

Supplementary information

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2 I. Reactions and rate coefficients used in the current study

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

4 $k(T) = A \times e^{(-E/RT)}$ Eq. S1

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

6 $k_0(T) = k_{0298} \times (T/298)^{-n} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$ Eq. S2

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

8 $k_\infty(T) = k_{\infty298} \times (T/298)^{-m} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ Eq. S3

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

10 $k_f(T, [M]) = \left\{ \frac{k_\infty(T)k_0(T)[M]}{k_\infty(T) + k_0(T)[M]} \right\} 0.6^{\left\{ 1 + \left[\log_{10} \left(\frac{k_0(T)[M]}{k_\infty(T)} \right) \right]^2 \right\}^{-1}}$ Eq. S4

11 Where $[M]$ is the total gas concentration.

12 Table S1: Reactions and corresponding rate coefficients taken from Burkholder et al., 2019. The radical intermediate formed during OVCO oxidation and photolysis
13 are assumed to be converted to RO_2^* , and the oxidation reaction or the photolysis is taken as the rate-determining step.

Number	Reaction	A-Factor	E/R	k (298 K) or k _{total} (298K, 1atm)	$k_0(T) = k_{0298} \times (T/298)^{-n}$		$k_\infty(T) = k_{\infty298} \times (T/298)^{-m}$	
					k_{0298}	n	$k_{\infty298}$	m
R1	$^{(a)}\text{O}_3 + \text{hv} \rightarrow \text{O}(\text{^1D}) + \text{O}_2$							
R2a	$\text{O}(\text{^1D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	1.63×10^{-10}	-60	2.0×10^{-10}				

Number	Reaction	A-Factor	E/R	k (298 K) or k _{total} (298K, 1atm)	k ₀ (T) = k ₀ ²⁹⁸ × (T/298) ⁻ⁿ		k _∞ (T) = k _∞ ²⁹⁸ × (T/298) ^{-m}	
					k ₀ ²⁹⁸	n	k _∞ ²⁹⁸	m
R2b	O(¹ D) + O ₂ → O(³ P) + O ₂	3.3 × 10 ⁻¹¹	-55	3.95 × 10 ⁻¹¹				
R2c	O(¹ D) + N ₂ → O(³ P) + N ₂	2.15 × 10 ⁻¹¹	-110	3.1 × 10 ⁻¹¹				
R3	HONO + hν → OH + NO							
R4	H ₂ O ₂ + hν → 2OH							
R5	OH + O ₃ → HO ₂ + O ₂	1.7 × 10 ⁻¹²	940	7.3 × 10 ⁻¹⁴				
R6	OH + CO + O ₂ \xrightarrow{M} HO ₂ + CO ₂			2.4 × 10 ⁻¹³	6.9 × 10 ⁻³³	2.1	1.1 × 10 ⁻¹²	-1.3
R7	^(b) OH + CH ₄ + O ₂ → CH ₃ O ₂ + H ₂ O	2.45 × 10 ⁻¹²	1775	6.3 × 10 ⁻¹⁵				
R8	^(c) HCHO + hν + 2O ₂ → 2HO ₂ + CO							
R9	^(d) CH ₃ CHO + hν + 2O ₂ → CH ₃ O ₂ + HO ₂ + CO							
R10a	^(e) CH ₃ C(O)CH ₃ + hν + 2O ₂ → CH ₃ C(O)O ₂ + CH ₃ O ₂							
R10b	CH ₃ C(O)CH ₃ + hν + 2O ₂ → 2 CH ₃ O ₂ + CO							
R11	CHOCHO + hν + 2O ₂ → 2HO ₂ + 2CO							
R12a	OH + HCHO + O ₂ → HO ₂ + CO + H ₂ O	5.5 × 10 ⁻¹²	-125	8.5 × 10 ⁻¹²				
R12b	^(f) OH + CH ₃ CHO + O ₂ \xrightarrow{M} CH ₃ C(O)O ₂ + H ₂ O	4.63 × 10 ⁻¹²	-350	1.5 × 10 ⁻¹¹				
R12c	^(g) OH + CH ₃ C(O)CH ₃ → H ₂ O + CH ₃ C(O)CH ₂			See note				
R12d	OH + CH ₃ OH + O ₂ → CH ₂ O + HO ₂ + H ₂ O	2.9 × 10 ⁻¹²	345	9.1 × 10 ⁻¹³				
R12e	OH + CHOCHO + O ₂ → HO ₂ + H ₂ O + 2CO	1.15 × 10 ⁻¹¹	0	1.15 × 10 ⁻¹¹				
R13	^(h) O ₃ + CH ₂ =C(CH ₃)CH=CH ₂ → products	1.1 × 10 ⁻¹⁴	2000	1.3 × 10 ⁻¹⁷				

