow R6O_2$	2.6×10^{9}	2.6×10^{9}
11	$R1O_2 + R1O_2 \rightarrow R1O + R1O + O_2$	1.4×10^{8}	1.4×10^{8}
12	$R2O_2 + R2O_2 \rightarrow R2O + R2O + O_2$	4.2×10^{6}	4.2×10^{8}
13	$R3O_2 + R3O_2 \rightarrow R3O + R3O + O_2$	1.7×10^{8}	1.7×10^{8}
14	$R4O_2 + R4O_2 \rightarrow R4O + R4O + O_2$	1.7×10^{8}	1.7×10^{8}
15	$R5O_2 + R5O_2 \rightarrow R5O + R5O + O_2$	1.0×10^{8}	1.0×10^{8}
16	$R6O_2 + R6O_2 \rightarrow R6O + R6O + O_2$	2.8×10^{8}	2.8×10^{8}
17	$R1O_2 + R2O_2 \rightarrow R1O + R2O + O_2$	1.2×10^{8}	2.0×10^{8}
18	$R1O_2 + R3O_2 \rightarrow R1O + R3O + O_2$	1.7×10^{8}	1.7×10^{8}
19	$R1O_2 + R4O_2 \rightarrow R1O + R4O + O_2$	1.7×10^{8}	1.7×10^{8}
20	$R1O_2 + R5O_2 \rightarrow R1O + R5O + O_2$	1.2×10^{8}	1.2×10^{8}
21	$R1O_2 + R6O_2 \rightarrow R1O + R6O + O_2$	1.7×10^{8}	1.7×10^{8}
22	$R2O_2 + R3O_2 \rightarrow R2O + R3O + O_2$	1.2×10^{8}	2.2×10^{8}

23	$R2O_2 + R4O_2 \rightarrow R2O + R4O + O_2$	1.2×10^{8}	2.2×10^{8}
24	$R2O_2 + R5O_2 \rightarrow R2O + R5O + O_2$	1.2×10^{8}	2.2×10^{8}
25	$R2O_2 + R6O_2 \rightarrow R2O + R6O + O_2$	1.7×10^{8}	2.6×10^{8}
26	$R3O_2 + R4O_2 \rightarrow R3O + R4O + O_2$	1.7×10^{8}	1.7×10^{8}
27	$R3O_2 + R5O_2 \rightarrow R3O + R5O + O_2$	1.3×10^{8}	1.3×10^{8}
28	$R3O_2 + R6O_2 \rightarrow R3O + R6O + O_2$	2.2×10^{8}	2.2×10^{8}
29	$R4O_2 + R5O_2 \rightarrow R4O + R5O + O_2$	1.3×10^{8}	1.3×10^{8}
30	$R4O_2 + R6O_2 \rightarrow R4O + R6O + O_2$	2.2×10^{8}	2.2×10^{8}
31	$R5O_2 + R6O_2 \rightarrow R5O + R6O + O_2$	1.7×10^{8}	1.7×10^{8}
32	$R1O_2 + R1O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + O_2$	9.2×10^{7}	9.2×10^{7}
33	$R3O_2 + R3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + O_2$	1.2×10^{8}	1.2×10^{8}
34	$R4O_2 + R4O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + O_2$	1.2×10^{8}	1.2×10^{8}
35	$R5O_2 + R5O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + O_2$	6.5×10^{7}	6.5×10^{7}

36	$R6O_2 + R6O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	6.9×10^{7}	6.9×10^{7}
37	$R1O_2 + R2O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	2.9×10^{7}	4.0×10^{7}
38	$R1O_2 + R3O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	1.1×10^{8}	1.1×10^{8}
39	$R1O_2 + R4O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	1.1×10^{8}	1.1×10^{8}
40	$R1O_2 + R5O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	7.7×10^{7}	7.7×10^{7}
41	$R1O_2 + R6O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	7.0×10^{7}	7.0×10^{7}
42	$R2O_2 + R3O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	3.1×10^{7}	5.7×10^{7}
43	$R2O_2 + R4O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	3.1×10^{7}	5.7×10^{7}
44	$R2O_2 + R5O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	2.9×10^{7}	5.3×10^{7}
45	$R2O_2 + R6O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	1.9×10^{7}	3.5×10^{7}
46	$R3O_2 + R4O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	1.2×10^{8}	1.2×10^{8}
47	$R3O_2 + R5O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	8.7×10^{7}	8.7×10^{7}
48	$R3O_2 + R6O_2 \rightarrow C_5$ alcohol + C_5 carbonyl + O_2	9.3×10^{7}	9.3×10^{7}

