



24 **Table S1.** The aqueous phase chemical mechanism and corresponding rate constants used in TM4-  
 25 ECPL. Units for the photolysis frequencies are s<sup>-1</sup>, and for the second order aqueous reactions are expressed  
 26 in L mol<sup>-1</sup> s<sup>-1</sup>. Reaction rates are taken from Lim et al. (2005), unless referred differently. Reactions rates are  
 27 calculated as follows:

$$k = k_{298} \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right]$$

Aqueous Phase Reactions			K <sub>298</sub>	E/R	
1	O <sub>3</sub> + <i>hν</i> (+ H <sub>2</sub> O)	→	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	a	
2	H <sub>2</sub> O <sub>2</sub> + <i>hν</i>	→	2OH	a	
3	HO <sub>2</sub> + HO <sub>2</sub>	→	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	9.7 10 <sup>5</sup>	2500
4	HO <sub>2</sub> + O <sub>2</sub> <sup>-</sup>	→	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.0 10 <sup>8</sup>	900
5	O <sub>3</sub> + O <sub>2</sub> <sup>-</sup> (+ H <sup>+</sup> )	→	OH + 2O <sub>2</sub> (+HO <sup>-</sup> )	1.5 10 <sup>9</sup>	
6	O <sub>3</sub> + OH	→	HO <sub>2</sub> + O <sub>2</sub>	1.1 10 <sup>8</sup>	
7	HO <sub>2</sub> + OH	→	O <sub>2</sub> + H <sub>2</sub> O	7.1 10 <sup>9</sup>	
8	OH + OH	→	H <sub>2</sub> O <sub>2</sub>	5.5 10 <sup>9</sup>	
9	H <sub>2</sub> O <sub>2</sub> + OH	→	HO <sub>2</sub> + H <sub>2</sub> O	2.7 10 <sup>7</sup>	
10	GLYAL + OH (+ O <sub>2</sub> )	→	GLY + HO <sub>2</sub>	1.0 10 <sup>9</sup>	1564 <sup>b</sup>
11	GLYAL + OH (+ O <sub>2</sub> )	→	GLX <sup>-</sup> + HO <sub>2</sub> + H <sub>2</sub> O	5.0 10 <sup>8</sup>	1564 <sup>b</sup>
12	GLY + OH (+ O <sub>2</sub> )	→	GLX <sup>-</sup> + HO <sub>2</sub>	1.1 10 <sup>9</sup>	1564 <sup>c</sup>
13	GLY + OH	→	PRODUCTS (0.03GLX <sup>-</sup> + 0.97OXL <sup>-</sup> )	3.1 10 <sup>9g</sup>	
14	GLY ( <i>aerosol water</i> )	→	PRODUCTS (0.2OXL <sup>-2</sup> + 0.8SOA)	h 1.3 10 <sup>-7</sup> (pH = 2) 2.4 10 <sup>-4</sup> (pH = 5) 0.43 (pH = 7)	
15	GLY + NH <sub>4</sub> <sup>+</sup> ( <i>aerosol water</i> )	→	PRODUCTS (SOA) <sup>i</sup>		
16	MGLY + OH	→	0.92PRV <sup>-</sup> + 0.08GLX <sup>-</sup> + HO <sub>2</sub> + H <sub>2</sub> O	1.1 10 <sup>9d</sup>	1600
17	HCOOH + OH	→	CO <sub>2</sub> + HO <sub>2</sub> + H <sub>2</sub> O	1.2 10 <sup>8</sup>	990
18	HCOO <sup>-</sup> + OH	→	CO <sub>2</sub> + H <sub>2</sub> O	3.1 10 <sup>9</sup>	1240
19	CH <sub>3</sub> COOH + OH	→	0.85GLX <sup>-</sup> + 0.15HCOO <sup>-</sup>	1.5 10 <sup>7</sup>	1330
20	CH <sub>3</sub> COO <sup>-</sup> + OH	→	0.85GLX <sup>-</sup> + 0.15HCOO <sup>-</sup>	1.9 10 <sup>9</sup>	1800
21	PRV + OH	→	CH <sub>3</sub> COOH + HO <sub>2</sub> + CO <sub>2</sub>	1.2 10 <sup>8</sup>	2766
22	PRV <sup>-</sup> + OH	→	CH <sub>3</sub> COOH + HO <sub>2</sub> + CO <sub>2</sub>	7.0 10 <sup>8</sup>	2285
23	GLX + OH (+ O <sub>2</sub> )	→	OXL <sup>-</sup> + HO <sub>2</sub>	3.6 10 <sup>8e</sup>	962 <sup>e</sup>
24	GLX <sup>-</sup> + OH	→	OXL <sup>-</sup> + HO <sub>2</sub>	2.8 10 <sup>9e</sup>	4330 <sup>e</sup>
25	OXL + 2OH	→	2CO <sub>2</sub> + 2H <sub>2</sub> O	1.4 10 <sup>6</sup>	2766 <sup>f</sup>
26	OXL <sup>-</sup> + OH	→	2CO <sub>2</sub> + 2H <sub>2</sub> O	1.9 10 <sup>8e</sup>	2766 <sup>e</sup>
27	OXL <sup>=</sup> + OH	→	2CO <sub>2</sub> + 2H <sub>2</sub> O	1.6 10 <sup>8e</sup>	4330 <sup>e</sup>