Number	Reaction	A-Factor	E/R	k (298 K) or k _{total} (298K, 1atm)	k ₀ (T) = k _{0²⁹⁸} × (T/298) ⁻ⁿ		k _∞ (T) = k _{∞²⁹⁸} × (T/298) ^{-m}	
					k _{0²⁹⁸}	n	k _{∞²⁹⁸}	m
R14	⁽ⁱ⁾ HO ₂ + HO ₂ → H ₂ O ₂ + O ₂ \xrightarrow{M} H ₂ O ₂ + O ₂	3.0 × 10 ⁻¹³	-460	1.4 × 10 ⁻¹²	See note			
		2.1 × 10 ⁻³³ [M]	-920	4.6 × 10 ⁻³² [M]				
R15	HO ₂ + CH ₃ O ₂ → CH ₃ OOH + O ₂	4.1 × 10 ⁻¹³	-750	5.2 × 10 ⁻¹²				
R16a	^(j) CH ₃ O ₂ + CH ₃ O ₂ → CH ₃ OH + HCHO + O ₂	9.5 × 10 ⁻¹⁴	-390	3.5 × 10 ⁻¹³				
R16b	CH ₃ O ₂ + CH ₃ O ₂ → 2CH ₃ O + O ₂	9.5 × 10 ⁻¹⁴	-390	3.5 × 10 ⁻¹³				
R17	OH + HO ₂ → H ₂ O + O ₂	4.8 × 10 ⁻¹¹	-250	1.1 × 10 ⁻¹⁰				
R18a	OH + OH \xrightarrow{M} H ₂ O ₂			6.3 × 10 ⁻¹²	6.9 × 10 ⁻³¹	1.0	2.6 × 10 ⁻¹¹	0
R18b	OH + OH → H ₂ O + O(³ P)	1.8 × 10 ⁻¹²	0	1.8 × 10 ⁻¹²				
R19	OH + NO \xrightarrow{M} HONO			7.4 × 10 ⁻¹²	7.1 × 10 ⁻³¹	2.6	3.6 × 10 ⁻¹¹	0.1
R20	OH + NO ₂ \xrightarrow{M} HNO ₃			1.1 × 10 ⁻¹¹	1.8 × 10 ⁻³⁰	3.0	2.8 × 10 ⁻¹¹	0
R21	OH + HONO → H ₂ O + NO ₂	3.0 × 10 ⁻¹²	-250	6.9 × 10 ⁻¹²				
R22	CH ₃ O + NO \xrightarrow{M} CH ₃ ONO			2.9 × 10 ⁻¹¹	2.3 × 10 ⁻²⁹	2.8	3.8 × 10 ⁻¹¹	0.6
R23	^(k) HO ₂ + NO → OH + NO ₂	3.44 × 10 ⁻¹²	-260	8.2 × 10 ⁻¹²				

Number	Reaction	A-Factor	E/R	k (298 K) or k _{total} (298K, 1atm)	k ₀ (T) = k _{0²⁹⁸} × (T/298) ⁻ⁿ		k _∞ (T) = k _{∞²⁹⁸} × (T/298) ^{-m}	
					k _{0²⁹⁸}	n	k _{∞²⁹⁸}	m
R24	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	1.0×10^{-14}	490	1.9×10^{-15}				
R25	^(l) $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	2.8×10^{-12}	-300	7.7×10^{-12}				
R26	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	3.9×10^{-14}	900	1.9×10^{-15}				

14 (a) The O_3 photolysis has a second channel $\text{O}_3 + \text{hv} (\lambda < 320 \text{ nm}) \rightarrow \text{O}(\text{P}) + \text{O}_2$. So, only the photolysis rate for R1 is used in the calculation.

