I. Reactions and rate coefficients used in the current study

The temperature dependent rate coefficients of the bimolecular reactions are calculated using the Arrhenius expression:

\[ k(T) = A \times e^{\left(-\frac{E}{RT}\right)} \]  

Eq. S1

The low-pressure-limiting rate coefficients for termolecular reactions are given in the form:

\[ k_0(T) = k_{0,298} \times \left(\frac{T}{298}\right)^{-n} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \]  

Eq. S2

The high-pressure-limiting rate coefficients for termolecular reactions are given in the form:

\[ k_\infty(T) = k_{\infty,298} \times \left(\frac{T}{298}\right)^{-m} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \]  

Eq. S3

The following formula calculates the effective second-order rate coefficients for a given condition of temperature and pressure (altitude) (Burkholder et al., 2019).

\[ k_f(T, [M]) = \left\{ \frac{k_\infty(T)k_0(T)[M]}{k_{0,298}(T)+k_0(T)[M]} \right\} 0.6^{\left[1+\log_2 \left(\frac{k_0(T)[M]}{k_{0,298}(T)}\right)^2\right]} \]  

Eq. S4

Where [M] is the total gas concentration.

Table S1: Reactions and corresponding rate coefficients taken from Burkholder et al., 2019. The radical intermediate formed during OVCO oxidation and photolysis are assumed to be converted to RO₂*, and the oxidation reaction or the photolysis is taken as the rate-determining step.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>A-Factor</th>
<th>E/R</th>
<th>k (298 K) or k&lt;sub&gt;\text{total}&lt;/sub&gt; (298K, 1 atm)</th>
<th>k&lt;sub&gt;0&lt;/sub&gt;(T) = k&lt;sub&gt;0,298&lt;/sub&gt; × (T/298)&lt;sup&gt;-n&lt;/sup&gt;</th>
<th>k&lt;sub&gt;\infty&lt;/sub&gt;(T) = k&lt;sub&gt;\infty,298&lt;/sub&gt; × (T/298)&lt;sup&gt;-m&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>^10O₃ + hv → O(^1D) + O₂</td>
<td></td>
<td></td>
<td></td>
<td>k&lt;sub&gt;0,298&lt;/sub&gt;</td>
<td>n</td>
</tr>
<tr>
<td>R2a</td>
<td>O(^1D) + H₂O → 2OH</td>
<td>1.63 × 10⁻¹⁰</td>
<td>-60</td>
<td>2.0 × 10⁻¹⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number</td>
<td>Reaction</td>
<td>A-Factor</td>
<td>E/R</td>
<td>( k_{\text{298}} ) or ( k_{\text{total}} ) (298K, 1atm)</td>
<td>( k_0(T) = k_{298}^n \times (T/298)^{-n} )</td>
<td>( k_{\infty}^n(T) = k_{\infty298}^m \times (T/298)^{-m} )</td>
</tr>
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</tr>
<tr>
<td>R2b</td>
<td>( \text{O}^1(\text{D}) + \text{O}_2 \rightarrow \text{O}^3(\text{P}) + \text{O}_2 )</td>
<td>( 3.3 \times 10^{-11} )</td>
<td>-55</td>
<td>( 3.95 \times 10^{-11} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R2c</td>
<td>( \text{O}^1(\text{D}) + \text{N}_2 \rightarrow \text{O}^3(\text{P}) + \text{N}_2 )</td>
<td>( 2.15 \times 10^{-11} )</td>
<td>-110</td>
<td>( 3.1 \times 10^{-11} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R3</td>
<td>( \text{HONO} + \text{hv} \rightarrow \text{OH} + \text{NO} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>( \text{H}_2\text{O}_2 ) + ( \text{hv} ) ( \rightarrow \text{2OH} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>( \text{OH} + \text{O}_3 ) ( \rightarrow \text{HO}_2 + \text{O}_2 )</td>
<td>( 1.7 \times 10^{-12} )</td>
<td>940</td>
<td>( 7.3 \times 10^{-14} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R6</td>
<td>( \text{OH} + \text{CO} + \text{O}_2 ) ( \rightarrow \text{HO}_2 + \text{CO}_2 )</td>
