Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: Significance to the in-cloud SOA production

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Supplementary material

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Table S1. Mechanisms for the photooxidation of MACR and MVK in the box model.

No	Reaction	Rate constant (M^{-1} s^{-1}) 298 K	Reference
1	$H_2O_2 + hv \rightarrow 2 \cdot OH$	2.2×10^{-5} (s^{-1}) [a]	Warneck, 1999
2	$H_2O_2 + \cdot OH \rightarrow HO_2 \cdot + H_2O$	2.7×10^{7}	Liao and Gurol, 1995
3	$HO_2 \cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH$	3.7	Liao and Gurol, 1995
4	$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$	8.3×10^{5}	Liao and Gurol, 1995
5	$MACR + \cdot OH \rightarrow 0.5 * CH_2(OH)C \cdot (CH_3)CHO + 0.5 * \cdot CH_2C(OH)(CH_3)CHO$	1.5×10^{9} [b]	Gligorovski et al., 2009
6	$MVK + \cdot OH \rightarrow 0.7 * CH_2(OH)C \cdot HC(O)CH_3 + 0.3 * CH_2CH(OH)C(O)CH_3$	8.0×10^{8} [b]	Fitted
7	$CH_2(OH)C \cdot (CH_3)CHO + O_2 \rightarrow CH_2(OH)C(OO\cdot)(CH_3)CHO$	3.2×10^{9} [c]	Marchaj et al., 1991
8	$\cdot CH_2C(OH)(CH_3)CHO + O_2 \rightarrow \cdot OOCH_2C(OH)(CH_3)CHO$	1.8×10^{9} [c]	Marchaj et al., 1991
9	$CH_2(OH)C \cdot HC(O)CH_3 + O_2 \rightarrow CH_2(OH)C(OO\cdot)HC(O)CH_3$	3.2×10^{9} [c]	Marchaj et al., 1991

10	$\cdot CH_2CH(OH)C(O)CH_3 + O_2 \rightarrow \cdot OOCH_2CH(OH)C(O)CH_3$	1.8×10^{9} [c]	Marchaj et al., 1991
11	$2*CH_2(OH)C(OO\cdot)(CH_3)CHO \rightarrow O_2 + 0.8*CH_2(OH)C(O)CH_3 + 0.8*CHO + CH_3C(O)CHO + CH_2OH + 0.2*CH_2(OH)C(O)CHO + 0.2*CH_3$	4.0×10^{7} [d]	Glowa et al., 2000
12	$2*OOCH_2C(OH)(CH_3)CHO \rightarrow 2OHCC(OH)(CH_3)CHO + H_2O_2$	2.0×10^{8} [d]	Glowa et al., 2000
13	$2*OOCH_2C(OH)(CH_3)CHO \rightarrow OHCC(OH)(CH_3)CHO + CH_2(OH)C(OH)(CH_3)CHO + O_2$	2.0×10^{8} [d]	Glowa et al., 2000
14	$2*OOCH_2C(OH)(CH_3)CHO \rightarrow 2*HCHO + 2*CH_3C\cdot(OH)CHO + O_2$	4.0×10^{7} [d]	Glowa et al., 2000
15	$\cdot CHO + O_2 \rightarrow CO_2 + \cdot OH$	4.5×10^{9}	Hart et al., 1964
16	$2*\cdot CHO \rightarrow HCHO + HCOOH$	3.0×10^{8}	Hart et al., 1964
17	$CH_3C\cdot(OH)CHO + O_2 \rightarrow CH_3C(OO\cdot)(OH)CHO$	2.0×10^{9} [e]	von Sonntag, 1987
18	$2*CH_3C(OO\cdot)(OH)CHO \rightarrow 0.8*CH_3COOH + 0.8*\cdot CHO + 0.8*OHCCOOH + 0.8*\cdot CH_3 + 0.2*CH_3C(O)CHO + 0.2*\cdot OH$	1.0×10^{8} [f]	Glowa et al., 2000
19	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow 2*CH_2(OH)C(O)C(O)CH_3 + H_2O_2$	1.0×10^{8} [d]	Glowa et al., 2000
20	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow CH_2(OH)C(O)C(O)CH_3 + CH_2(OH)CH(OH)C(O)CH_3 + O_2$	1.0×10^{8} [d]	Glowa et al., 2000
21	$2*CH_2(OH)C(OO\cdot)HC(O)CH_3 \rightarrow O_2 + 0.6*\cdot CH_2OH + 0.6*CH_3C(O)CHO + 1.4*CH_2(OH)CHO + 1.4*CH_3CO\cdot$	8.0×10^{7} [d]	Glowa et al., 2000