49	$R4O_2 + R5O_2 \rightarrow C_5\ \text{alcohol} + C_5\ \text{carbonyl} + O_2$	8.7×10^{7}	8.7×10^{7}
50	$R4O_2 + R6O_2 \rightarrow C_5\ \text{alcohol} + C_5\ \text{carbonyl} + O_2$	9.3×10^{7}	9.3×10^{7}
51	$R5O_2 + R6O_2 \rightarrow C_5\ \text{alcohol} + C_5\ \text{carbonyl} + O_2$	7.0×10^{7}	7.0×10^{7}
52	$R1O_2 + HO_2 \rightarrow R1OOH + O_2$	9.8×10^{8}	9.8×10^{8}
53	$R2O_2 + HO_2 \rightarrow R2OOH + O_2$	9.8×10^{8}	9.8×10^{8}
54	$R3O_2 + HO_2 \rightarrow R3OOH + O_2$	9.8×10^{8}	9.8×10^{8}
55	$R4O_2 + HO_2 \rightarrow R4OOH + O_2$	9.8×10^{8}	9.8×10^{8}
56	$R5O_2 + HO_2 \rightarrow R5OOH + O_2$	9.8×10^{8}	9.8×10^{8}
57	$R6O_2 + HO_2 \rightarrow R6OOH + O_2$	9.8×10^{8}	9.8×10^{8}
58	$MVKAOO + R1O_2 \rightarrow 0.3*MACR + 0.3*MVK + 0.6*MG + HCHO + 1.2*HO_2$	3.0×10^{6}	3.0×10^{6}
59	$MVKAOO + R2O_2 \rightarrow 0.3*MACR + 0.3*MVK + 0.6*MG + HCHO + 1.2*HO_2$	3.0×10^{6}	3.0×10^{6}
60	$MVKAOO + R3O_2 \rightarrow 0.3*MACR + 0.3*MVK + 0.6*MG + HCHO + 1.2*HO_2$	3.0×10^{6}	3.0×10^{6}
61	$MVKAOO + R4O_2 \rightarrow 0.3*MACR + 0.3*MVK + 0.6*MG + HCHO + 1.2*HO_2$	3.0×10^{6}	3.0×10^{6}

62	$MVKAOO + R5O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
63	$MVKAOO + R6O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
64	$MVKBOO + R1O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
65	$MVKBOO + R2O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
66	$MVKBOO + R3O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
67	$MVKBOO + R4O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
68	$MVKBOO + R5O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
69	$MVKBOO + R6O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
70	$MACRAOO + R1O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
71	$MACRAOO + R2O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
72	$MACRAOO + R3O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
73	$MACRAOO + R4O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
74	$MACRAOO + R5O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}

75	$MACRAOO + R6O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
76	$MACRBOO + R1O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
77	$MACRBOO + R2O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
78	$MACRBOO + R3O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
79	$MACRBOO + R4O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
80	$MACRBOO + R5O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
81	$MACRBOO + R6O_2 \rightarrow 0.3 * MACR + 0.3 * MVK + 0.6 * MG + HCHO + 1.2 * HO_2$	3.0×10^{6}	3.0×10^{6}
82	$R1O_2 \rightarrow C_5H_8O_2$	3.3×10^{5}	3.3×10^{5}
83	$R5O_2 \rightarrow C_5H_8O_2$	3.3×10^{5}	3.3×10^{5}
84	$R1OOH + OH \rightarrow C_5H_8O_2 + OH$	6.4×10^{9}	6.4×10^{9}
85	$R5OOH + OH \rightarrow C_5H_8O_2 + OH$	6.4×10^{9}	6.4×10^{9}
86	$R1OOH \rightarrow C_5H_8O_2 + HO_2 + OH$	5.8×10^{-6}	5.8×10^{-6}
87	$R5OOH \rightarrow C_5H_8O_2 + HO_2 + OH$	5.8×10^{-6}	5.8×10^{-6}