<td>( 1.7 \times 10^{-12} )</td>
<td>940</td>
<td>( 7.3 \times 10^{-14} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R7</td>
<td>( \text{H}_2\text{C} = \text{C} + \text{O}_2 \rightarrow \text{H}_2\text{C} = \text{C} + \text{O}_2 )</td>
<td>( 2.45 \times 10^{-12} )</td>
<td>1775</td>
<td>( 6.3 \times 10^{-15} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R8</td>
<td>( \text{H}_2\text{C} = \text{O} + \text{hv} \rightarrow \text{H}_2\text{O} )</td>
<td>( 1.7 \times 10^{-12} )</td>
<td>940</td>
<td>( 7.3 \times 10^{-14} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R9</td>
<td>( \text{CH}_3\text{CHO} + \text{hv} \rightarrow \text{CH}_3\text{C} = \text{O} + \text{CO} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R10a</td>
<td>( \text{CH}_3\text{C}(\text{O})\text{CH}_3 ) + ( \text{hv} ) ( + \text{2O}_2 ) ( \rightarrow \text{2CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R10b</td>
<td>( \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{hv} + \text{2O}_2 \rightarrow \text{2CH}_3\text{C}(\text{O})\text{O}_2 + \text{CO}_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R11</td>
<td>( \text{CHOCHO} ) + ( \text{hv} ) ( + \text{2O}_2 ) ( \rightarrow \text{2HO}_2 + \text{2CO} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12a</td>
<td>( \text{OH} + \text{HCHO} + \text{O}_2 ) ( \rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O} )</td>
<td>( 5.5 \times 10^{-12} )</td>
<td>-125</td>
<td>( 8.5 \times 10^{-12} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R12b</td>
<td>( \text{OH} + \text{CH}_3\text{CHO} + \text{O}_2 ) ( \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{H}_2\text{O} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12c</td>
<td>( \text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3 ) ( \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{C}(\text{O})\text{CH}_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12d</td>
<td>( \text{OH} + \text{CH}_3\text{OH} + \text{O}_2 ) ( \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{H}_2\text{O} )</td>
<td>( 2.9 \times 10^{-12} )</td>
<td>345</td>
<td>( 9.1 \times 10^{-13} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R12e</td>
<td>( \text{OH} + \text{CHOCHO} + \text{O}_2 ) ( \rightarrow \text{HO}_2 + \text{H}_2\text{O} + \text{2CO} )</td>
<td>( 1.15 \times 10^{-11} )</td>
<td>0</td>
<td>( 1.15 \times 10^{-11} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>R13</td>
<td>( \text{H}_2\text{C} = \text{C} + \text{C}(\text{H}_3)\text{CH} = \text{CH}_3 ) ( \rightarrow \text{products} )</td>
<td>( 1.1 \times 10^{-14} )</td>
<td>2000</td>
<td>( 1.3 \times 10^{-17} )</td>
<td>( k_0 )</td>
<td>( k_{\infty} )</td>
</tr>
<tr>
<td>Number</td>
<td>Reaction</td>
<td>A-Factor</td>
<td>E/R</td>
<td>k (298 K) or k_{total} (298 K, 1 atm)</td>
<td>k_{o_2} (T) = k_{o_2}^{298} \times (T/298)^{-n}</td>
<td>k_{o_2} (T) = k_{o_2}^{298} \times (T/298)^{-m}</td>
</tr>
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<td>--------</td>
<td>--------------------------------------------------------------------------</td>
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<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>R14</td>
<td>^{14}\text{H}_2\text{O} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad M \rightarrow \text{H}_2\text{O}_2 + \text{O}_2</td>
<td>3.0 \times 10^{-13}</td>
<td>-460</td>