22	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow 2*OHCCH(OH)C(O)CH_3 + H_2O_2$	1.0×10^{8} [d]	Glowa et al., 2000
23	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow OHCCH(OH)C(O)CH_3 + CH_2(OH)CH(OH)C(O)CH_3 + O_2$	1.0×10^{8} [d]	Glowa et al., 2000
24	$2*\cdot OOCH_2CH(OH)C(O)CH_3 \rightarrow 2*HCHO + 2*CH_3C(O)C\cdot H(OH) + O_2$	8.0×10^{7} [d]	Glowa et al., 2000
25	$CH_3CO\cdot + O_2 \rightarrow CH_3CO_3\cdot$	5.0×10^{9}	Glowa et al., 2000
26	$2*CH_3CO_3\cdot \rightarrow O_2 + 2CO_2 + 2\cdot CH_3$	1.0×10^{7}	Glowa et al., 2000
27	$CH_3CO\cdot + \cdot OH \rightarrow CH_3COOH$	1.0×10^{9}	Glowa et al., 2000
28	$2*CH_3CO\cdot \rightarrow CH_3COCOCH_3$	1.0×10^{9}	Glowa et al., 2000
29	$CH_3CO_3\cdot + CH_3O_2\cdot \rightarrow O_2 + HCHO + CH_3COOH$	1.7×10^{8} [g]	Herrmann et al., 1999
30	$CH_2(OH)CHO + \cdot OH \rightarrow CH_2(OH)COOH + HO_2\cdot + H_2O$	5.0×10^{8}	Warneck, 2003
31	$CH_2(OH)COOH + \cdot OH \rightarrow \cdot CH(OH)COOH + H_2O$	5.4×10^{8}	Scholes and Willson, 1967
32	$\cdot CH(OH)COOH + O_2 \rightarrow \cdot OOCH(OH)COOH$	2.0×10^{9}	Herrmann et al., 2000
33	$\cdot OOCH(OH)COOH + H_2O \rightarrow CH(OH)_2COOH + HO_2\cdot$	52	Herrmann et al., 2000
34	$CH(OH)_2COOH + \cdot OH \rightarrow HOOCCOOH + HO_2\cdot + H_2O$	3.6×10^{8}	Ervens et al., 2003

35	$CH_2(OH)CHO + \cdot OH \rightarrow (OH)_2CHCH(OH)_2 + HO_2\cdot$	1.0×10^{9}	Warneck, 2003
36	$CH(OH)_2COOH + H_2O_2 \rightarrow HCOOH + CO_2 + H_2O$	0.3	Tan et al., 2009
37	$(OH)_2CHCH(OH)_2 + \cdot OH \rightarrow CHOCOOH + HO_2\cdot$	1.1×10^{9}	Buxton et al., 1988
38	$CH_3C(O)CH(OH)\cdot + O_2 \rightarrow CH_3C(O)CH(OH)OO\cdot$	2.0×10^{9}	von Sonntag, 1987 Herrmann et al., 2000
39	$CH_3C(O)CH(OH)OO\cdot \rightarrow CH_3C(O)CHO + HO_2$	2.1×10^{2}	Bothe et al., 1978 Herrmann et al., 2000
40	$2*CH_3C(O)CH(OH)OO\cdot \rightarrow 2*CH_3C(O)COOH + H_2O_2$	3.5×10^{8}	Bothe et al., 1978 Herrmann et al., 2000
41	$CHOCOOH + \cdot OH \rightarrow HOOCCOOH + HO_2\cdot + H_2O$	1.2×10^{9}	Stefan and Bolton, 1999
42	$HCHO + H_2O \rightarrow CH_2(OH)_2$	0.18 (F) 5.1×10^{-3} (B)	Bell and Evans, 1966
43	$CH_2(OH)_2 + \cdot OH \rightarrow H_2O + HO_2\cdot + HCOOH$	1.0×10^{9}	Chin and Wine, 1994
44	$HCOOH \leftrightarrow HCOO^- + H^+$	8.9×10^{6} (F) 5.0×10^{10} (B)	Harned and Owen, 1958 Graedel and Weschler, 1981
45	$HCOOH + \cdot OH \rightarrow H_2O + HO_2\cdot + CO_2$	1.3×10^{8}	Chin and Wine, 1994
46	$HCOO^- + \cdot OH \rightarrow OH^- + HO_2\cdot + CO_2$	4.0×10^{9}	Buxton et al., 1988

