

24 **Table S1.** The aqueous phase chemical mechanism and corresponding rate constants used in TM4-
 25 ECPL. Units for the photolysis frequencies are s⁻¹, and for the second order aqueous reactions are expressed
 26 in L mol⁻¹ s⁻¹. 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 ₂₉₈	E/R	
1	O ₃ + <i>hν</i> (+ H ₂ O)	→	H ₂ O ₂ + O ₂	a	
2	H ₂ O ₂ + <i>hν</i>	→	2OH	a	
3	HO ₂ + HO ₂	→	H ₂ O ₂ + O ₂	9.7 10 ⁵	2500
4	HO ₂ + O ₂ ⁻	→	H ₂ O ₂ + O ₂	1.0 10 ⁸	900
5	O ₃ + O ₂ ⁻ (+ H ⁺)	→	OH + 2O ₂ (+HO ⁻)	1.5 10 ⁹	
6	O ₃ + OH	→	HO ₂ + O ₂	1.1 10 ⁸	
7	HO ₂ + OH	→	O ₂ + H ₂ O	7.1 10 ⁹	
8	OH + OH	→	H ₂ O ₂	5.5 10 ⁹	
9	H ₂ O ₂ + OH	→	HO ₂ + H ₂ O	2.7 10 ⁷	
10	GLYAL + OH (+ O ₂)	→	GLY + HO ₂	1.0 10 ⁹	1564 ^b
11	GLYAL + OH (+ O ₂)	→	GLX ⁻ + HO ₂ + H ₂ O	5.0 10 ⁸	1564 ^b
12	GLY + OH (+ O ₂)	→	GLX ⁻ + HO ₂	1.1 10 ⁹	1564 ^c
13	GLY + OH	→	PRODUCTS (0.03GLX ⁻ + 0.97OXL ⁻)	3.1 10 ^{9g}	
14	GLY (<i>aerosol water</i>)	→	PRODUCTS (0.2OXL ⁻² + 0.8SOA)	h 1.3 10 ⁻⁷ (pH = 2) 2.4 10 ⁻⁴ (pH = 5) 0.43 (pH = 7)	
15	GLY + NH ₄ ⁺ (<i>aerosol water</i>)	→	PRODUCTS (SOA) ⁱ		
16	MGLY + OH	→	0.92PRV ⁻ + 0.08GLX ⁻ + HO ₂ + H ₂ O	1.1 10 ^{9d}	1600
17	HCOOH + OH	→	CO ₂ + HO ₂ + H ₂ O	1.2 10 ⁸	990
18	HCOO ⁻ + OH	→	CO ₂ + H ₂ O	3.1 10 ⁹	1240
19	CH ₃ COOH + OH	→	0.85GLX ⁻ + 0.15HCOO ⁻	1.5 10 ⁷	1330
20	CH ₃ COO ⁻ + OH	→	0.85GLX ⁻ + 0.15HCOO ⁻	1.9 10 ⁹	1800
21	PRV + OH	→	CH ₃ COOH + HO ₂ + CO ₂	1.2 10 ⁸	2766
22	PRV ⁻ + OH	→	CH ₃ COOH + HO ₂ + CO ₂	7.0 10 ⁸	2285
23	GLX + OH (+ O ₂)	→	OXL ⁻ + HO ₂	3.6 10 ^{8e}	962 ^e
24	GLX ⁻ + OH	→	OXL ⁻ + HO ₂	2.8 10 ^{9e}	4330 ^e
25	OXL + 2OH	→	2CO ₂ + 2H ₂ O	1.4 10 ⁶	2766 ^f
26	OXL ⁻ + OH	→	2CO ₂ + 2H ₂ O	1.9 10 ^{8e}	2766 ^e
27	OXL ⁼ + OH	→	2CO ₂ + 2H ₂ O	1.6 10 ^{8e}	4330 ^e

29 ^aUsing 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); ^b as for GLY; ^c Herrmann (2003); ^d rate constant from
 31 Ervens et al. (2004); ^e Herrmann (2003); ^f as for OXL⁻; ^g lumped reactions based on Carlton et al. (2007); ^h
 32 photochemical lumped reaction in aerosol water content based on Ervens and Volkamer (2010) with rate of
 33 4s⁻¹ scaled on the photolysis frequencies of H₂O₂; ⁱ 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⁻¹ 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 ₂₉₈	-ΔH/R
HO ₂	↔	HO ⁻ + H ⁺	1.6 10 ⁻⁵ ^a	
H ₂ O ₂	↔	HO ₂ ⁻ + H ⁺	2.2 10 ⁻¹²	3700
HCOOH	↔	HCOO ⁻ + H ⁺	1.77 10 ⁻⁴	-12
GLX	↔	GLX ⁻ + H ⁺	3.47 10 ⁻⁴	267
OXL	↔	OXL ⁻ + H ⁺	5.6 10 ⁻³	453
OXL ⁻	↔	OXL ⁼ + H ⁺	5.42 10 ⁻⁵	805