<td>1.4 \times 10^{-12}</td>
<td>See note</td>
<td></td>
</tr>
<tr>
<td>R15</td>
<td>\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2</td>
<td>4.1 \times 10^{-11}</td>
<td>-750</td>
<td>5.2 \times 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R16a</td>
<td>\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2</td>
<td>9.5 \times 10^{-14}</td>
<td>-390</td>
<td>3.5 \times 10^{-13}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R16b</td>
<td>\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2</td>
<td>9.5 \times 10^{-14}</td>
<td>-390</td>
<td>3.5 \times 10^{-13}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R17</td>
<td>\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2</td>
<td>4.8 \times 10^{-11}</td>
<td>-250</td>
<td>1.1 \times 10^{-10}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R18a</td>
<td>\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2</td>
<td>6.3 \times 10^{-12}</td>
<td>6.9 \times 10^{-31}</td>
<td>1.0</td>
<td>2.6 \times 10^{-11}</td>
<td>0</td>
</tr>
<tr>
<td>R18b</td>
<td>\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(^3\text{P})</td>
<td>1.8 \times 10^{-12}</td>
<td>0</td>
<td>1.8 \times 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R19</td>
<td>\text{OH} + \text{NO} \rightarrow \text{HONO}</td>
<td>7.4 \times 10^{-12}</td>
<td>7.1 \times 10^{-31}</td>
<td>2.6</td>
<td>3.6 \times 10^{-11}</td>
<td>0.1</td>
</tr>
<tr>
<td>R20</td>
<td>\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3</td>
<td>1.1 \times 10^{-11}</td>
<td>1.8 \times 10^{-30}</td>
<td>3.0</td>
<td>2.8 \times 10^{-11}</td>
<td>0</td>
</tr>
<tr>
<td>R21</td>
<td>\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2</td>
<td>3.0 \times 10^{-12}</td>
<td>-250</td>
<td>6.9 \times 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R22</td>
<td>\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}</td>
<td>2.9 \times 10^{-11}</td>
<td>2.3 \times 10^{-29}</td>
<td>2.8</td>
<td>3.8 \times 10^{-11}</td>
<td>0.6</td>
</tr>
<tr>
<td>R23</td>
<td>^{k}\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2</td>
<td>3.44 \times 10^{-12}</td>
<td>-260</td>
<td>8.2 \times 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number</td>
<td>Reaction</td>
<td>A-Factor</td>
<td>E/R</td>
<td>( k(298\text{ K}) ) ( / k_{\text{total}}(298\text{ K}, 1\text{ atm}) )</td>
<td>( k_0(T) = k_0^{298} \times (T/298)^{-n} )</td>
<td>( k_\infty(T) = k_\infty^{298} \times (T/298)^{-m} )</td>
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</tr>
<tr>
<td>R24</td>
<td>( \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 )</td>
<td>1.0 \times 10^{-14}</td>
<td>490</td>
<td>1.9 \times 10^{15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R25</td>
<td>(^1\text{CH}_2\text{O} + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{NO}_2 )</td>
<td>2.8 \times 10^{-12}</td>
<td>-300</td>
<td>7.7 \times 10^{-12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R26</td>
<td>( \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 )</td>
<td>3.9 \times 10^{-14}</td>
<td>900</td>
<td>1.9 \times 10^{15}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) The \( \text{O}_3 \) photolysis has a second channel \( \text{O}_3 + \text{hv} (\lambda < 320 \text{ nm}) \rightarrow \text{O}_2(\text{P}) + \text{O}_2 \). So, only the photolysis rate for R1 is used in the calculation.