29 <sup>a</sup> Using the gas-phase photolysis rates (Myriokefalitakis et al. (2008) supplementary material.), increased by  
 30 a factor of 1.5 as recommended by Barth et al. (2003); <sup>b</sup> as for GLY; <sup>c</sup> Herrmann (2003); <sup>d</sup> rate constant from  
 31 Ervens et al. (2004); <sup>e</sup> Herrmann (2003); <sup>f</sup> as for OXL<sup>-</sup>; <sup>g</sup> lumped reactions based on Carlton et al. (2007); <sup>h</sup>  
 32 photochemical lumped reaction in aerosol water content based on Ervens and Volkamer (2010) with rate of  
 33 4s<sup>-1</sup> scaled on the photolysis frequencies of H<sub>2</sub>O<sub>2</sub>; <sup>i</sup> Noziere et al. (2009)

34

35 **Table S2.** Aqueous phase equilibrium used in TM4-ECPL. Dissociation constants are taken from Lim  
 36 et al. (2005) unless referred differently. Dissociation constants are expressed in mol L<sup>-1</sup> and are calculated as  
 37 follows:

$$k_{eq} = k_{eq298} \exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

38

Aqueous Phase Equilibrium			Keq <sub>298</sub>	-ΔH/R
HO <sub>2</sub>	↔	HO <sup>-</sup> + H <sup>+</sup>	1.6 10 <sup>-5</sup> <sup>a</sup>	
H <sub>2</sub> O <sub>2</sub>	↔	HO <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	2.2 10 <sup>-12</sup>	3700
HCOOH	↔	HCOO <sup>-</sup> + H <sup>+</sup>	1.77 10 <sup>-4</sup>	-12
GLX	↔	GLX <sup>-</sup> + H <sup>+</sup>	3.47 10 <sup>-4</sup>	267
OXL	↔	OXL <sup>-</sup> + H <sup>+</sup>	5.6 10 <sup>-3</sup>	453
OXL <sup>-</sup>	↔	OXL <sup>=</sup> + H <sup>+</sup>	5.42 10 <sup>-5</sup>	805

39 <sup>a</sup> Seinfeld and Pandis (1998)

40

41 **Table S3.** Henry's law constants used in TM4-ECPL. Henry constants are taken from Sander (1999)  
 42 unless referred differently. Henry constants are expressed in mol L<sup>-1</sup> atm<sup>-1</sup> and are calculated as  
 43 follows:

$$H = H_{298} \exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

44

Species	H <sub>298</sub>	-ΔH/R
OH	9.0 10 <sup>3</sup>	4500
HO <sub>2</sub>	4.6 10 <sup>3</sup>	4800
H <sub>2</sub> O <sub>2</sub>	8.6 10 <sup>4</sup>	6500
HCOOH	8.9 10 <sup>3</sup>	6100
CH <sub>3</sub> COOH	4.1 10 <sup>3</sup>	6300
PRV	3.1 10 <sup>5</sup>	5100
GLYAL	4.1 10 <sup>4</sup>	4600
GLY <sup>(a)</sup>	4.19 10 <sup>5</sup>	62200/R
MGLY	3.7 10 <sup>3</sup>	7500
GLX <sup>a</sup>	1.09 10 <sup>4</sup>	40000/R
OXL <sup>b</sup>	3.26 10 <sup>6</sup>	

45 <sup>a</sup> Ip et al. (2009); R=8.314 J mol<sup>-1</sup> K<sup>-1</sup>, is the universal gas constant; <sup>b</sup> Brimblecombe et al. (1992) ; The  
 46 temperature dependence Henry's value is calculated following :  $\ln(H) = -9.45 + 7285/T$