88	$C_5H_8O_2 + OH \rightarrow 0.52 * C_5H_9O_5$	2.7×10^{9}	2.7×10^{9}
89	$C_5H_9O_5 \rightarrow 0.73 * MG + 0.27 * GL$	1.3×10^{4}	1.3×10^{4}
90	$C_5H_9O_5 + HO_2 \rightarrow C_5H_9O_5H$	1.2×10^{9}	1.2×10^{9}
91	$C_5H_9O_5H + OH \rightarrow C_5H_9O_5$	1.9×10^{9}	1.9×10^{9}
92	$C_5H_9O_5H \rightarrow 0.5 * MG + 0.5 * GL$	5.8×10^{-6}	5.8×10^{-6}
93	$R1O + O_2 \rightarrow C_5\,\text{carbonyl} + HO_2$	1.0×10^{5}	1.0×10^{5}
94	$R1O \rightarrow C_5\,\text{carbonyl} + HO_2$	1.0×10^{5}	1.0×10^{5}
95	$R2O + O_2 \rightarrow MVK + HCHO + HO_2$	7.5×10^{4}	7.5×10^{4}
96	$R2O \rightarrow MVK + HCHO + HO_2$	7.5×10^{4}	7.5×10^{4}
97	$R2O + O_2 \rightarrow HMVK + CH_3O_2$	2.5×10^{4}	2.5×10^{4}
98	$R2O \rightarrow HMVK + CH_3O_2$	2.5×10^{4}	2.5×10^{4}
99	$R3O + O_2 \rightarrow MVK + HCHO + HO_2$	5.0×10^{4}	5.0×10^{4}
100	$R3O \rightarrow MVK + HCHO + HO_2$	5.0×10^{4}	5.0×10^{4}

101	$R3O + O_2 \rightarrow MF + HCHO + HO_2$	2.5×10^{4}	2.5×10^{4}
102	$R3O \rightarrow MF + HCHO + HO_2$	2.5×10^{4}	2.5×10^{4}
103	$R4O + O_2 \rightarrow MACR + HCHO + HO_2$	5.0×10^{4}	5.0×10^{4}
104	$R4O \rightarrow MACR + HCHO + HO_2$	5.0×10^{4}	5.0×10^{4}
105	$R4O + O_2 \rightarrow MF + HCHO + HO_2$	2.5×10^{4}	2.5×10^{4}
106	$R4O \rightarrow MF + HCHO + HO_2$	2.5×10^{4}	2.5×10^{4}
107	$R5O + O_2 \rightarrow C_5\,\text{carbonyl} + HO_2$	1.0×10^{5}	1.0×10^{5}
108	$R5O \rightarrow C_5\,\text{carbonyl} + HO_2$	1.0×10^{5}	1.0×10^{5}
109	$R6O + O_2 \rightarrow MACR + HCHO + HO_2$	1.0×10^{5}	1.0×10^{5}
110	$R6O \rightarrow MACR + HCHO + HO_2$	1.0×10^{5}	1.0×10^{5}
111	$CH_3O_2 + O_2 \rightarrow HO_2 + HCHO$	1.0×10^{5}	1.0×10^{5}
112	$R1O_2 + CH_3O_2 \rightarrow R1O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
113	$R1O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}

114	$R2O_2 + CH_3O_2 \rightarrow R2O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
115	$R2O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}
116	$R3O_2 + CH_3O_2 \rightarrow R3O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
117	$R3O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}
118	$R4O_2 + CH_3O_2 \rightarrow R4O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
119	$R4O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}
120	$R5O_2 + CH_3O_2 \rightarrow R5O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
121	$R5O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}
122	$R6O_2 + CH_3O_2 \rightarrow R6O + CH_3O + O_2$	6.0×10^{7}	6.0×10^{7}
123	$R6O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	6.0×10^{7}	6.0×10^{7}
124	$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$	7.3×10^{5}	7.3×10^{5}
125	$CH_3O_2 + CH_3O_2 \rightarrow C_5\,\text{alcohol} + C_5\,\text{carbonyl} + HCHO + O_2$	1.5×10^{6}	1.5×10^{6}
126	$MACR + \cdot OH \rightarrow 0.5 * CH_2(OH)C\cdot(CH_3)CHO + 0.5 * \cdot CH_2C(OH)(CH_3)CHO$	1.3×10^{10}	1.3×10^{10}