(b) Reaction \( \text{OH} \) with \( \text{CH}_3 \) produces \( \text{CH}_3_2\text{O} \) and \( \text{H}_2 \). The \( \text{CH}_3 \) formed further reacts with \( \text{O}_2 \) to form \( \text{CH}_3\text{O}_2 \). The formation of \( \text{CH}_3\text{O}_2 \) is assumed to be much faster than the \( \text{CH}_3 \) formation due to the high amount of \( \text{O}_2 \) present in the atmosphere. So the reaction of \( \text{OH} \) with \( \text{CH}_3 \) is taken as the rate-determining step for R7.

(c) The \( \text{HCHO} \) photolysis has a second channel, \( \text{HCHO} + \text{hv} (\lambda < 320 \text{ nm}) \rightarrow \text{H}_2 + \text{CO} \). So, only the photolysis rate for R8 is used in the calculation.

(d) The \( \text{CH}_3\text{CHO} \) photolysis has a second channel \( \text{CH}_3\text{CHO} + \text{hv} (\lambda < 320 \text{ nm}) \rightarrow \text{CH}_4 + \text{CO} \). So, only the photolysis rate for R9 is used in the calculation.

(e) To simplify the calculation, the \( \text{CH}_3\text{C(O)}\text{O}_2 \) produced is treated as a \( \text{CH}_2\text{O}_2 \) molecule during the calculation.

(f) The reaction of \( \text{OH} \) with \( \text{CH}_3\text{CHO} \) produces \( \text{CH}_3\text{C(O)}\text{O}_2 \) and \( \text{H}_2 \). The \( \text{CH}_3\text{C(O)}\text{O}_2 \) formed reacts with \( \text{O}_2 \) in a three-body reaction to form \( \text{CH}_3\text{C(O)}\text{O}_3 \). The formation of \( \text{CH}_3\text{C(O)}\text{O}_2 \) is assumed to be much faster than the \( \text{CH}_3\text{C(O)}\text{O}_2 \) formation due to the high amount of \( \text{O}_2 \) present in the atmosphere. So the reaction of \( \text{OH} \) with \( \text{CH}_3\text{CHO} \) is taken as the rate-determining step for R12b. To simplify the calculation, the \( \text{CH}_3\text{C(O)}\text{O}_2 \) produced is treated as a \( \text{CH}_2\text{O}_2 \) molecule during the calculation.

(g) The temperature-dependent reaction rate coefficient is given by: \( k_{12}(T) = 1.33 \times 10^{13} + 3.82 \times 10^{11} \times e^{(-2000/T)} \) cm\(^3\) molecules\(^{-1}\) s\(^{-1}\). \( \text{CH}_3\text{C(O)}\text{O}_2 \text{CH}_3 \) formed reacts with \( \text{O}_2 \) in a three-body reaction to form \( \text{CH}_3\text{C(O)}\text{C(O)}\text{H}_2 \). The formation of \( \text{CH}_3\text{C(O)}\text{C(O)}\text{H}_2 \) is assumed to be much faster than the \( \text{CH}_3\text{C(O)}\text{C(O)}\text{H}_2 \) formation due to the high amount of \( \text{O}_2 \) present in the atmosphere. So the reaction of \( \text{OH} \) with \( \text{CH}_3\text{C(O)}\text{O}_2 \) is taken as the rate-determining step for R12c. To simplify the calculation, the \( \text{CH}_3\text{C(O)}\text{C(O)}\text{H}_2 \) produced is treated as a \( \text{CH}_2\text{O}_2 \) molecule during the calculation.

(h) The reaction R13 shows an example of an ozonolysis reaction. To simplify the calculation, the ozonolysis reactions are not considered in this study.

(i) Reaction R14 exhibits a dependence on \( \text{H}_2\text{O} \) concentration. So the overall rate coefficient is given by the sum of the bimolecular component and a pressure-dependent termolecular component multiplied by the \( \text{H}_2\text{O} \) enhancement term, i.e.,

\[
(1.4 \times 10^{-1} + 4.6 \times 10^{-23}[\text{M}]) (1 + 1.4 \times 10^{-21}[\text{H}_2\text{O}]) e^{(2200/T)}. 
\]

(j) The \( \text{CH}_3\text{O}_2 \) self-reaction has a second channel with relative product yield \( \frac{k_{14}}{k_{14, \text{total}}} = (26.2 \pm 6.6) e^{(-1.13 \times 240)T} \) (Tyndall et al., 2001).

(k) Note that the \( \text{HO}_2 + \text{NO} \) reaction have another channel producing \( \text{HNO}_2 \). The probability of this channel is less than 1% and therefore negligible.

