

Supplementary information

1

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:

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

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

$$6 \quad k_0(T) = k_{0,298} \times (T/298)^{-n} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \quad \text{Eq. S2}$$

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

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

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

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

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 _{0,298} × (T/298) ⁻ⁿ		k _∞ (T) = k _{∞,298} × (T/298) ^{-m}	
					k _{0,298}	n	k _{∞,298}	m
R1	^(a) O ₃ + hv → O(¹ D) + O ₂							
R2a	O(¹ D) + H ₂ O → 2OH	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 + hv → OH + NO							
R4	H ₂ O ₂ + hv → 2OH							
R5	OH + O ₃ → HO ₂ + O ₂	1.7 × 10 ⁻¹²	940	7.3 × 10 ⁻¹⁴				
R6	OH + CO + O ₂ ^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 + hv + 2O ₂ → 2HO ₂ + CO							
R9	^(d) CH ₃ CHO + hv + 2O ₂ → CH ₃ O ₂ + HO ₂ + CO							
R10a	^(e) CH ₃ C(O)CH ₃ + hv + 2O ₂ → CH ₃ C(O)O ₂ + CH ₃ O ₂							
R10b	CH ₃ C(O)CH ₃ + hv + 2O ₂ → 2 CH ₃ O ₂ + CO							
R11	CHOCHO + hv + 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 ^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 ₀ ²⁹⁸ × (T/298) ⁻ⁿ		k _∞ (T) = k _∞ ²⁹⁸ × (T/298) ^{-m}	
					k ₀ ²⁹⁸	n	k _∞ ²⁹⁸	m
R14	⁽ⁱ⁾ HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	3.0 × 10 ⁻¹³	-460	1.4 × 10 ⁻¹²	See note			
	\xrightarrow{M} H ₂ O ₂ + O ₂	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 ₀ ²⁹⁸ × (T/298) ⁻ⁿ		k _∞ (T) = k _∞ ²⁹⁸ × (T/298) ^{-m}	
					k ₀ ²⁹⁸	n	k _∞ ²⁹⁸	m
R24	HO ₂ + O ₃ → OH + 2O ₂	1.0 × 10 ⁻¹⁴	490	1.9 × 10 ⁻¹⁵				
R25	^(l) CH ₃ O ₂ + NO → CH ₃ O + NO ₂	2.8 × 10 ⁻¹²	-300	7.7 × 10 ⁻¹²				
R26	CH ₃ O + O ₂ → CH ₂ O + HO ₂	3.9 × 10 ⁻¹⁴	900	1.9 × 10 ⁻¹⁵				

- 14 (a) The O₃ photolysis has a second channel O₃ + hv (λ < 320 nm) → O(³P) + O₂. So, only the photolysis rate for R1 is used in the calculation.
- 15 (b) Reaction OH with CH₄ produces CH₃ and H₂O. The CH₃ formed further reacts with O₂ to form CH₃O₂. The formation of CH₃O₂ is assumed to be much faster than the CH₃ formation due to the high
- 16 amount of O₂ present in the atmosphere. So the reaction of OH with CH₃ is taken as the rate-determining step for R7.
- 17 (c) The HCHO photolysis has a second channel, HCHO + hv (λ < 320 nm) → H₂ + CO. So, only the photolysis rate for R8 is used in the calculation.
- 18 (d) The CH₃CHO photolysis has a second channel CH₃CHO + hv (λ < 320 nm) → CH₄ + CO. So, only the photolysis rate for R9 is used in the calculation.
- 19 (e) To simplify the calculation, the CH₃C(O)O₂ produced is treated as a CH₃O₂ molecule during the calculation.
- 20 (f) The reaction of OH with CH₃CHO produces CH₃C(O) and H₂O. The CH₃C(O) formed reacts with O₂ in a three-body reaction to form CH₃C(O)O₂. The formation of CH₃C(O)O₂ is assumed to be
- 21 much faster than the CH₃C(O) formation due to the high amount of O₂ present in the atmosphere. So the reaction of OH with CH₃CHO is taken as the rate-determining step for R12b. To simplify the
- 22 calculation, the CH₃C(O)O₂ produced is treated as a CH₃O₂ molecule during the calculation.
- 23 (g) The temperature-dependent reaction rate coefficient is given by: k_{12c}(T) = 1.33 × 10⁻¹³ + 3.82 × 10⁻¹¹ × e^(-2000/T) cm³molecules⁻¹s⁻¹. CH₃C(O)CH₂ formed reacts with O₂ in a three-body reaction to
- 24 form CH₃C(O)CH₂O₂. The formation of CH₃C(O)CH₂O₂ is assumed to be much faster than the CH₃C(O)CH₂ formation due to the high amount of O₂ present in the atmosphere. So the reaction of OH
- 25 with CH₃C(O)CH₃ is taken as the rate-determining step for R12c. To simplify the calculation, the CH₃C(O)CH₂O₂ produced is treated as a CH₃O₂ molecule during the calculation.
- 26 (h) The reaction R13 shows an example of an ozonolysis reaction. To simplify the calculation, the ozonolysis reactions are not considered in this study.
- 27 (i) Reaction R14 exhibits a dependence on H₂O concentration. So the overall rate coefficient is given by the sum of the bimolecular component and a pressure-dependent termolecular component
- 28 multiplied by the H₂O enhancement term. i.e.,
- 29 $(1.4 \times 10^{-12} + 4.6 \times 10^{-32}[\text{M}])(1 + 1.4 \times 10^{-21}[\text{H}_2\text{O}]\text{exp}^{(2200/T)})$.
- 30 (j) The CH₃O₂ 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).
- 31 (k) Note that the HO₂ + NO reaction have another channel producing HNO₃. The probability of this channel is less than 1% and therefore negligible.
- 32 (l) Note that the CH₃O₂ + NO reaction have another channel producing CH₃NO₂. 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 RO_2^*
 35 $- RO_2^*$ reactions, and the radical interconversion reactions between OH, RO and RO_2^* occurs without losses. Based on the results of previous airborne campaigns
 36 (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
 37 and are excluded from this study. In addition, CH_3O_2 reactions were taken as a surrogate for all RO_2 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 $[RO_2^*]$ is given by