127	$MVK + \cdot OH \rightarrow 0.7 * CH_2(OH)C \cdot HC(O)CH_3 + 0.3 * CH_2CH(OH)C(O)CH_3$	1.2×10^{10}	1.2×10^{10}
128	$CH_2(OH)C \cdot (CH_3)CHO + O_2 \rightarrow CH_2(OH)C(OO\cdot)(CH_3)CHO$	3.2×10^{9}	3.2×10^{9}
129	$\cdot CH_2C(OH)(CH_3)CHO + O_2 \rightarrow \cdot OOCH_2C(OH)(CH_3)CHO$	1.8×10^{9}	1.8×10^{9}
130	$CH_2(OH)C \cdot HC(O)CH_3 + O_2 \rightarrow CH_2(OH)C(OO\cdot)HC(O)CH_3$	3.2×10^{9}	3.2×10^{9}
131	$\cdot CH_2CH(OH)C(O)CH_3 + O_2 \rightarrow \cdot OOCH_2CH(OH)C(O)CH_3$	1.8×10^{9}	1.8×10^{9}
132	$2 * CH_2(OH)C(OO\cdot)(CH_3)CHO \rightarrow O_2 + 0.8 * CH_2(OH)C(O)CH_3 + 0.8 * CHO + CH_3C(O)CHO + CH_2OH + 0.2 * CH_2(OH)C(O)CHO + 0.2 * CH_3$	4.0×10^{7}	4.0×10^{7}
133	$2 * OOCH_2C(OH)(CH_3)CHO \rightarrow 2OHCC(OH)(CH_3)CHO + H_2O_2$	2.0×10^{8}	2.0×10^{8}
134	$2 * OOCH_2C(OH)(CH_3)CHO \rightarrow OHCC(OH)(CH_3)CHO + CH_2(OH)C(OH)(CH_3)CHO + O_2$	2.0×10^{8}	2.0×10^{8}
135	$2 * OOCH_2C(OH)(CH_3)CHO \rightarrow 2 * HCHO + 2 * CH_3C \cdot (OH)CHO + O_2$	4.0×10^{7}	4.0×10^{7}
136	$\cdot CHO + O_2 \rightarrow CO_2 + \cdot OH$	4.5×10^{9}	4.5×10^{9}
137	$2 * \cdot CHO \rightarrow HCHO + HCOOH$	3.0×10^{8}	3.0×10^{8}
138	$CH_3C \cdot (OH)CHO + O_2 \rightarrow CH_3C(OO\cdot)(OH)CHO$	2.0×10^{9}	2.0×10^{9}

139	$2*CH_3C(OO\cdot)(OH)CHO \rightarrow 0.8*CH_3COOH + 0.8*\cdot CHO + 0.8*OHCCOOH + 0.8*\cdot CH_3 + 0.2*CH_3C(O)CHO + 0.2*\cdot OH$	1.0×10^{8}	1.0×10^{8}
140	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow 2*CH_2(OH)C(O)C(O)CH_3 + H_2O_2$	1.0×10^{8}	1.0×10^{8}
141	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow CH_2(OH)C(O)C(O)CH_3 + CH_2(OH)CH(OH)C(O)CH_3 + O_2$	1.0×10^{8}	1.0×10^{8}
142	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow O_2 + 0.6*\cdot CH_2OH + 0.6*CH_3C(O)CHO + 1.4*CH_2(OH)CHO + 1.4*CH_3CO\cdot$	8.0×10^{7}	8.0×10^{7}
143	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow 2*OHCCH(OH)C(O)CH_3 + H_2O_2$	1.0×10^{8}	1.0×10^{8}
144	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow OHCCH(OH)C(O)CH_3 + CH_2(OH)CH(OH)C(O)CH_3 + O_2$	1.0×10^{8}	1.0×10^{8}
145	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow 2*HCHO + 2*CH_3C(O)C\cdot H(OH) + O_2$	8.0×10^{7}	8.0×10^{7}
146	$CH_3CO\cdot + O_2 \rightarrow CH_3CO_3\cdot$	5.0×10^{9}	5.0×10^{9}
147	$2*CH_3CO_3\cdot \rightarrow O_2 + 2CO_2 + 2\cdot CH_3$	1.0×10^{7}	1.0×10^{7}
148	$CH_3CO\cdot + \cdot OH \rightarrow CH_3COOH$	1.0×10^{9}	1.0×10^{9}
149	$2*CH_3CO\cdot \rightarrow CH_3COCOCH_3$	1.0×10^{9}	1.0×10^{9}
150	$CH_3CO_3\cdot + CH_3O_2\cdot \rightarrow O_2 + HCHO + CH_3COOH$	1.7×10^{8}	1.7×10^{8}

