



Supplement of

The number fraction of iron-containing particles affects OH, HO_2 and H_2O_2 budgets in the atmospheric aqueous phase

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S1 Chemical mechanism and model input parameters

Table S1. Irreversible aqueous reactions

	Reactants		Products	k [M ⁻¹ s ⁻¹]	$E_a/R[K]$
R1	$SO_2 + O_3$	\rightarrow	$S(VI) + O_2$	$2.4 \cdot 10^4$	
R2	$HSO_3^- + O_3$	\rightarrow	$S(VI) + O_2$	$3.7 \cdot 10^5$	5530
R3	$SO_3^{2-} + O_3$	\rightarrow	$S(VI) + O_2$	$1.5 \cdot 10^9$	5280
R4	$H_2O_2 + HSO_3 + H^+$	\rightarrow	$S(VI) + H_2O$	$7.2 \cdot 10^7 \text{ M}^{-2} \text{ s}^{-1}$	4000
R5	$HO_2 + HO_2$	\rightarrow	$H_2O_2 + O_2$	$8.3 \cdot 10^5$	2720
R6	$O_2^- + HO_2$	\rightarrow	$H_2O_2 + O_2$	$9.7 \cdot 10^7$	1060
R7	$OH + CH_2O$	\rightarrow	$HO_2 + HCOOH$	1.10^{9}	1000
R8	$OH + CH_3OOH$	\rightarrow	$CH_3O_2 + H_2O$	$2.4 \cdot 10^7$	1680
R9	OH + CH ₃ OOH	\rightarrow	$HO_2 + HCOOH$	6.10^{6}	1680
R10	$O_3 + O_2^- (+ H^+)$	\rightarrow	$OH + 2 O_2$	$1.5 \cdot 10^9$	2200
R11	OH + CHOCHO	\rightarrow	HO ₂ + CHOCOOH	$1.1 \cdot 10^{9}$	1516
R12	OH + CHOCOOH	\rightarrow	$HO_2 + H_2C_2O_4$	$3.6 \cdot 10^8$	1000
R13	OH + CHOCOO ⁻	\rightarrow	$H_2C_2O_4$ -	$2.9 \cdot 10^9$	4300
R14	$OH + C_2 O_4^{2-}$	\rightarrow	$O_2^- + 2 CO_2 + OH^-$	$1.6 \cdot 10^8$	4300
R15	$OH + HC_2O_4^-$	\rightarrow	$HO_2 + 2 CO_2 + OH^2$	$1.9 \cdot 10^8$	2800
R16	$OH + H_2C_2O_4$	\rightarrow	$HO_2 + 2 CO_2 + H_2O$	$1.4 \cdot 10^{6}$	
R17	$OH + CH_3C(O)COOH$	\rightarrow	$HO_2 + CO_2 + CH_3COO^-$	7.10^{8}	
R18	OH + CH ₃ COCOOH	\rightarrow	$HO_2 + H_2O + CH_3COOH$	$1.2 \cdot 10^8$	
R19	OH + CHOCHO	\rightarrow	$HO_2 + CHOCOOH$	$1.1 \cdot 10^9$	1516
R20	OH + HCOO ⁻	\rightarrow	$HO_2 + CO_2 + H_2O$	$3.2 \cdot 10^9$	1000
R21	OH + HCOOH	\rightarrow	$HO_2 + CO_2 + H_2O$	$1.3 \cdot 10^8$	1000
R22	$CH_3O_2 + CH_3O_2$	\rightarrow	$CH_2O + CH_3OH + HO_2$	$1.7 \cdot 10^8$	2200
R23	$H_2O_2 + OH$	\rightarrow	$HO_2 + H_2O$	3.10^{7}	1680
R24	OH + WSOC	\rightarrow	WSOC + HO_2	$3.8 \cdot 10^8$	
R25	$Fe^{2+} + H_2O_2$	\rightarrow	Fe ³⁺ +OH+OH ⁻	55	
R26	$Fe^{3+} + HO_2$	\rightarrow	$Fe^{2+} + O_2 + H^+$	$1.3 \cdot 10^5$	
R27	$Fe^{3+} + O_2^{-}$	\rightarrow	$Fe^{2+} + O_2$	$1.5 \cdot 10^8$	
R28	$Fe^{3+} + H_2O_2$	\rightarrow	$Fe^{2+} + HO_2 + H^+$	0.002	
R29	$Fe^{2+} + H_2O_2$	\rightarrow	$Fe^{4+} + H_2O$	0.06	
R30	$Fe^{2+} + O_2$	\rightarrow	$O_2^- + Fe^{3+}$	200	
R31	$Fe^{2+} + O_2^- (+2H^+)$	\rightarrow	$Fe^{3+} + H_2O_2$	1.10^{7}	
R32	$Fe^{3+}+C_2O_4^{2-}$	\rightarrow	$[Fe(C_2O_4)]^+$	$2.9 \cdot 10^{9}$	
R33	$[Fe(C_2O_4)^+] + C_2O_4^{2-}$	\rightarrow	$[Fe(C_2O_4)]^{2-}$	$1.89 \cdot 10^4$	
R34	$[Fe(C_2O_4)^{2-}] + C_2O_4^{2-}$	\rightarrow	$[Fe(C_2O_4)_2]^{3-1}$	114	
R35	$[Fe(OH)]^{2+} + O_2^{-}$	\rightarrow	$O_2 + Fe^{2+} + OH^{-}$	$1.5 \cdot 10^8$	
R36	[Fe(OH)]2++ HO ₂	\rightarrow	$O_2 + Fe^{2+} + H_2O$	$1.3 \cdot 10^5$	
R37	$[Fe(OH)_2] + + O_2^-$	\rightarrow	$O_2 + Fe^{2+} + 2 OH^{-}$	$1.5 \cdot 10^8$	
R38	$[Fe(OH)_2] + HO_2$	\rightarrow	$O_2^- + Fe^{2+} + H_2O$	$1.3 \cdot 10^5$	
R39	$Fe^{3+} + H_2O$	\rightarrow	$[Fe(OH)]^{2+} + H^+$	$4.7 \cdot 10^4$	
R40	$[Fe(OH)]^{2+} + H_2O$	\rightarrow	$[Fe(OH)_2]^+ + H^+$	$1.1 \cdot 10^3$	
R41	$[Fe(OH)]^{2+} + H^{+}$	\rightarrow	$Fe^{3+} + +H_2O$	$4.3 \cdot 10^8$	
R42	$[Fe(OH)_2]^+ + H^+$	\rightarrow	$[Fe(OH)]^{2+}$ +H ₂ O	$8 \cdot 10^{7}$	
R43	$Fe^{2+} + OH$	\rightarrow	$[Fe(OH)]^{2+}$	$4.3 \cdot 10^8$	