39 ^a 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⁻¹ atm⁻¹ 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 ₂₉₈	-ΔH/R
OH	9.0·10 ³	4500
HO ₂	4.6·10 ³	4800
H ₂ O ₂	8.6·10 ⁴	6500
HCOOH	8.9·10 ³	6100
CH ₃ COOH	4.1·10 ³	6300
PRV	3.1 10 ⁵	5100
GLYAL	4.1·10 ⁴	4600
GLY ^(a)	4.19·10 ⁵	62200/R
MGLY	3.7·10 ³	7500
GLX ^a	1.09·10 ⁴	40000/R
OXL ^b	3.26·10 ⁶	

45 ^a Ip et al. (2009); R=8.314 J mol⁻¹ K⁻¹, is the universal gas constant; ^b 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, Δt 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 (Φ_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 (cm^3
68 $\text{H}_2\text{O cm}^{-3} \text{ air}$). The concentration of a species i ($C_{i,liq}$ in molecule cm^{-3}) in the liquid phase in
69 connection with the total concentration (C_{tot} in molecule cm^{-3}) is calculated using the Φ_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 α 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 HO₂ radicals are considered to be subjected to kinetic
83 limitations. Barth et al. (2003) suggested that OH and HO₂ 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 μm and mass accommodation coefficients of 0.05 and 0.01 for OH and
86 HO₂ radicals, respectively, as suggested by Herrmann et al. (2000).

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88 References

- 89 Brimblecombe, P., Clegg, S.L., Khan, I.: Thermodynamic properties of carboxylic acids relevant to
90 their solubility in aqueous solutions, *J. Aeros. Sci.*, 23, suppl. I, S901-S904, 1992.
- 91 Barth, M.C., Sillman, S., Hudman, R., Jacobson, M.Z., Kim, C.-H., Monod, A., Liang, J.: Summary
92 of the cloud chemistry modeling intercomparison: Photochemical box model simulation, *J.*
93 *Geophys. Res.*, 108, 4214, doi:10.1029/2002JD002673, 2003.
- 94 Carlton, A.G., Turpin, B.J., Altieri, K.E., Seitzinger, S., Reff, A., Lim, H.-J., Ervens, B.:
95 Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous
96 photooxidation experiments, *Atmos. Environ.*, 41, 7588–7602,
97 doi:10.1016/j.atmosenv.2007.05.035, 2007.
- 98 Ervens, B., Feingold, G., Frost, G.J., Kreidenweis S.M.: A modeling study of aqueous production of
99 dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys.*
100 *Res.*, 109, D15205, doi:10.1029/2003JD004387, 2004.
- 101 Ervens, B., and Volkamer, R.: Glyoxal processing outside clouds: towards a kinetic modeling
102 framework of secondary organic aerosol formation in aqueous particles, *Atmos. Chem. Phys.*,
103 10, 8219-8244, doi:10.5194/acp-10-8219-2010, 2010.
- 104 Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke R., Nowacki P., Zellner R.: CAPRAM2.3: A
105 Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, *J. Atmos.*
106 *Chem.*36, 231–284, 2000.
- 107 Herrmann, H.: Kinetics of Aqueous Phase Reactions Relevant for Atmospheric Chemistry, *Chem.*
108 *Rev.* 2003, 103, 4691-4716, doi: 10.1021/cr020658q, 2003.
- 109 Ip, H.S.S., Huang, X.H.H., Yu J.Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and
110 glycolic acid, *Geophys. Res. Lett.*, 36, L01802, doi:10.1029/2008GL036212, 2009.
- 111 Lelieveld J. and Crutzen, P.J.: The role of clouds in tropospheric photochemistry, *J. Atmos. Chem.*,
112 12, 229-267, 1991.
- 113 Lim, H.-J., Carlton, A.G., Turpin, B.J.: Isoprene forms secondary organic aerosol through cloud
114 processing: Model simulations, *Environ. Sci. Technol.*, 39, 4441–4446, 2005.
- 115 Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Brühl, C., Volkamer,
116 R., Burrows, J.P., Kanakidou, M.: The influence of natural and anthropogenic secondary
117 sources on the glyoxal global distribution, *Atmos. Chem. Phys.*, 8, 4965–4981, 2008.
- 118 Noziere, B., Dziedzic, P., Cordova, A.: Products and Kinetics of the Liquid-Phase Reaction of
119 Glyoxal Catalyzed by Ammonium Ions (NH_4^+), *J. Phys. Chem. A.*, 113, 231–237, doi:
120 10.1021/jp8078293, 2009.
- 121 Sander, R.: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential
122 Importance in Environmental Chemistry, available at [http://www.mpch-](http://www.mpch-mainz.mpg.de/~sander/res/henry.html)
123 [mainz.mpg.de/~sander/res/henry.html](http://www.mpch-mainz.mpg.de/~sander/res/henry.html), 1999.
- 124 Schwartz, S.E.: Mass-transport considerations pertinent to aqueous phase reactions of gases on
125 liquid water clouds, in *Chemistry of Multiphase Atmospheric Systems*, NATO ASI Ser.,
126 edited by W. Jaeschke, Springer, Berlin, 1986.
- 127 Seinfeld J. H. and Pandis S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate*
128 *Change*, A Wiley-Interscience publication, USA, 1998.