47	$CH_3C(O)CHO + H_2O \leftrightarrow CH_3C(O)CH(OH)_2$	21.5 (F) 0.5 (B)	Betterton and Hoffmann, 1988
48	$CH_3C(O)CH(OH)_2 + OH \rightarrow CH_3C(O)C(OH)_2 \cdot + H_2O$	1.1×10^9	Ervens et al., 2003
49	$CH_3C(O)C(OH)_2 \cdot + O_2 \rightarrow CH_3C(O)C(OH)_2OO\cdot$	2.0×10^9	von Sonntag, 1987
50	$CH_3C(O)C(OH)_2OO\cdot \rightarrow CH_3C(O)COOH + HO_2\cdot$	$1.0\times10^{7\,h}$	Buxton et al., 1988
51	$CH_3C(O)COOH \leftrightarrow CH_2C(O)COO^- + H^+$	1.8×10^8 (F) 5.0×10^{10} (B)	Herrmann et al., 2005
52	$CH_3C(O)COO^- + hv \leftrightarrow CH_3COO^-$	5.0×10^{-4} (s^{-1})	Lim et al., 2005
53	$CH_3C(O)COO^- + H_2O_2 \leftrightarrow CH_3COO^- + H_2O + CO_2$	0.11	Carlton et al., 2006
54	$CH_3C(O)COOH + \cdot OH \rightarrow \cdot CH_2C(O)COOH + H_2O$	1.2×10^8	Ervens et al., 2003
55	$\cdot CH_2C(O)COOH + O_2 \rightarrow \cdot O_2CH_2C(O)COOH$	1.9×10^7	Herrmann et al., 2005
56	$2 * \cdot O_2CH_2C(O)COOH \rightarrow 2 * OHCC(O)COOH + H_2O_2$	2.0×10^7	Herrmann et al., 2005
57	$CH_3COOH \leftrightarrow CH_3COO^- + H^+$	8.8×10^5 (F) 5.0×10^{10} (B)	Herrmann et al., 2000
58	$CH_3COOH + \cdot OH \leftrightarrow HOOCCOOH$	1.6×10^7	Stefan et al., 1996
59	$CH_3COO^- + \cdot OH \rightarrow HOOCCOO^-$	8.5×10^7	Stefan et al., 1996

60	$HOOCCOOH + \cdot OH \rightarrow 2*CO_2 + H_2O + HO_2\cdot$	1.4×10^{6}	Buxton et al., 1988
61	$HOOCCOO^{-} + \cdot OH \rightarrow 2*CO_2 + H_2O + O_2^{-}\cdot$	4.7×10^{7}	Buxton et al., 1988
62	$HOOCCOOH \leftrightarrow HOOCCOO^{-} + H^{+}$	3.2×10^{9} (F) 5.0×10^{10} (B)	Meyerstein, 1971
63	$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$	4.1×10^{9}	Marchaj et al., 1991
64	$CH_3O_2\cdot + CH_3O_2\cdot \rightarrow CH_3OH + HCHO + O_2$	1.7×10^{8}	Herrmann et al., 1999
65	$\cdot CH_2OH + O_2 \rightarrow \cdot OOCH_2OH$	2.0×10^{9}	von Sonntag, 1987
66	$2*\cdot OOCH_2OH \rightarrow CH_3OH + HCHO + O_2$	1.1×10^{9}	von Sonntag, 1987

a: Estimated according to the Warneck, 1999 parameterization;
b: The branching ratios were in analogy to those of gas-phase reactions. The rate constant was estimated in analogy to that of MACR;
c: Estimated in analogy to the addition O_2 to 1-C_4H_9 and 2-C_4H_9 radical;
d: Estimated in analogy to the methyl ethyl ketone peroxy radical reaction;
e: Estimated in analogy to isopropanol;
f: Estimated in analogy to the combination of $CH_3C(O_2)(OH)COCH_3$ radical;
g: Estimated in analogy to the combination of CH_3O_2 radical;
h: Estimated in analogy to glyoxal;