				K_a [M]
E1	H_2O	\rightleftharpoons	OH^-+H^+	$1.0 \cdot 10^{-14}$
E2	HO_2	\rightleftharpoons	$O_2^- + H^+$	$1.60 \cdot 10^{-5}$
E3	CHOCOOH	\rightleftharpoons	$CHOCOO^{-} + H^{+}$	$6.60 \cdot 10^{-4}$
E4	HCOOH	\rightleftharpoons	$HCOO^{-} + H^{+}$	$1.77 \cdot 10^{-4}$
E5	$H_2C_2O_4$	\rightleftharpoons	$HC_2O_4^- + H^+$	$6.40 \cdot 10^{-2}$
E6	$HC_2O_4^-$	\rightleftharpoons	$C_2O_4^{2-} + H^+$	$5.25 \cdot 10^{-5}$
E7	HNO_3	\rightleftharpoons	$NO_{3}^{-} + H^{+}$	22
E8	$SO_2 + H_2O$	\rightleftharpoons	$HSO_3^- + H^+$	0.013
E9	HSO ₃ ⁻	\rightleftharpoons	$SO_3^{2-} + H^+$	$6.60 \cdot 10^{-8}$
E10	H_2SO_4	\rightleftharpoons	$HSO_4^- + H^+$	1000
E11	HSO_4	\rightleftharpoons	$SO_4^{2-} + H^+$	0.102
E12	NH_3	\rightleftharpoons	$\mathrm{NH_4^+} + \mathrm{OH^-}$	$1.76 \cdot 10^{-5}$