151	$CH_2(OH)CHO + \cdot OH \rightarrow CH_2(OH)COOH + HO_2\cdot + H_2O$	5.0×10^{8}	5.0×10^{8}
152	$CH_2(OH)COOH + \cdot OH \rightarrow \cdot CH(OH)COOH + H_2O$	5.4×10^{8}	5.4×10^{8}
153	$\cdot CH(OH)COOH + O_2 \rightarrow \cdot OOCH(OH)COOH$	2.0×10^{9}	2.0×10^{9}
154	$\cdot OOCH(OH)COOH + H_2O \rightarrow CH(OH)_2COOH + HO_2\cdot$	52	52
155	$CH(OH)_2COOH + \cdot OH \rightarrow HOOCCOOH + HO_2\cdot + H_2O$	3.6×10^{8}	3.6×10^{8}
156	$CH_2(OH)CHO + \cdot OH \rightarrow (OH)_2CHCH(OH)_2 + HO_2\cdot$	1.0×10^{9}	1.0×10^{9}
157	$CH(OH)_2COOH + H_2O_2 \rightarrow HCOOH + CO_2 + H_2O$	0.3	0.3
158	$(OH)_2CHCH(OH)_2 + \cdot OH \rightarrow CHOCOOH + HO_2\cdot$	1.1×10^{9}	1.1×10^{9}
159	$CH_3C(O)CH(OH)\cdot + O_2 \rightarrow CH_3C(O)CH(OH)OO\cdot$	2.0×10^{9}	2.0×10^{9}
160	$CH_3C(O)CH(OH)OO\cdot \rightarrow CH_3C(O)CHO + HO_2$	2.1×10^{2}	2.1×10^{2}
161	$2 * CH_3C(O)CH(OH)OO\cdot \rightarrow 2 * CH_3C(O)COOH + H_2O_2$	3.5×10^{8}	3.5×10^{8}
162	$CHOCOOH + \cdot OH \rightarrow HOOCCOOH + HO_2\cdot + H_2O$	1.2×10^{9}	1.2×10^{9}
163	$HCHO + H_2O \rightarrow CH_2(OH)_2$	0.18 (F) 5.1×10^{-3}	0.18 (F) 5.1×10^{-3}

		(B)	(B)
164	$CH_2(OH)_2 + \cdot OH \rightarrow H_2O + HO_2\cdot + HCOOH$	1.0×10^{9}	1.0×10^{9}
165	$HCOOH \leftrightarrow HCOO^- + H^+$	8.9×10^{6} (F) 5.0×10^{10} (B)	8.9×10^{6} (F) 5.0×10^{10} (B)
166	$HCOOH + \cdot OH \rightarrow H_2O + HO_2\cdot + CO_2$	1.3×10^{8}	1.3×10^{8}
167	$HCOO^- + \cdot OH \rightarrow OH^- + HO_2\cdot + CO_2$	4.0×10^{9}	4.0×10^{9}
168	$CH_3C(O)CHO + H_2O \leftrightarrow CH_3C(O)CH(OH)_2$	21.5 (F) 0.5 (B)	21.5 (F) 0.5 (B)
169	$CH_3C(O)CH(OH)_2 + OH \rightarrow CH_3C(O)C(OH)_2\cdot + H_2O$	1.1×10^{9}	1.1×10^{9}
170	$CH_3C(O)C(OH)_2\cdot + O_2 \rightarrow CH_3C(O)C(OH)_2OO\cdot$	2.0×10^{9}	2.0×10^{9}
171	$CH_3C(O)C(OH)_2OO\cdot \rightarrow CH_3C(O)COOH + HO_2\cdot$	1.0×10^{7}	1.0×10^{7}
172	$CH_3C(O)COOH \leftrightarrow CH_2C(O)COO^- + H^+$	1.8×10^{8} (F) 5.0×10^{10} (B)	1.8×10^{8} (F) 5.0×10^{10} (B)
173	$CH_3C(O)COO^- + h\nu \leftrightarrow CH_3COO^-$	5.0×10^{-4} (s^{-1})	5.0×10^{-4} (s^{-1})