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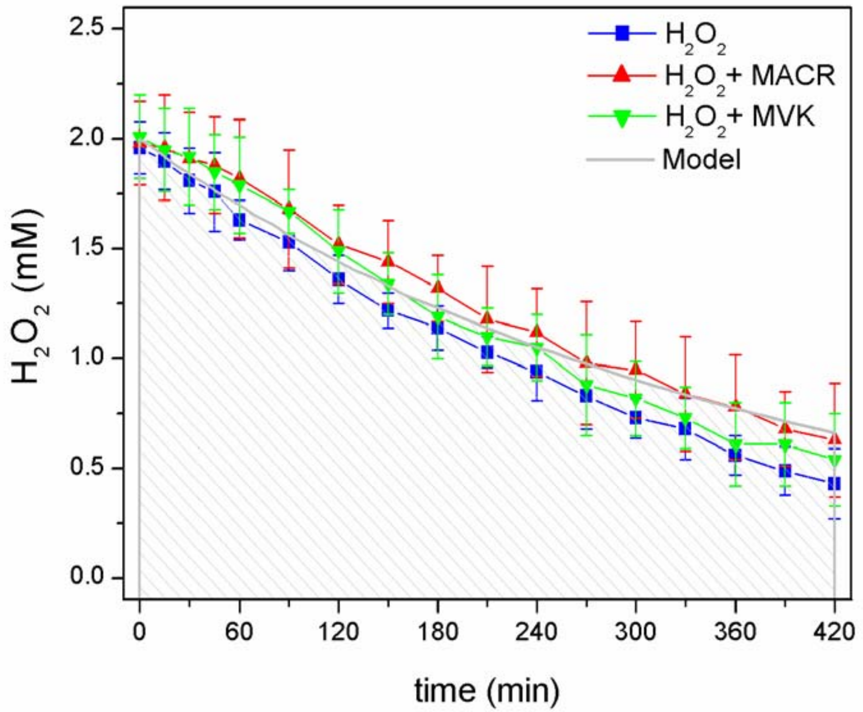

Fig. S1. Direct photolysis of hydrogen peroxide (experimental and simulated data).

