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

X. Zhang, Z. M. Chen*, and Y. Zhao

State Key Laboratory of Environmental Simulation and Pollution Control,
College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

Supplementary material

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

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

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

* Correspondence to: Z.M. Chen
  (zmchen@pku.edu.cn)
<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate constant (M$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}$</td>
<td>$2.2 \times 10^{-5}$ s$^{-1}$</td>
<td>Warneck, 1999</td>
</tr>
<tr>
<td>2</td>
<td>$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{HO}_2 \cdot +\text{H}_2\text{O}$</td>
<td>$2.7 \times 10^7$</td>
<td>Liao and Gurol, 1995</td>
</tr>
<tr>
<td>3</td>
<td>$\text{HO}_2 \cdot +\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \cdot\text{OH}$</td>
<td>$3.7$</td>
<td>Liao and Gurol, 1995</td>
</tr>
<tr>
<td>4</td>
<td>$\text{HO}_2 \cdot +\text{HO}_2 \cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$8.3 \times 10^5$</td>
<td>Liao and Gurol, 1995</td>
</tr>
<tr>
<td>5</td>
<td>$\text{MACR} + \cdot\text{OH} \rightarrow 0.5 \cdot \text{CH}_2(\text{OH})\text{C} \cdot (\text{CH}_3)\text{CHO} + 0.5 \cdot \text{CH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CHO}$</td>
<td>$1.5 \times 10^9$ $^b$</td>
<td>Gligorovski et al., 2009</td>
</tr>
<tr>
<td>6</td>
<td>$\text{MVK} + \cdot\text{OH} \rightarrow 0.7 \cdot \text{CH}_2(\text{OH})\text{C} \cdot \text{HC(O)CH}_3 + 0.3 \cdot \text{CH}_2\text{CH(\text{OH})C(O)CH}_3$</td>
<td>$8.0 \times 10^8$ $^b$</td>
<td>Fitted</td>
</tr>
<tr>
<td>7</td>
<td>$\text{CH}_2(\text{OH})\text{C} \cdot (\text{CH}_3)\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})\text{C(OO-)CH}_3)\text{CHO}$</td>
<td>$3.2 \times 10^9$ $^c$</td>
<td>Marchaj et al., 1991</td>
</tr>
<tr>
<td>8</td>
<td>$\cdot\text{CH}_2\text{C(OH)}(\text{CH}_3)\text{CHO} + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{C(OH)}(\text{CH}_3)\text{CHO}$</td>
<td>$1.8 \times 10^9$ $^c$</td>
<td>Marchaj et al., 1991</td>
</tr>
<tr>
<td>9</td>
<td>$\text{CH}_2(\text{OH})\text{C} \cdot \text{HC(O)CH}_3 + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})\text{C(OO-)HC(O)CH}_3$</td>
<td>$3.2 \times 10^9$ $^c$</td>
<td>Marchaj et al., 1991</td>
</tr>
<tr>
<td>10</td>
<td>$\cdot\text{CH}_2\text{CH(OH)C(O)CH}_3 + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{CH(OH)C(O)CH}_3$</td>
<td>$1.8 \times 10^9$ $^c$</td>
<td>Marchaj et al., 1991</td>
</tr>
</tbody>
</table>
11 \[2 \cdot \text{CH}_2(\text{OH})\text{C(OO)}(\text{CH}_3)\text{CHO} \rightarrow \text{O}_2 + 0.8 \cdot \text{CH}_2(\text{OH})\text{C(O)}\text{CH}_3 + 0.8 \cdot \text{CHO} + \text{CH}_3\text{C(O)CHO} + \text{CH}_2\text{OH} + 0.2 \cdot \text{CH}_2(\text{OH})\text{C(O)CHO} + 0.2 \cdot \text{CH}_3\]
\[4.0 \times 10^7 \] d
Glowa et al., 2000

12 \[2 \cdot \text{OOCH}_2\text{C(OH)}(\text{CH}_3)\text{CHO} \rightarrow 2\text{OHCC(OH)}(\text{CH}_3)\text{CHO} + \text{H}_2\text{O}_2\]
\[2.0 \times 10^8 \] d
Glowa et al., 2000