(l) Note that the \( \text{CH}_3\text{O}_2 + \text{NO} \) reaction have another channel producing \( \text{CH}_2\text{NO}_2 \). The probability of this channel is less than 0.5% and therefore negligible.
II. Deviation of Eq. 6 and Eq. 7

An analytical equation to calculate RO$_2^*$ was derived, assuming the primary source of RO$_2^*$ production is precursor photolysis, the loss of RO$_2^*$ is only through RO$_2^*$ - RO$_2^*$ reactions, and the radical interconversion reactions between OH, RO and RO$_2^*$ occurs without losses. Based on the results of previous airborne campaigns (Tan et al., 2001 and Cantrell et al., 2003b), the production of RO$_2^*$ from the photolysis of H$_2$O$_2$ and ozonolysis of alkenes were assumed to have minor contribution and are excluded from this study. In addition, CH$_3$O reactions were taken as a surrogate for all RO$_2$ reactions to reduce the complexity of the calculations.

Under these assumptions and based on the reactions in Table S1

- The rate of change of [RO$_2^*$] is given by

\[
\frac{d}{dt} ([RO_2^*]) = \frac{d}{dt} ([OH] + [CH_3O] + [HO_2] + [CH_3O_2])
\]

\[
\frac{d}{dt} ([RO_2^*]) = 2j_1 [O_3] \beta + j_3 [HONO] + 2j_6 [HCHO] + 2j_1 \{CHOCHO\} + 2j_9 [CH_3CHO] + 2(j_1 + j_1 \Phi) [CH_3C(O)CH_3] - 2k_1 [HO_2] [CH_3O_2] - 2k_1 [HO_2]^2
\]

\[
- 2k_1 \alpha [CH_3O_2]^2
\]

Where \( \beta \) is the fraction of O(1D) reacts with H$_2$O to form OH and is given by

\[
\beta = \frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_2] + k_{2c}[N_2]}
\]

Now substituting [HO$_2$] = \( \delta \) [RO$_2^*$] and [CH$_3$O$_2$] = (1 - \( \delta \)) [RO$_2^*$] in Eq. S5

\[
\frac{d}{dt} ([RO_2^*]) = 2j_1 [O_3] \beta + j_3 [HONO] + 2j_6 [HCHO] + 2j_1 \{CHOCHO\} + 2j_9 [CH_3CHO] + 2(j_1 + j_1 \Phi) [CH_3C(O)CH_3] - 2k_1 \delta (1 - \delta) [RO_2^*]^2
\]

\[
- 2k_1 \alpha (1 - \delta) [RO_2^*]^2 - 2k_1 \delta [RO_2^*]^2
\]

Under photostationary steady-state (PSS)

\[
\frac{d}{dt} ([RO_2^*]) = 0
\]

\[
\Rightarrow 2j_1 [O_3] \beta + j_3 [HONO] + 2j_6 [HCHO] + 2j_1 \{CHOCHO\} + 2j_9 [CH_3CHO] + 2(j_1 + j_1 \Phi) [CH_3C(O)CH_3] = 2k_1 \delta (1 - \delta) [RO_2^*]^2 + 2k_1 \alpha (1 - \delta) [RO_2^*]^2
\]

Eq. S6 is a quadratic equation of [RO$_2^*$] without a linear term. The solution is given by

\[
[RO_2^*]_c = \sqrt{\frac{P_{RO_2^*}^2}{2k_{RO_2}}}
\]

Eq. S7
3. Derivation of Eq. 8 and Eq. 9

51 If the radical interconversion and the loss of OH and CH$_3$O through the reaction with NO$_x$ during the interconversion are considered, then