174	$CH_3C(O)COO^- + H_2O_2 \leftrightarrow CH_3COO^- + H_2O + CO_2$	0.11	0.11
175	$CH_3C(O)COOH + \cdot OH \rightarrow \cdot CH_2C(O)COOH + H_2O$	1.2×10^{8}	1.2×10^{8}
176	$\cdot CH_2C(O)COOH + O_2 \rightarrow \cdot O_2CH_2C(O)COOH$	1.9×10^{7}	1.9×10^{7}
177	$2*\cdot O_2CH_2C(O)COOH \rightarrow 2*OHCC(O)COOH + H_2O_2$	2.0×10^{7}	2.0×10^{7}
178	$CH_3COOH \leftrightarrow CH_3COO^- + H^+$	8.8×10^{5} (F) 5.0×10^{10} (B)	8.8×10^{5} (F) 5.0×10^{10} (B)
179	$CH_3COOH + \cdot OH \leftrightarrow HOOCCOOH$	1.6×10^{7}	1.6×10^{7}
180	$CH_3COO^- + \cdot OH \rightarrow HOOCCOO^-$	8.5×10^{7}	8.5×10^{7}
181	$HOOCCOOH + \cdot OH \rightarrow 2*CO_2 + H_2O + HO_2\cdot$	1.4×10^{6}	1.4×10^{6}
182	$HOOCCOO^- + \cdot OH \rightarrow 2*CO_2 + H_2O + O_2^-\cdot$	4.7×10^{7}	4.7×10^{7}
183	$HOOCCOOH \leftrightarrow HOOCCOO^- + H^+$	3.2×10^{9} (F) 5.0×10^{10} (B)	3.2×10^{9} (F) 5.0×10^{10} (B)
184	$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$	4.1×10^{9}	4.1×10^{9}

185	$CH_3O_2\cdot + CH_3O_2\cdot \rightarrow CH_3OH + HCHO + O_2$	1.7×10^{8}	1.7×10^{8}
186	$\cdot CH_2OH + O_2 \rightarrow \cdot OOCH_2OH$	2.0×10^{9}	2.0×10^{9}
187	$2* \cdot OOCH_2OH \rightarrow CH_3OH + HCHO + O_2$	1.1×10^{9}	1.1×10^{9}

The formula or description of the simplified name in Table.1 are as follows:

Name	Formula/description	Name	Formula/description
$R1O_2$	$HOCH_2C(CH_3)=CHCH_2OO\cdot$	R5O	$\cdot OCH_2C(CH_3)=CHCH_2OH$
$R2O_2$	$HOCH_2C(CH_3)(OO\cdot)CH=CH_2$	R6O	$CH_2=C(CH_3)CH(O\cdot)CH_2OH$
$R3O_2$	$CH_2=CHC(CH_3)(OH)CH_2OO\cdot$	MACAOO	$CH_2(OH)C(OO\cdot)(CH_3)CHO$
$R4O_2$	$CH_2=C(CH_3)CH(OH)CH_2OO\cdot$	MACBOO	$\cdot OOCH_2C(OH)(CH_3)CHO$
$R5O_2$	$\cdot OOCH_2C(CH_3)=CHCH_2OH$	MVKAOO	$CH_2(OH)C(OO\cdot)HC(O)CH_3$
$R6O_2$	$CH_2=C(CH_3)CH(OO\cdot)CH_2OH$	MVKBOO	$\cdot OOCH_2CH(OH)C(O)CH_3$
R1O	$HOCH_2C(CH_3)=CHCH_2O\cdot$	HMVK	$CH_2(OH)C\cdot HC(O)CH_3$ $CH_2CH(OH)C(O)CH_3$
R2O	$HOCH_2C(CH_3)(O\cdot)CH=CH_2$	$C_5H_8O_2$	Carbonyls (internal double bond)

R3O	$CH_2=CHC(CH_3)(OH)CH_2O\cdot$	$C_5H_9O_5$	Peroxy radicals from C_5-hydroxy aldehydes
R4O	$CH_2=C(CH_3)CH(OH)CH_2O\cdot$	$C_5H_9O_5H$	Hydroperoxides from $C_5H_9O_5$