13 \[2 \cdot \text{OOCH}_2\text{C(OH)}(\text{CH}_3)\text{CHO} \rightarrow \text{OHCC(OH)}(\text{CH}_3)\text{CHO} + \text{CH}_2(\text{OH})\text{C(OH)}(\text{CH}_3)\text{CHO} + \text{O}_2\]
\[2.0 \times 10^8 \] d
Glowa et al., 2000

14 \[2 \cdot \text{OOCH}_2\text{C(OH)}(\text{CH}_3)\text{CHO} \rightarrow 2 \cdot \text{HCHO} + 2 \cdot \text{CH}_3\text{C(OH)CHO} + \text{O}_2\]
\[4.0 \times 10^7 \] d
Glowa et al., 2000

15 \[\cdot \text{CHO} + \text{O}_2 \rightarrow \text{CO}_2 + \cdot \text{OH}\]
\[4.5 \times 10^9 \]
Hart et al., 1964

16 \[2 \cdot \cdot \text{CHO} \rightarrow \text{HCHO} + \text{HCOOH}\]
\[3.0 \times 10^8 \]
Hart et al., 1964

17 \[\text{CH}_3\text{C(OH)CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(OO)O(OH)CHO}\]
\[2.0 \times 10^9 \] e
von Sonntag, 1987

18 \[2 \cdot \text{CH}_3\text{C(OO)O(OH)CHO} \rightarrow 0.8 \cdot \text{CH}_3\text{COOH} + 0.8 \cdot \cdot \text{CHO} + 0.8 \cdot \text{OHCCOOH} + 0.8 \cdot \cdot \text{CH}_3 + 0.2 \cdot \text{CH}_3\text{C(O)CHO} + 0.2 \cdot \cdot \text{OH}\]
\[1.0 \times 10^8 \] f
Glowa et al., 2000

19 \[2 \cdot \text{CH}_2(\text{OH})\text{C(OO)HC(O)CH}_3 \rightarrow 2 \cdot \text{CH}_2(\text{OH})\text{C(O)C(O)CH}_3 + \text{H}_2\text{O}_2\]
\[1.0 \times 10^8 \] d
Glowa et al., 2000

20 \[2 \cdot \text{CH}_2(\text{OH})\text{C(OO)HC(O)CH}_3 \rightarrow \text{CH}_2(\text{OH})\text{C(O)C(O)CH}_3 + \text{CH}_2(\text{OH})\text{CH(OH)C(O)CH}_3 + \text{O}_2\]
\[1.0 \times 10^8 \] d
Glowa et al., 2000

21 \[2 \cdot \text{CH}_2(\text{OH})\text{C(OO)HC(O)CH}_3 \rightarrow \text{O}_2 + 0.6 \cdot \text{CH}_2\text{OH} + 0.6 \cdot \text{CH}_3\text{C(O)CHO} + 1.4 \cdot \text{CH}_2(\text{OH})\text{CHO} + 1.4 \cdot \text{CH}_3\text{CO\cdot}\]
\[8.0 \times 10^7 \] d
Glowa et al., 2000

22 \[2 \cdot \cdot \text{OOCH}_2\text{CH(OH)C(O)CH}_3 \rightarrow 2 \cdot \text{OHCC(HOH)C(O)CH}_3 + \text{H}_2\text{O}_2\]
\[1.0 \times 10^8 \] d
Glowa et al., 2000
23 \[2 \cdot \text{OOC(OH)C(O)CH}_3 \rightarrow \text{OHCCH(OH)C(O)CH}_3 + \text{CH}_2(\text{OH})\text{CH(OH)C(O)CH}_3 + \text{O}_2\] 
\[1.0 \times 10^8 \text{ d}\] 
Glowa et al., 2000

24 \[2 \cdot \text{OOC(OH)C(O)CH}_3 \rightarrow 2 \cdot \text{HCHO} + 2 \cdot \text{CH}_3\text{C(O)C·H(OH)} + \text{O}_2\] 
\[8.0 \times 10^7 \text{ d}\] 
Glowa et al., 2000

25 \[\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO} + \cdot\] 
\[5.0 \times 10^9 \] 
Glowa et al., 2000