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

$$\frac{d}{dt}([RO_2^*]) = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] - 2k_{15}[HO_2][CH_3O_2] - 2k_{14}[HO_2]^2 - 2k_{16a}[CH_3O_2]^2$$

40

Eq. S5

41 Where β is the fraction of $O(^1D)$ reacts with H_2O to form OH and is given by $\beta = \left(\frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_2] + k_{2c}[N_2]} \right)$

42 Now substituting $[HO_2] = \delta[RO_2^*]$ and $[CH_3O_2] = (1 - \delta)[RO_2^*]$ in Eq. S5

$$\frac{d}{dt}([RO_2^*]) = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] - 2k_{15}\delta(1 - \delta)[RO_2^*]^2 - 2k_{16a}((1 - \delta)[RO_2^*])^2 - 2k_{14}(\delta[RO_2^*])^2$$

43 Under photostationary steady-state (PSS)

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

$$\Rightarrow 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] = 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2$$

Eq. S6

46 Eq. S6 is a quadratic equation of $[RO_2^*]$ without a linear term. The solution is given by

$$47 [RO_2^*]_c = \sqrt{\frac{P_{RO_2^*}}{2k_{RO_2^*}}}$$

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 $2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] - [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] +$
 55 $k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b}) [OH]^2$ Eq. S8

56 Under photostationary steady-state

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

57 i.e.,

58 $2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] = [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] +$
 59 $k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b}) [OH]^2$ 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 $[OH] = \frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])}$ Eq. S10

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

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

65 Under PSS

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

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

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

$$68 \frac{d}{dt}([HO_2]) =$$

$$69 \quad 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] -$$

$$70 \quad [HO_2](k_{15}[CH_3O_2] + k_{17}[OH] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2$$

71 Based on the assumption made for Eq. S10, the reaction R17 (OH – HO₂ reaction) is assumed to have a negligible contribution in the HO₂ loss process. So

$$72 \frac{d}{dt}([HO_2]) =$$

$$73 \quad 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] -$$

$$74 \quad [HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 \quad \text{Eq. S13}$$

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

$$76 \frac{d}{dt}([CH_3O_2]) = j_9[CH_3CHO] + 2j_{11}[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) -$$

$$77 \quad 2(k_{16a} + k_{16b})[CH_3O_2]^2 \quad \text{Eq. S14}$$

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

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

$$79 = 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] -$$

$$80 \quad [HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCHO] +$$

$$81 \quad k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 \quad \text{Eq. S15}$$

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.

$$83 \frac{d}{dt}([RO_2^*]) =$$

$$84 \quad 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] +$$

$$85 \quad \frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])} (k_5[O_3] + k_6[CO] +$$

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 – RO₂^{*} interconversion

95 On rearranging

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

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

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

$$\begin{aligned} 100 \quad & \Rightarrow (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = [HO_2](k_{23}[NO] + k_{24}[O_3])\rho + \\ 101 \quad & (2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + 2k_{15}[HO_2][CH_3O_2] + 2k_{16a}[CH_3O_2]^2 + 2k_{14}[HO_2]^2 \end{aligned} \quad \text{Eq. S19}$$

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

$$\begin{aligned} 103 \quad & (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = \delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho + \\ 104 \quad & \left(2k_{16b}((1 - \delta)[RO_2^*])^2 + k_{25}(1 - \delta)[RO_2^*][NO] \right) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2 \\ 105 \quad & \end{aligned} \quad \text{Eq. S20}$$

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

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

108 Where

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

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

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

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 $(2j_1[O_3]\beta + j_3[HONO]) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = (2k_{16b}((1 - \delta)[RO_2^*])^2 + k_{25}(1 -$
 116 $\delta)[RO_2^*][NO]) \left(\frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) + 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2$

117

Eq. S22

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