15 (b) Reaction OH with CH_4 produces CH_3 and H_2O . The CH_3 formed further reacts with O_2 to form CH_3O_2 . The formation of CH_3O_2 is assumed to be much faster than the CH_3 formation due to the high amount of O_2 present in the atmosphere. So the reaction of OH with CH_3 is taken as the rate-determining step for R7.

16 (c) The 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.

17 (d) The CH_3CHO 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.

18 (e) To simplify the calculation, the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ produced is treated as a CH_3O_2 molecule during the calculation.

19 (f) The reaction of OH with CH_3CHO produces $\text{CH}_3\text{C}(\text{O})$ and H_2O . The $\text{CH}_3\text{C}(\text{O})$ formed reacts with O_2 in a three-body reaction to form $\text{CH}_3\text{C}(\text{O})\text{O}_2$. The formation of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is assumed to be much faster than the $\text{CH}_3\text{C}(\text{O})$ formation due to the high amount of O_2 present in the atmosphere. So the reaction of OH with CH_3CHO is taken as the rate-determining step for R12b. To simplify the calculation, the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ produced is treated as a CH_3O_2 molecule during the calculation.

20 (g) The temperature-dependent reaction rate coefficient is given by: $k_{12c}(T) = 1.33 \times 10^{-13} + 3.82 \times 10^{-11} \times e^{(-2000/T)}$ $\text{cm}^3\text{molecules}^{-1}\text{s}^{-1}$. $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ formed reacts with O_2 in a three-body reaction to form $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$. The formation of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ is assumed to be much faster than the $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ formation due to the high amount of O_2 present in the atmosphere. So the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ is taken as the rate-determining step for R12c. To simplify the calculation, the $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ produced is treated as a CH_3O_2 molecule during the calculation.

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

22 (i) Reaction R14 exhibits a dependence on H_2O concentration. So the overall rate coefficient is given by the sum of the bimolecular component and a pressure-dependent termolecular component multiplied by the H_2O enhancement term. i.e.,

23
$$(1.4 \times 10^{-12} + 4.6 \times 10^{-32}[\text{M}]) (1 + 1.4 \times 10^{-21}[\text{H}_2\text{O}] \exp^{(2200/T)})$$
.

24 (j) The CH_3O_2 self-reaction has a second channel with relative product yield, $\frac{k_{16b}}{k_{16a}} = (26.2 \pm 6.6) e^{(-1130 \pm 240)/T}$ (Tyndall et al., 2001).

25 (k) Note that the $\text{HO}_2 + \text{NO}$ reaction have another channel producing HNO_3 . The probability of this channel is less than 1% and therefore negligible.

26 (l) Note that the $\text{CH}_3\text{O}_2 + \text{NO}$ reaction have another channel producing CH_3NO_2 . The probability of this channel is less than 0.5% and therefore negligible.

33 II. Deviation of Eq. 6 and Eq. 7

34 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 $\text{RO}_2^* - \text{RO}_2^*$ 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_2O_2 and ozonolysis of alkenes were assumed to have minor contribution and are excluded from this study. In addition, CH_3O_2 reactions were taken as a surrogate for all RO₂ reactions to reduce the complexity of the calculations.

38 Under these assumptions and based on the reactions in Table S1

39 • The rate of change of $[\text{RO}_2^*]$ is given by

$$\frac{d}{dt}([\text{RO}_2^*]) = \frac{d}{dt}([\text{OH}] + [\text{CH}_3\text{O}] + [\text{HO}_2] + [\text{CH}_3\text{O}_2])$$

$$\frac{d}{dt}([\text{RO}_2^*]) = 2j_1[\text{O}_3]\beta + j_3[\text{HONO}] + 2j_8[\text{HCHO}] + 2j_{11}[\text{CHOCHO}] + 2j_9[\text{CH}_3\text{CHO}] + 2(j_{10a} + j_{10b})[\text{CH}_3\text{C}(\text{O})\text{CH}_3] - 2k_{15}[\text{HO}_2][\text{CH}_3\text{O}_2] - 2k_{14}[\text{HO}_2]^2 - 2k_{16a}[\text{CH}_3\text{O}_2]^2$$

