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 into MACR and MVK 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. The temporal profile of ln[isoprene] and reaction time (t)

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Table S1. Mechanisms for the OH oxidation of isoprene into MACR and MVK in the box model.

NO.	Reaction	Initial Rate constant (M^{-1} s^{-1}) 298 K	Adjusted Rate onstant (M^{-1} s^{-1}) 298 K
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	$isoprene + \cdot OH \rightarrow R1O_2$	5.2×10^{8}	5.2×10^{8}
6	$isoprene + \cdot OH \rightarrow R2O_2$	1.6×10^{9}	1.6×10^{9}
7	$isoprene + \cdot OH \rightarrow R3O_2$	1.8×10^{8}	1.8×10^{8}
8	$isoprene + \cdot OH \rightarrow R4O_2$	1.8×10^{8}	1.8×10^{8}
9	$isoprene + \cdot OH \rightarrow R5O_2$	2.6×10^{7}	2.6×10^{7}

10	$\text{isoprene} + \cdot\text{OH} \rightarrow \text{R6O}_2$	7.9×10^{8}	7.9×10^{8}
11	$\text{R1O}_2 + \text{R1O}_2 \rightarrow \text{R1O} + \text{R1O} + \text{O}_2$	1.4×10^{8}	1.4×10^{8}
12	$\text{R2O}_2 + \text{R2O}_2 \rightarrow \text{R2O} + \text{R2O} + \text{O}_2$	4.2×10^{6}	4.2×10^{8}
13	$\text{R3O}_2 + \text{R3O}_2 \rightarrow \text{R3O} + \text{R3O} + \text{O}_2$	1.7×10^{8}	1.7×10^{8}
14	$\text{R4O}_2 + \text{R4O}_2 \rightarrow \text{R4O} + \text{R4O} + \text{O}_2$	1.7×10^{8}	1.7×10^{8}
15	$\text{R5O}_2 + \text{R5O}_2 \rightarrow \text{R5O} + \text{R5O} + \text{O}_2$	1.0×10^{8}	1.0×10^{8}
16	$\text{R6O}_2 + \text{R6O}_2 \rightarrow \text{R6O} + \text{R6O} + \text{O}_2$	2.8×10^{8}	2.8×10^{8}
17	$\text{R1O}_2 + \text{R2O}_2 \rightarrow \text{R1O} + \text{R2O} + \text{O}_2$	1.2×10^{8}	2.0×10^{8}
18	$\text{R1O}_2 + \text{R3O}_2 \rightarrow \text{R1O} + \text{R3O} + \text{O}_2$	1.7×10^{8}	1.7×10^{8}
19	$\text{R1O}_2 + \text{R4O}_2 \rightarrow \text{R1O} + \text{R4O} + \text{O}_2$	1.7×10^{8}	1.7×10^{8}
20	$\text{R1O}_2 + \text{R5O}_2 \rightarrow \text{R1O} + \text{R5O} + \text{O}_2$	1.2×10^{8}	1.2×10^{8}
21	$\text{R1O}_2 + \text{R6O}_2 \rightarrow \text{R1O} + \text{R6O} + \text{O}_2$	1.7×10^{8}	1.7×10^{8}
22	$\text{R2O}_2 + \text{R3O}_2 \rightarrow \text{R2O} + \text{R3O} + \text{O}_2$	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	$R1O + O_2 \rightarrow C_5\ carbonyl + HO_2$	1.0×10^{5}	1.0×10^{5}
94	$R1O \rightarrow C_5\ carbonyl + HO_2$	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}

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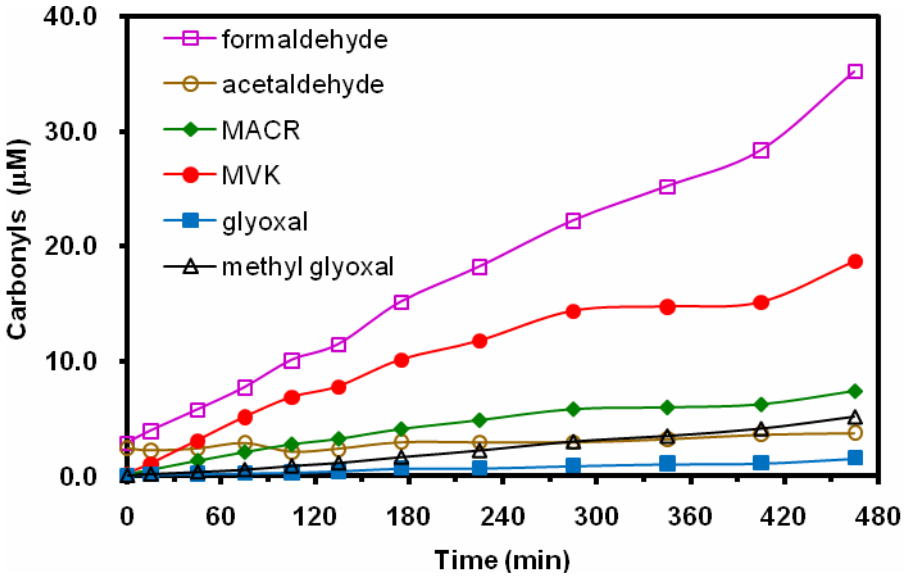

Fig.S1. The time series of products in an aqueous isoprene-OH reaction under the condition of 1.5 L top space in the 2.1 L reactor.

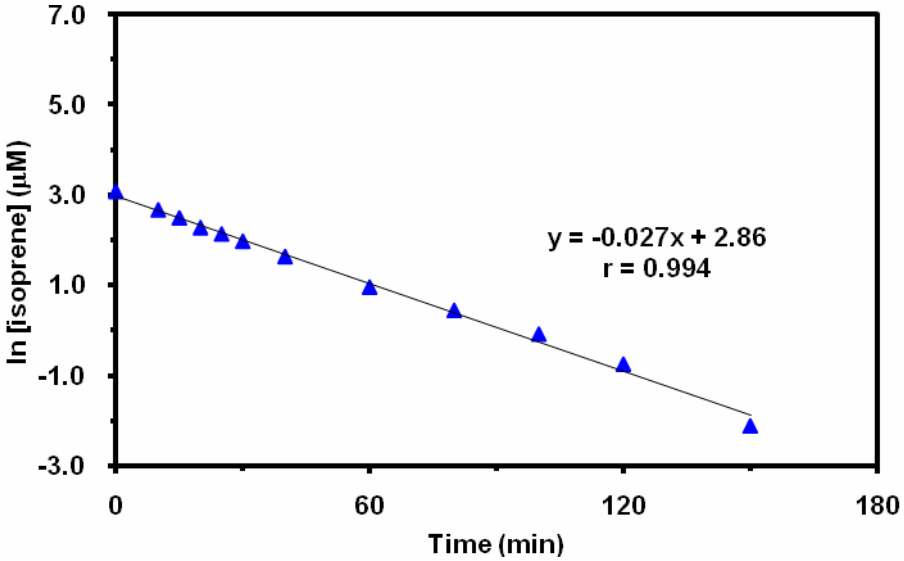

Fig.S2. The temporal profile of isoprene in an aqueous isoprene oxidation