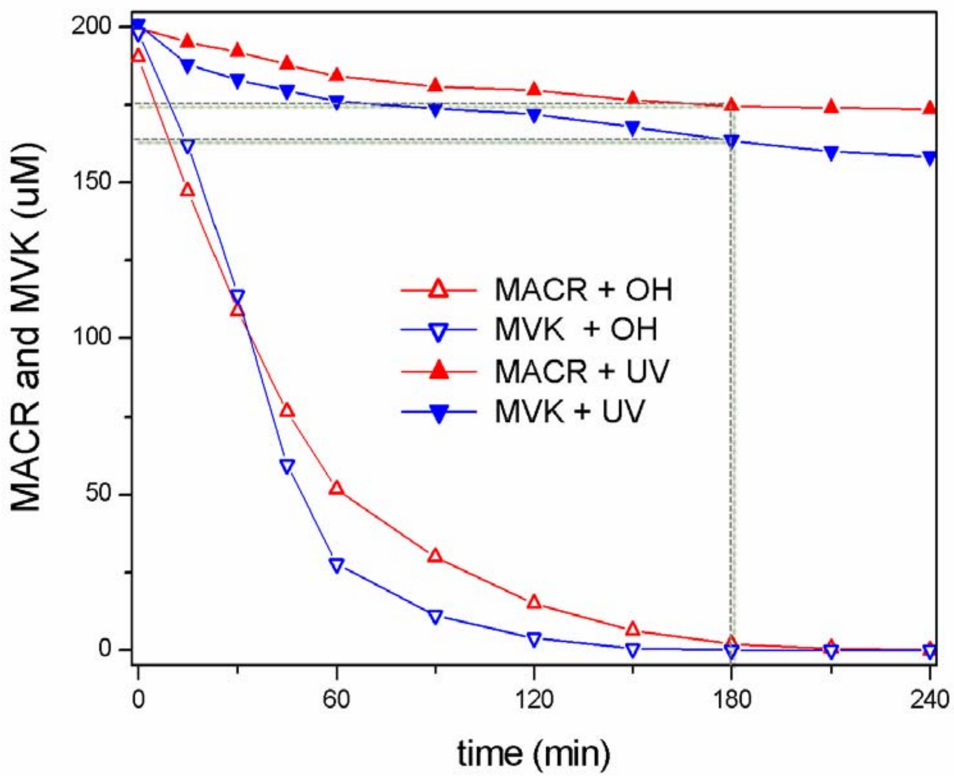

Fig. S2. MACR/MVK decay via UV-photolysis and OH-oxidation.

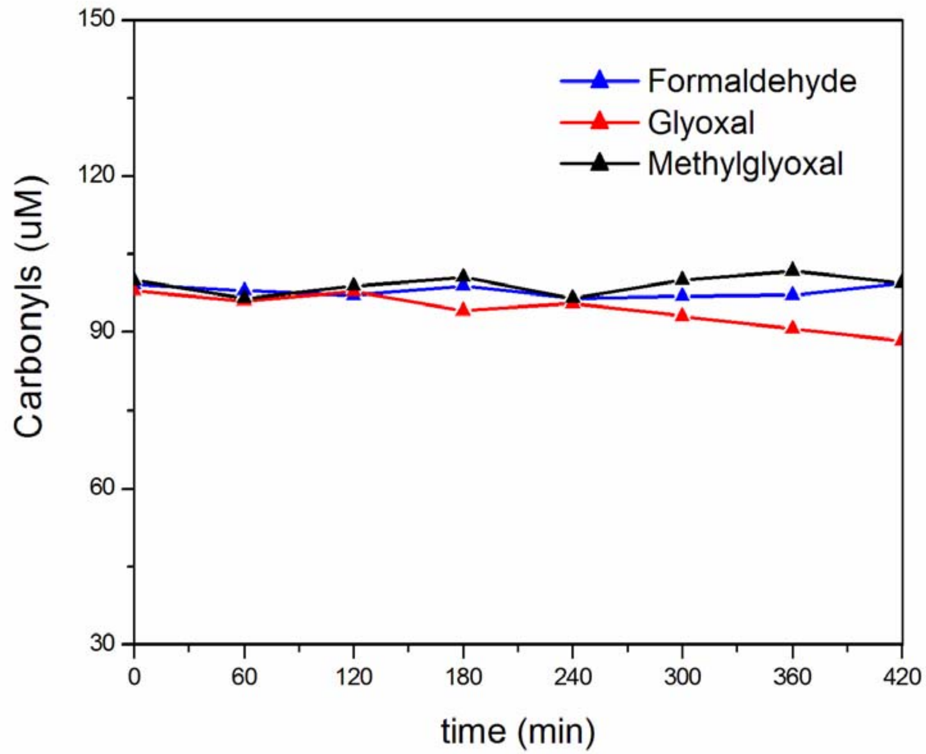

Fig. S3. Time series of standard carbonyls in 2 mM H_2O_2 solution in darkness.