40 Eq. S5

41 Where β is the fraction of $\text{O}(\text{^1D})$ reacts with H_2O to form OH and is given by $\beta = \left(\frac{k_{2a}[\text{H}_2\text{O}]}{k_{2a}[\text{H}_2\text{O}] + k_{2b}[\text{O}_2] + k_{2c}[\text{N}_2]} \right)$

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

$$\frac{d}{dt}([\text{RO}_2^*]) = 2j_1[\text{O}_3]\beta + j_3[\text{HONO}] + 2j_8[\text{HCHO}] + 2j_{11}[\text{CHOCHO}] + 2j_9[\text{CH}_3\text{CHO}] + 2(j_{10a} + j_{10b})[\text{CH}_3\text{C}(\text{O})\text{CH}_3] - 2k_{15}\delta(1 - \delta)[\text{RO}_2^*]^2 - 2k_{16a}((1 - \delta)[\text{RO}_2^*])^2 - 2k_{14}(\delta[\text{RO}_2^*])^2$$

43 Under photostationary steady-state (PSS)

$$\frac{d}{dt}([\text{RO}_2^*]) = 0$$

$$\Rightarrow 2j_1[\text{O}_3]\beta + j_3[\text{HONO}] + 2j_8[\text{HCHO}] + 2j_{11}[\text{CHOCHO}] + 2j_9[\text{CH}_3\text{CHO}] + 2(j_{10a} + j_{10b})[\text{CH}_3\text{C}(\text{O})\text{CH}_3] = 2k_{15}\delta(1 - \delta)[\text{RO}_2^*]^2 + 2k_{16a}((1 - \delta)[\text{RO}_2^*])^2 + 2k_{14}(\delta[\text{RO}_2^*])^2$$

45 Eq. S6

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

$$47 [\text{RO}_2^*]_c = \sqrt[2]{\frac{\text{P}_{\text{RO}_2^*}}{2k_{\text{RO}_2^*}}}$$

47 Eq. S7

48 $k_{RO_2^*} = (k_{15}\delta(1-\delta) + k_{16a}(1-\delta)^2 + k_{14}\delta^2)$

$$P_{RO_2^*} = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3]$$

49 Since the amount of OH and RO is much smaller than that of HO₂ and RO₂ in the atmosphere, RO₂^{*} to a good approximation is the sum of HO₂ and RO₂ radicals.

50 III. Derivation of Eq. 8 and Eq. 9

51 If the radical interconversion and the loss of OH and CH₃O through the reaction with NO_x during the interconversion are considered, then

52 • The rate of change of [OH] is given by

$$53 \frac{d}{dt}([OH]) =$$

$$54 2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] - [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b})[OH]^2 \quad \text{Eq. S8}$$

56 Under photostationary steady-state

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

57 i.e.,

$$58 2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] = [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b})[OH]^2 \quad \text{Eq. S9}$$

60 Since the atmospheric [OH] and [HO₂] << [NO] and [NO₂], as a first approximation, the reactions R18 (OH – OH reaction) and R17 (OH – HO₂ reaction) are 61 assumed to be negligible in the loss process of OH compared to the OH – NO_x reactions. So Eq. S9 can be modified as:

$$62 [OH] = \frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]}) \quad \text{Eq. S10}$$

63 • The rate of change of [CH₃O] is given by

$$64 \frac{d}{dt}([CH_3O]) = 2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO] - [CH_3O](k_{22}[NO] + k_{26}[O_2]) \quad \text{Eq. S11}$$

65 Under PSS

$$\frac{d}{dt}([CH_3O]) = 0$$

66 $\Rightarrow [CH_3O] = \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])}$ Eq. S12

67 • The rate of change of $[HO_2]$ is given by

68 $\frac{d}{dt}([HO_2]) =$
 69 $2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCCHO]) + k_{26}[CH_3O][O_2] -$
 70 $[HO_2](k_{15}[CH_3O_2] + k_{17}[OH] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2$

71 Based on the assumption made for Eq. S10, the reaction R17 ($OH - HO_2$ reaction) is assumed to have a negligible contribution in the HO_2 loss process. So

72 $\frac{d}{dt}([HO_2]) =$
 73 $2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCCHO]) + k_{26}[CH_3O][O_2] -$
 74 $[HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2$ Eq. S13

75 • The rate of change of $[CH_3O_2]$ is given by

76 $\frac{d}{dt}([CH_3O_2]) = j_9[CH_3CHO] + 2j_{11}[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCCHO] + k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) -$
 77 $2(k_{16a} + k_{16b})[CH_3O_2]^2$ Eq. S14

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

$$\frac{d}{dt}([RO_2^*]) = \frac{d}{dt}([HO_2] + [CH_3O_2]) = 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCCHO]) + k_{26}[CH_3O][O_2] - [HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCCHO] + k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2$$
 Eq. S15

82 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.