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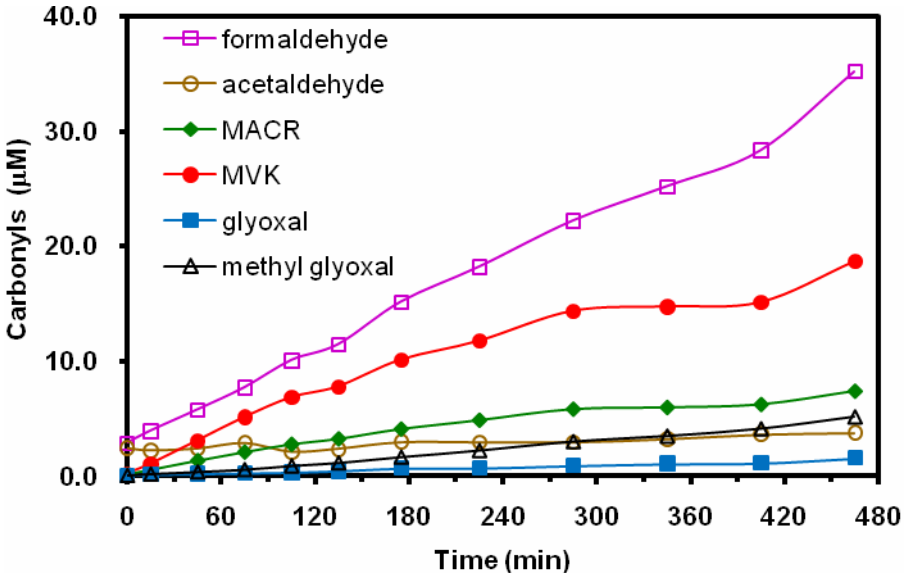

Fig.S1. The time series of products in the aqueous isoprene-OH reaction under the condition of 1.5 L top space in the 2.1 L reactor.

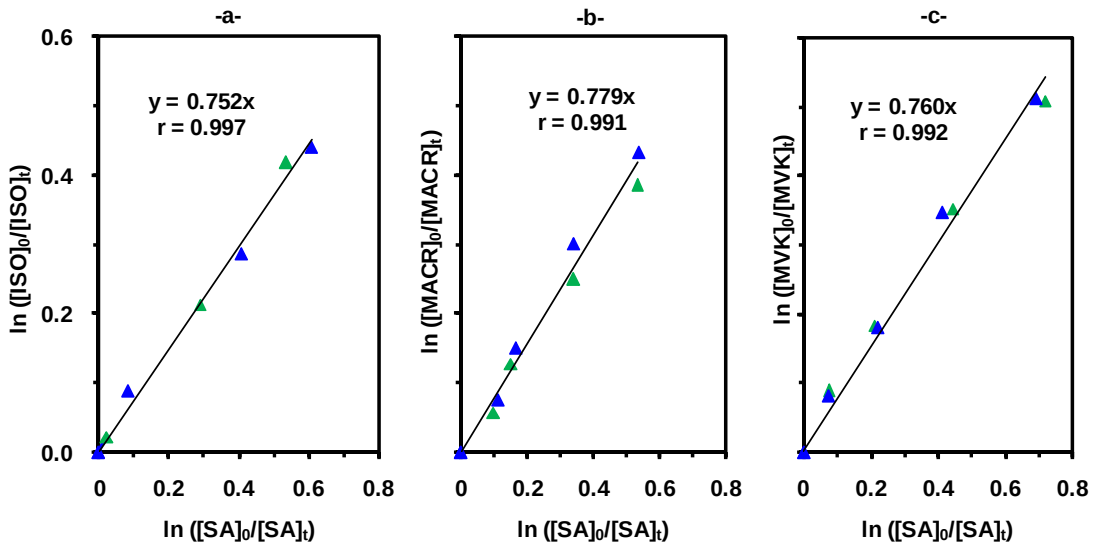

Fig.S2. Experiments 1 and 2 (green and blue) for the kinetics of aqueous OH-initiated oxidation of isoprene (ISO), methacrolein (MACR), and methyl vinyl ketone (MVK) relative to salicylic acid at 283 K. (a) ISO/SA; (b) MACR/SA; (c) MVK/SA.