47

## 48 **A1 Exchange between gas and aqueous phase**

49 Aqueous-phase chemistry is simulated in the model as a first-order, first degree homogeneous,  
50 ordinary equation:

$$51 \quad \frac{dC_i}{dt} = P_i - L_i C_i \quad (1)$$

52 where  $C_i$  is the concentration,  $P_i$  is the chemical production of the species  $i$ , and  $L_i$  is the pseudo-  
53 first-order loss term of the species  $i$ . Because of the stiffness of the simultaneous solution of  
54 gaseous and aqueous phase chemistry (lifetime of the species differs by many orders of magnitude),  
55 the Euler backward iterative (EBI) method is used, as suggested by Barth et al. (2003). The Barth-  
56 EBI approximation is a stable, implicit method which solves Equation 1 as

$$57 \quad C^{n+1,i+1} = \frac{C^n + P^{n+1,i} \Delta t}{1 + L^{n+1,i} \Delta t} \quad (2)$$

58 where  $n$  is the current time step,  $n+1$  is the next time step,  $\Delta t$  is the time step duration, and  $i$   
59 represents the number of iterations. This method uses 0.01% for the threshold convergence criterion  
60 for all species. Important parameters for the solubility of gases in cloud droplets are the liquid water  
61 content ( $LWC$ ) and the temperature ( $T$ ). The solubility of gases in water is governed by the Henry's  
62 law constant ( $H$ ) (Table S3). For a given  $T$ ,  $H$  and  $LWC$ , the phase ratio ( $\Phi_x$ ), which represents the  
63 amount of gas in a given volume of air which resides in the aqueous-phase relative to the amount in  
64 the interstitial gas-phase (Lelieveld and Crutzen, 1991; Barth et al., 2003), is calculated by:

$$65 \quad \Phi_x = H(T) \cdot R \cdot T \cdot LWC \quad (3)$$

66 where  $H(T)$  is the temperature dependent effective Henry's law constant,  $R$  is the universal gas  
67 constant ( $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature ( $K$ ) and  $LWC$  is the liquid water content ( $\text{cm}^3$   
68  $\text{H}_2\text{O cm}^{-3} \text{ air}$ ). The concentration of a species  $i$  ( $C_{i,liq}$  in  $\text{molecule cm}^{-3}$ ) in the liquid phase in  
69 connection with the total concentration ( $C_{tot}$  in  $\text{molecule cm}^{-3}$ ) is calculated using the  $\Phi_x$  as,

$$70 \quad C_{i,liq} = \frac{\Phi_x}{1 + \Phi_x} C_{i,tot} \quad (4)$$

71 However, a chemical species may not achieve equilibrium on the timescales of the model's time  
72 step because of mass transfer kinetic limitations between phases (Schwartz, 1986). The rate of  
73 change of a chemical species  $i$ , due to mass transfer between gas and liquid phase can be defined as

$$74 \quad k_{t,i} = \left( \frac{r^2}{3D_g} + \frac{4r}{3va} \right)^{-1} \quad (5)$$

75 where  $k_{t,i}$  is the transfer coefficient ( $s^{-1}$ ),  $r$  the droplet radius ( $m$ ),  $D_g$  the gas-phase diffusion  
76 coefficient ( $m^2 s^{-1}$ ),  $v$  the mean molecular speed ( $m s^{-1}$ ) and  $\alpha$  the mass accommodation coefficient  
77 (Table S3). The  $D_g$  and the  $v$  are defined as:

$$D_g = 1.9(MW)^{-\frac{2}{3}} \quad (6)$$

$$v = \left( \frac{8k_B T N_a}{\pi(MW)} \right)^{-\frac{1}{2}} \quad (7)$$

78

79

80 where  $MW$  is the molecular weight,  $k_B$  the Boltzmann constant ( $1.38 \times 10^{-16} \text{ dyn cm K}^{-1}$ ) and  $N_a$  the  
81 Avogadro number ( $6.023 \times 10^{23} \text{ molecule mol}^{-1}$ ).

82 For the present study only OH and HO<sub>2</sub> radicals are considered to be subjected to kinetic  
83 limitations. Barth et al. (2003) suggested that OH and HO<sub>2</sub> radicals are not in equilibrium between  
84 the gas and aqueous phases. For those two radicals, the model calculates the  $k_t$  taking into account a  
85 cloud droplet radius of 5  $\mu\text{m}$  and mass accommodation coefficients of 0.05 and 0.01 for OH and  
86 HO<sub>2</sub> radicals, respectively, as suggested by Herrmann et al. (2000).

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