83 $\frac{d}{dt}([RO_2^*]) =$
 84 $2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCCHO] + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] +$
 85 $\frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])} (k_5[O_3] + k_6[CO] +$

86 $k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] -$
 87 $[HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2$ Eq. S16

88 Now substituting

89 $(1 - \rho) = \frac{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO])}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])}$ in Eq. S16 gives

90 $\frac{d}{dt}([RO_2^*]) =$
 91 $2j_8[HCHO] + 2j_9[CH_3CHO] + 2j_{11}[CHOCHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + (2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3])(1 - \rho) +$
 92 $k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 - [HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) -$
 93 $2k_{14}[HO_2]^2$ Eq. S17

94 Where ρ is the OH loss during the $OH - RO_2^*$ interconversion

95 On rearranging

$$\frac{d}{dt}([RO_2^*]) = (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] + [HO_2](k_{23}[NO] + k_{24}[O_3])(1 - \rho) + k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] - [HO_2](k_{23}[NO] + k_{24}[O_3]) - k_{15}[HO_2][CH_3O_2] - k_{15}[HO_2][CH_3O_2] - (2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) - 2k_{16a}[CH_3O_2]^2 - 2k_{14}[HO_2]^2$$

96 Combining common terms indicated by the same colours gives

97 $\frac{d}{dt}([RO_2^*]) = (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] - [HO_2](k_{23}[NO] +$
 98 $k_{24}[O_3])\rho - (2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) - 2k_{15}[HO_2][CH_3O_2] - 2k_{16a}[CH_3O_2]^2 - 2k_{14}[HO_2]^2$ Eq. S18

99 Under steady-state

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

100
$$\Rightarrow (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = [HO_2](k_{23}[NO] + k_{24}[O_3])\rho +$$

101
$$(2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + 2k_{15}[HO_2][CH_3O_2] + 2k_{16a}[CH_3O_2]^2 + 2k_{14}[HO_2]^2$$
 Eq. S19

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

103
$$(2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = \delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho +$$

104
$$(2k_{16b}((1 - \delta)[RO_2^*])^2 + k_{25}(1 - \delta)[RO_2^*][NO]) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2$$
 Eq. S20

106 Eq. S20 is a quadratic equation of $[RO_2^*]$. The solution is given by

107
$$[RO_2^*] = \frac{-(-L_{RO_2^*}) - 2\sqrt{L_{RO_2^*}^2 - 4(-2k_{RO_2^*})P_{RO_2^*}}}{2(-2k_{RO_2^*})}$$
 Eq. S21

108 Where

109
$$k_{RO_2^*} = \left(\left(k_{16b} \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + k_{16a} \right) (1 - \delta)^2 + k_{15}\delta(1 - \delta) + k_{14}\delta^2 \right)$$

$$L_{RO_2^*} = \left(\delta(k_{23}[NO] + k_{24}[O_3])\rho + \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) k_{25}(1 - \delta)[NO] \right)$$

110
$$P_{RO_2^*} = (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO]$$

111 • Special case I

112 When $k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO] \ll$

113 $k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]$, i.e., $\rho \approx 0$, Eq. S19 can be
 114 simplified as:

115
$$(2j_1[O_3]\beta + j_3[HONO]) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = \left(2k_{16b}((1 - \delta)[RO_2^*])^2 + k_{25}(1 - \delta)[RO_2^*][NO]\right) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])}\right) + 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2$$

116 Eq. S22

117

118 $L_{RO_2^*}$ and $P_{RO_2^*}$ becomes

$$L_{RO_2^*} = \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])}\right)k_{25}(1 - \delta)[NO]$$

119 $P_{RO_2^*} = (2j_1[O_3]\beta + j_3[HONO]) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO]$

120 • Special case II

121

122 If $\rho \approx 0$ 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