52 The rate of change of $[\text{OH}]$ is given by

$$\frac{d}{dt}([\text{OH}]) = \ldots$$

53 i.e.,

$$\frac{d}{dt}([\text{OH}]) = 0$$

55 Under photostationary steady-state

$$\frac{d}{dt}([\text{OH}]) = 0$$

57 Since the atmospheric [OH] and [HO$_2$] $\ll$ [NO] and [NO$_2$], as a first approximation, the reactions R18 (OH – OH reaction) and R17 (OH – HO$_2$ reaction) are assumed to be negligible in the loss process of OH compared to the OH – NO$_x$ reactions. So Eq. 9 can be modified as:

$$[\text{OH}] = \frac{2j_1[\text{O}_3]\beta + j_3[\text{HONO}] + k_{23}[\text{HO}_2][\text{NO}] + k_{24}[\text{HO}_2][\text{O}_3]}{(k_5[\text{O}_3] + k_6[\text{CO}] + k_7[\text{CH}_4] + k_{12}[\text{HCHO}] + k_{12}[\text{CH}_3\text{CHO}] + k_{12}[\text{CH}_3\text{C(O)CH}_3] + k_{12}[\text{CH}_3\text{OH}] + k_{12}[\text{CHOCHO}] + k_{12}[\text{HO}_2] + k_{12}[\text{NO}] + k_{20}[\text{NO}_2] + k_{21}[\text{HONO}]) - 2(k_{18} + k_{19} + k_{20} + k_{21})[\text{OH}]^2}$$

59 The rate of change of $[\text{CH}_3\text{O}]$ is given by

$$\frac{d}{dt}([\text{CH}_3\text{O}]) = 2k_1 a[\text{CH}_3\text{O}_2]^2 + k_{25}[\text{CH}_3\text{O}_2][\text{NO}] - [\text{CH}_3\text{O}](k_{22}[\text{NO}] + k_{26}[O_2])$$
\[
\frac{d}{dt} ([CH_3O]) = 0
\]

\[
\Rightarrow [CH_3O] = \frac{2k_1[CH_3O]^2 + k_2[CH_3O][NO]}{(k_22[NO]+ k_26[O_2])} \quad \text{Eq. S12}
\]

- The rate of change of [HO_2] is given by

\[
\frac{d}{dt} ([HO_2]) = 2j_0[HCHO] + j_9[CH_3CHO] + 2j_1 [CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_1 \alpha[HCHO]+ k_1 \alpha[CH_3OH] + k_1 \alpha[CHOCHO]) + k_26[CH_3O][O_2] - [HO_2](k_1 \alpha[CH_3O] + k_1 \alpha[OH] + k_23[NO] + k_24[O_3]) - 2k_1[HO_2]^2 \quad \text{Eq. S13}
\]

- The rate of change of [CH_3O_2] is given by

\[
\frac{d}{dt} ([CH_3O_2]) = j_0[CH_3CHO] + 2j_1 [CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_1 \alpha[CHOCHO] + k_1 \alpha[CH_3C(O)CH_3]) - [CH_3O_2](k_1 \alpha[HO_2] + k_25[NO]) - 2(k_1 \alpha + k_1 \theta)[CH_3O_2]^2 \quad \text{Eq. S14}
\]

- If CH_3O_2 is assumed as a surrogate for all RO_2, then the rate of change of [RO_2^*] is given by

\[
\frac{d}{dt} ([RO_2^*]) = \frac{d}{dt} ([HO_2] + [CH_3O_2]) = 2j_0[HCHO] + j_9[CH_3CHO] + 2j_1 [CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_1 \alpha[HCHO] + k_1 \alpha[CH_3OH] + k_1 \alpha[CHOCHO]) + k_26[CH_3O][O_2] - [HO_2](k_1 \alpha[CH_3O] + k_23[NO] + k_24[O_3]) - 2k_1[HO_2]^2 + j_0[CH_3CHO] + 2(j_1 \alpha + j_1 \theta)[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_1 \alpha[CHOCHO] + k_1 \alpha[CH_3C(O)CH_3]) - [CH_3O_2](k_1 \alpha[HO_2] + k_25[NO]) - 2(k_1 \alpha + k_1 \theta)[CH_3O_2]^2 \quad \text{Eq. S15}
\]