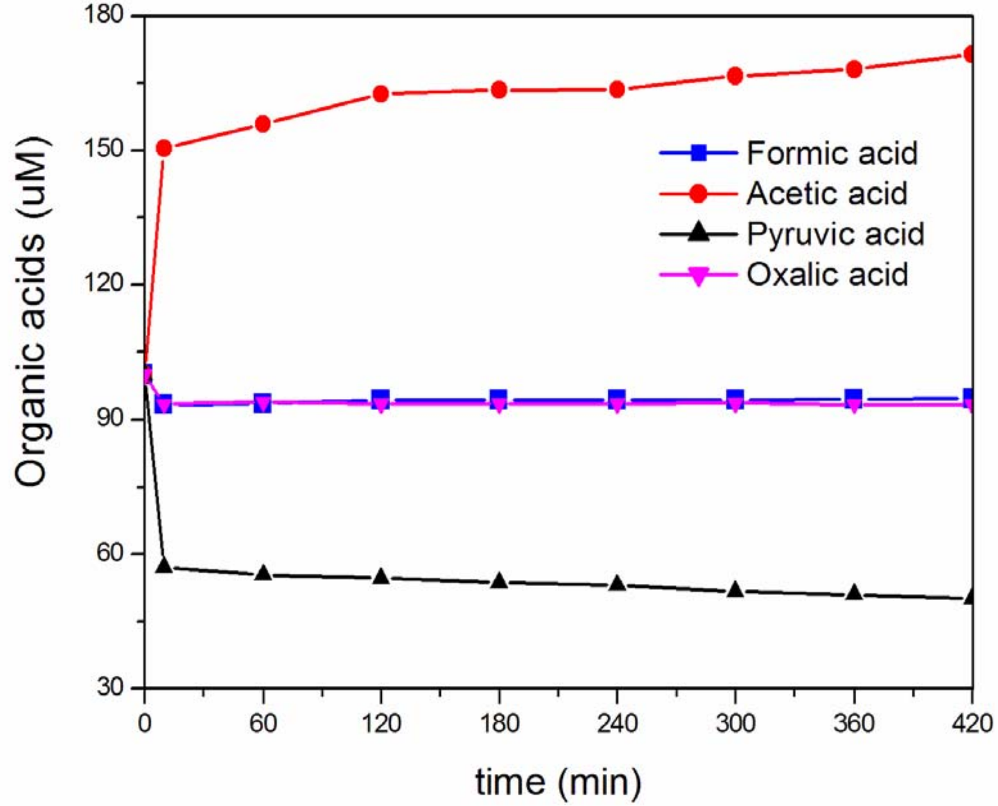

Fig. S4. Time series of standard organic acids in 2 mM H_2O_2 solution in darkness.

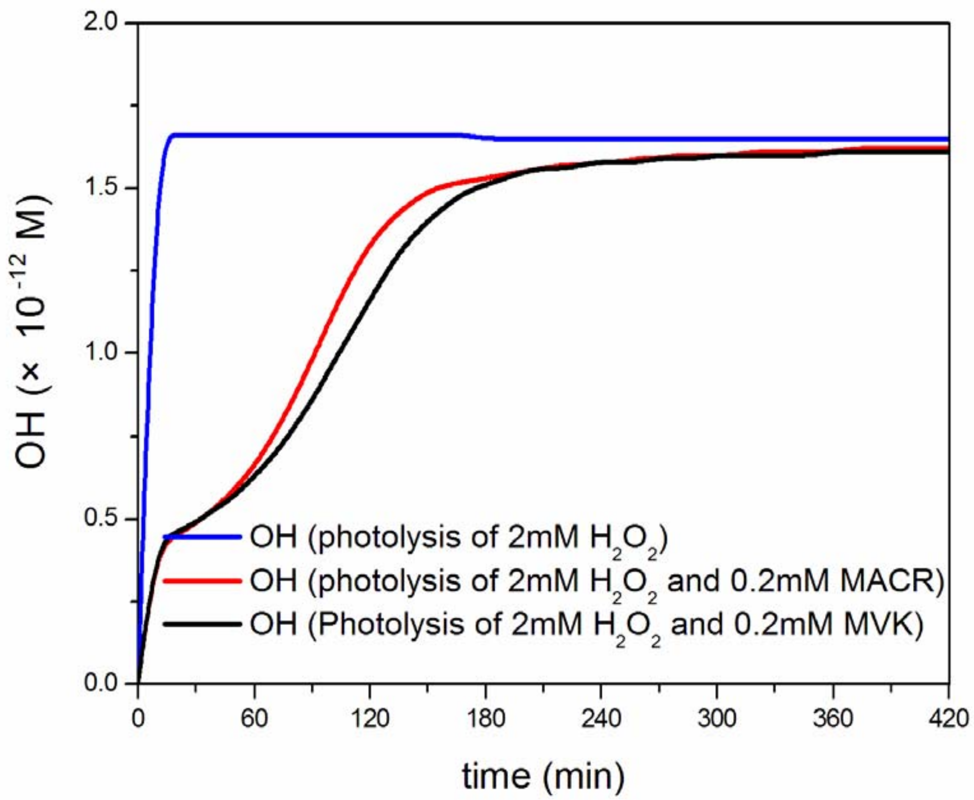

Fig. S5. Modeled OH via H_2O_2 photolysis.