26 \[2 \cdot \text{CH}_3\text{CO}_3 + \rightarrow \text{O}_2 + 2\text{CO}_2 + 2 \cdot \text{CH}_3\] 
\[1.0 \times 10^7 \] 
Glowa et al., 2000

27 \[\text{CH}_3\text{CO} + \cdot \text{OH} \rightarrow \text{CH}_3\text{COOH}\] 
\[1.0 \times 10^9 \] 
Glowa et al., 2000

28 \[2 \cdot \text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{COOCH}_3\] 
\[1.0 \times 10^9 \] 
Glowa et al., 2000

29 \[\text{CH}_3\text{CO}_3 + \text{CH}_3\text{O}_2 \rightarrow \text{O}_2 + \text{HCHO} + \text{CH}_3\text{COOH}\] 
\[1.7 \times 10^8 \text{ g}\] 
Herrmann et al., 1999

30 \[\text{CH}_2(\text{OH})\text{CHO} + \cdot \text{OH} \rightarrow \text{CH}_2(\text{OH})\text{COOH} + \text{HO}_2 + \cdot \text{H}_2\text{O}\] 
\[5.0 \times 10^8 \] 
Warneck, 2003

31 \[\text{CH}_2(\text{OH})\text{COOH} + \cdot \text{OH} \rightarrow \cdot \text{CH(OH)COOH} + \text{H}_2\text{O}\] 
\[5.4 \times 10^8 \] 
Scholes and Willson, 1967

32 \[\cdot \text{CH(OH)COOH} + \text{O}_2 \rightarrow \cdot \text{OOCH(OH)COOH}\] 
\[2.0 \times 10^9 \] 
Herrmann et al., 2000

33 \[\cdot \text{OOCH(OH)COOH} + \cdot \text{H}_2\text{O} \rightarrow \text{CH(OH)}_2\text{COOH} + \cdot \text{HO}_2\] 
\[52 \] 
Herrmann et al., 2000

34 \[\text{CH(OH)}_2\text{COOH} + \cdot \text{OH} \rightarrow \cdot \text{HOOC(OH)COOH} + \cdot \text{HO}_2 + \cdot \text{H}_2\text{O}\] 
\[3.6 \times 10^8 \] 
Ervens et al., 2003

35 \[\text{CH}_2(\text{OH})\text{CHO} + \cdot \text{OH} \rightarrow (\text{OH})_2\text{CHCH(OH)} + \cdot \text{HO}_2\] 
\[1.0 \times 10^9 \] 
Warneck, 2003
36 \((\text{OH})_2 \text{CHCH(OH)}_2 + \cdot \text{OH} \to \text{CHOOCOOH} + \text{HO}_2 \cdot\)  

1.1×10^9  

Buxton et al., 1988

37 \(\text{CH}_3\text{C(O)CH(OH)}_ \cdot + \text{O}_2 \to \text{CH}_3\text{C(O)CH(OH)OO} \cdot\)

2.0×10^9  

von Sonntag, 1987  
Herrmann et al., 2000

38 \(\text{CH}_3\text{C(O)CH(OH)OO} \cdot \to \text{CH}_3\text{C(O)CHO} + \text{HO}_2\)

2.1×10^2  

Bothe et al., 1978  
Herrmann et al., 2000

39 \(2 \cdot \text{CH}_3\text{C(O)CH(OH)OO} \cdot \to 2 \cdot \text{CH}_3\text{C(O)COOH} + \text{H}_2\text{O}_2\)

3.5×10^8  

Bothe et al., 1978  
Herrmann et al., 2000

40 \(\text{CHOOCOOH} + \cdot \text{OH} \to \text{HOOCOCOOH} + \text{HO}_2 \cdot + \text{H}_2\text{O}\)

1.2×10^9  

Stefan and Bolton, 1999

41 \(\text{HCHO} + \text{H}_2\text{O} \to \text{CH}_2(\text{OH})_2\)

0.18 (F)  
5.1×10^{-3} (B)  
Bell and Evans, 1966

42 \(\text{CH}_2(\text{OH})_2 + \cdot \text{OH} \to \text{H}_2\text{O} + \text{HO}_2 \cdot + \text{HCOOH}\)