Since OH and CH_3O are not measured on-board during EMeRGe, Eq. S10 and Eq. S12 are substituted in Eq. S15 and on rearranging.
\[ k_7[CH_4] + k_1[CHCHO] + k_1[CHOCHO] + k_1[CH_3C(O)CH_3] + k_1[CH_3OH] + k_1[CHOOCH] + k_{26} \frac{2k_1 \phi[CH_2O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO]+k_{26}[O_2])} [O_2] - \\
[HO_2](k_1[CH_3O_2] + k_2[NO] + k_2[O_3]) - 2k_1[HO_2]^2 - [CH_3O_2](k_1[HO_2] + k_{25}[NO]) - 2(k_1 \phi + k_1 \phi)[CH_3O_2]^2 \]  
Eq. S16

Now substituting

\[
(1 - \rho) = \frac{(k_3[O_3] + k_4[CO] + k_7[CH_4] + k_1[CHCHO] + k_1[CHOCHO] + k_1[CH_3C(O)CH_3] + k_1[CH_3OH] + k_1[CHOOCH] + k_{26} \frac{2k_1 \phi[CH_2O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO]+k_{26}[O_2])} [O_2] - [CH_3O_2](k_1[HO_2] + k_{25}[NO]) - 2(k_1 \phi + k_1 \phi)[CH_3O_2]^2 - [HO_2](k_1[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_1[HO_2]^2}{(k_3[O_3] + k_4[CO] + k_7[CH_4] + k_1[CHCHO] + k_1[CHOCHO] + k_1[CH_3C(O)CH_3] + k_1[CH_3OH] + k_1[CHOOCH] + k_1[HO_2] + k_1[NO] + k_{20}[NO_2] + k_{21}[HONO])} \]  
Eq. S16 gives

\[ \frac{d}{dt}([RO_2]^*) = 2j_9[CH_3CHO] + 2j_1[CHOCHO] + 2(j_1 \phi + j_1 \phi)[CH_3C(O)CH_3] + (2j_1[O_3] + 2j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3])(1 - \rho) + k_{26} \frac{2k_1 \phi[CH_2O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO]+k_{26}[O_2])} [O_2] - [CH_3O_2](k_1[HO_2] + k_{25}[NO]) - 2(k_1 \phi + k_1 \phi)[CH_3O_2]^2 - [HO_2](k_1[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_1[HO_2]^2 \]  
Eq. S17

Where \( \rho \) is the OH loss during the OH – RO\(_2\)\(^*\) interconversion

On rearranging

\[
\frac{d}{dt}([RO_2]^*) = (2j_1[O_3] + 2j_3[HONO])(1 - \rho) + 2j_9[CH_3CHO] + 2j_1[CHOCHO] + 2(j_1 \phi + j_1 \phi)[CH_3C(O)CH_3] + 2j_1[HO_2] - [HO_2](k_{23}[NO] + k_{24}[O_3])(1 - \rho) + k_{26} \frac{2k_1 \phi[CH_2O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO]+k_{26}[O_2])} [O_2] - [HO_2](k_{23}[NO] + k_{24}[O_3]) - k_1[HO_2][CH_3O_2] - k_1[HO_2][CH_3O_2] - 2k_1 \phi[CH_3O_2]^2 + 2k_{25}[CH_3O_2][NO] - 2k_1 \phi[CH_3O_2]^2 - 2k_1[HO_2]^2 \]  
Eq. S18

Combining common terms indicated by the same colours gives

\[
\frac{d}{dt}([RO_2]^*) = (2j_1[O_3] + 2j_3[HONO])(1 - \rho) + 2j_9[CH_3CHO] + 2j_1[CHOCHO] + 2(j_1 \phi + j_1 \phi)[CH_3C(O)CH_3] + 2j_1[HO_2] - [HO_2](k_{23}[NO] + k_{24}[O_3]) - k_1[HO_2][CH_3O_2] - [HO_2](k_{23}[NO] + k_{24}[O_3]) - k_{24}[O_3])\rho - 2k_1 \phi[CH_3O_2]^2 + k_{25}[CH_3O_2][NO] \left( \frac{k_{25}[NO]}{(k_{22}[NO]+k_{24}[O_3])} \right) - k_1[HO_2][CH_3O_2] - 2k_1 \phi[CH_3O_2]^2 - 2k_1[HO_2]^2 \]  
Eq. S18

Under steady-state

\[
\frac{d}{dt}([RO_2]^*) = 0
\]
\[ (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_0[HCHO] + 2j_0[CH_3CHO] + 2(j_1 a + j_1 a)[CH_3C(O)CH_3] + 2j_1 \text{CHOCHO} = [HO_2](k_{23}[NO] + k_{24}[O_3])\rho + \]

\[(2k_1 a[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) + 2k_1 [HO_2][CH_3O_2] + 2k_1 a[CH_3O_2]^2 + 2k_1 [HO_2]^2 \]

Eq. S19

Now substituting \([HO_2] = \delta [RO_2^+]\) and \([CH_3O_2] = (1 - \delta) [RO_2^+]\) in Eq. S19

\[ (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_0[HCHO] + 2j_0[CH_3CHO] + 2(j_1 a + j_1 a)[CH_3C(O)CH_3] + 2j_1 \text{CHOCHO} = \delta [RO_2^+](k_{23}[NO] + k_{24}[O_3])\rho + \]

\[ (2k_1 a((1 - \delta)[RO_2^+])^2 + k_{25}(1 - \delta)[RO_2^+][NO]) \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) + 2k_1 \varphi(1 - \delta)[RO_2^+]^2 + 2k_1 a((1 - \delta)[RO_2^+])^2 + 2k_1 \delta[RO_2^+]^2 \]

Eq. S20

Eq. S20 is a quadratic equation of \([RO_2^+]\). The solution is given by

\[ [RO_2^+] = \frac{-(-L_{RO_2^+}) \pm \sqrt{L_{RO_2^+}^2 - 4(-2k_{RO_2^+})^2}}{2(-2k_{RO_2^+})} \]

Eq. S21

Where

\[ k_{RO_2^+} = \left( k_1 a \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) + k_1 a \right)(1 - \delta)^2 + k_1 a(1 - \delta) + k_1 \delta^2 \]

\[ L_{RO_2^+} = \left( \delta(k_{23}[NO] + k_{24}[O_3])\rho + \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right)k_{25}(1 - \delta)[NO] \right) \]

\[ P_{RO_2^+} = (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_0[HCHO] + 2j_0[CH_3CHO] + 2(j_1 a + j_1 a)[CH_3C(O)CH_3] + 2j_1 \text{CHOCHO} \]

\[ \bullet \text{ Special case I} \]

When \( k_1 a[NO] + k_{20}[NO_2] + k_{21}[HONO] \ll \)

\[ k_{25}[O_3] + k_4[CO] + k_5[CH_4] + k_1 a[HCHO] + k_1 a[CH_3C(O)CH_3] + k_1 a[CH_3O_2] + k_1 a[CH_3OH] + k_1 a[CHOCHO], \text{ i.e., } \rho \approx 0, \text{ Eq. S19 can be simplified as:} \]
(2j_1[O_3]β + j_3[HONO]) + 2j_0[HCHO] + 2j_0[CH_3CHO] + 2(j_1 + j_1)[CH_3(C(O)CH_3) + 2j_1[CHOCHO] = (2k_1 a((1 − δ)[RO_2]^2 + k_25(1 − δ)[RO_2][NO]) + 2k_1 \delta(1 − δ)[RO_2]^2 + 2k_1 a((1 − δ)[RO_2]^2 + 2k_1 \delta[RO_2]^2)^2

\text{Eq. S22}

L_{RO_2} and P_{RO_2} becomes

L_{RO_2} = \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{24}[O_2])}\right)k_{25}(1 − δ)[NO]

P_{RO_2} = (2j_1[O_3]β + j_3[HONO]) + 2j_0[HCHO] + 2j_0[CH_3CHO] + 2(j_1 + j_1)[CH_3(C(O)CH_3) + 2j_1[CHOCHO]

\bullet \text{ Special case II}

If ρ ≈ 0 and OH and CH_3O are converted to RO_2^* without any losses, then Eq. S20 becomes Eq. S6 and the solution is given by Eq. S7