1.0×10^9  

Chin and Wine, 1994  
Harned and Owen, 1958

43 \(\text{HCOOH} \leftrightarrow \text{HCOO}^- + \text{H}^+\)

8.9×10^6 (F)  
5.0×10^{10} (B)  
Graedel and Weschler, 1981

44 \(\text{HCOOH} + \cdot \text{OH} \to \text{H}_2\text{O} + \text{HO}_2 \cdot + \text{CO}_2\)

1.3×10^8  

Chin and Wine, 1994  
Buxton et al., 1988

45 \(\text{HCOO}^- + \cdot \text{OH} \to \text{OH}^- + \text{HO}_2 \cdot + \text{CO}_2\)

4.0×10^9  

Betterton and Hoffmann, 1988

46 \(\text{CH}_3\text{C(O)CHO} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{C(O)CH(OH)}_2\)

21.5 (F)  
0.5 (B)  
Ervens et al., 2003

47 \(\text{CH}_3\text{C(O)CH(OH)}_2 + \cdot \text{OH} \to \text{CH}_3\text{C(O)C(OH)}_2 \cdot + \text{H}_2\text{O}\)

1.1×10^9  

Ervens et al., 2003
48. $\text{CH}_3\text{C(O)(OH)}_2 \cdot + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)(OH)}_2 \text{OO} \cdot$  
\[2.0 \times 10^9\] von Sonntag, 1987

49. $\text{CH}_3\text{C(O)(OH)}_2 \text{OO} \cdot \rightarrow \text{CH}_3\text{C(O)(COOH)} + \text{HO}_2 \cdot$  
\[1.0 \times 10^7\] h Buxton et al., 1988

50. $\text{CH}_3\text{C(O)(COOH)} + \cdot \text{OH} \rightarrow \text{CH}_2\text{C(O)(COOH)} + \text{H}_2\text{O}$  
\[1.2 \times 10^8\] Ervens et al., 2003

51. $\text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^\cdot + \text{H}^+$  
\[8.8 \times 10^5\] (F) \[5.0 \times 10^{10}\] (B) Herrmann et al., 2000

52. $\text{CH}_3\text{COOH} + \cdot \text{OH} \leftrightarrow \text{HOOC(COOH}$  
\[1.6 \times 10^7\] Stefan et al., 1996

53. $\text{CH}_3\text{COO}^\cdot + \cdot \text{OH} \rightarrow \text{HOOC(COOO}$  
\[8.5 \times 10^7\] Stefan et al., 1996

54. $\text{HOOC(COOH} + \cdot \text{OH} \rightarrow 2 \cdot \text{CO}_2 + \text{H}_2\text{O} + \text{HO}_2 \cdot$  
\[1.4 \times 10^6\] Buxton et al., 1988

55. $\text{HOOC(COOO}^\cdot + \cdot \text{OH} \rightarrow 2 \cdot \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2 \cdot$  
\[4.7 \times 10^7\] Buxton et al., 1988

56. $\text{HOOC(COOH} \leftrightarrow \text{HOOC(COOO}^\cdot + \text{H}^+$  
\[3.2 \times 10^9\] (F) \[5.0 \times 10^{10}\] (B) Meyerstein, 1971

57. $\text{CH}_3 \cdot + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \cdot$  
\[4.1 \times 10^9\] Marchaj et al., 1991

58. $\text{CH}_3\text{O}_2 \cdot + \text{CH}_3\text{O}_2 \cdot \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$  
\[1.7 \times 10^8\] Herrmann et al., 1999

59. $\cdot \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \cdot \text{OOCH}_2\text{OH}$  
\[2.0 \times 10^9\] von Sonntag, 1987

60. $2 \cdot \text{OOCH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$  
\[1.1 \times 10^9\] 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 O2 to 1-C4H9 and 2-C4H9 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 CH3C(O2)(OH)COCH3 radical;
g: Estimated in analogy to the combination of CH3O2 radical;
h: Estimated in analogy to glyoxal;

References:


Fig. S1. Direct photolysis of hydrogen peroxide (experimental and simulated data).
Fig. S2. MACR/MVK decay via UV-photolysis and OH-oxidation.