Table S3. Photolyses in the aqueous phase

	Reaction			J [s ⁻¹]
P1	$[Fe(OH)^{2+}] + h\nu$	\rightarrow	$Fe^{2+} + OH$	$1.83 \cdot 10^{-4}$
P2	$[Fe(OH)_2]^+ + h\nu$	\rightarrow	$Fe^{2+} + OH + OH^{-}$	$1.83 \cdot 10^{-4}$
P3	$[Fe(C_2O_4)_2]^- + h\nu$	\rightarrow	$Fe^{2+} + C_2O_4^{2-} + C_2O_4^{-}$	9.19·10 ⁻⁴
P4	$[Fe(C_2O_4)_3]^{3-} + h\nu$	\rightarrow	$Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{}$	9.19·10 ⁻⁴
P5	$H_2O_2 + h\nu$	\rightarrow	2 OH	8.13·10 ⁻⁶

Table S4. Phase transfer parameters, used in Eq-1 and Eq-2, molecular weight $M_g \text{ [mol g}^{-1}$, mass accommodation coefficient α (dimensionless), gas phase diffusion coefficient $D_g \text{ [cm s}^{-1}\text{]}$ and Henry's law constant $K_H \text{ [M atm}^{-1}\text{]}$

Species	M_{g}	α	D_g	K _H
O ₃	48	0.05	0.148	$1.14 \cdot 10^{-2}$
H_2O_2	34	0.1	0.118	$1.02 \cdot 10^5$
OH	17	0.05	0.153	25
HO ₂	33	0.05	0.104	9.10^{3}
HCHO	30	0.02	0.164	$4.99 \cdot 10^3$
CH ₃ O ₂	47	0.0038	0.135	310
CH ₃ OOH	48	0.0038	0.135	310
HNO ₃	63	0.054	0.132	$2.1 \cdot 10^5$
N_2O_5	108	0.0037	0.110	1.4
SO_2	64	0.035	0.128	1.23
HCOOH	46	0.012	0.153	$1.77 \cdot 10^{-4}$
(CHO) ₂	58	0.023	0.115	$4.19 \cdot 10^5$
CH ₃ COCHO	72	0.1	0.115	$3.2 \cdot 10^4$
NH ₃	17	0.1	0.1	60.7

Table S5. Initial gas phase mixing ratios [ppb]; all other species are not initialized

Species	Mixing ratio
O ₃	30
H_2O_2	1
HCHO	1
HNO ₃	1
SO_2	0.5
NH_3	1
NO	2
CO	150
C ₅ H ₈	2
C_7H_8	2
C_2H_4	0.5

S2 Aqueous phase diffusion

Gradients between the drop surface and the center of the droplets (or particles) can occur when highly reactive species (e.g. OH, HO_2) are taken up from the gas phase into the aqueous phase and are efficiently consumed faster by chemical reactions than aqueous phase diffusion can replenish their concentration throughout the aqueous phase volume. The deviation from a homogeneously mixed aqueous phase is commonly quantified by the diffuso-reactive parameter *q* (Seinfeld and Pandis, 1998):

$$q = 0.5 D \sqrt{\frac{k^{loss}}{D_{aq}}}$$
(S.1)

whereas D is the drop (particle) diameter (20 μ m for cloud droplets, 300 nm for aerosol particles in our study), D_{aq} is the aqueous phase diffusion coefficient 2.10² cm⁻² s⁻¹ and k^{loss} is the total chemical first-order loss rate in the aqueous phase $(k^{2nd} \cdot [reactant])$ [s⁻¹].

The main loss process of OH(aq) is the reaction with WSOC ([WSOC]= $1.3 \cdot 10^{-4}$ M in cloud water, 2.6 M in aerosol water). We assume that k^{loss} of OH is entirely determined by this reaction (Ervens et al., 2014). The main single loss process of the HO₂ radical is the reaction with Fe(III) that contributes to 20% for $F_{N,Fe} = 2\%$ and 80% for $F_{N,Fe} = 100\%$. In iron-free droplets and particles, the recombination of HO₂ is its main loss process (Section 3.2). Therefore, using the HO₂ concentrations as shown in Figures 2 and 3 ($2.4 \cdot 10^{-8}$ M and $2.2 \cdot 10^{-7}$ M) can be assumed, together with an average rate constant of $4.7 \cdot 10^{7}$ M⁻¹ s⁻¹ (($k_{HO2+O2} + k_{HO2+HO2}$)/2) is assumed to account for the approximately equal proportions of HO₂ and O₂⁻ at pH = 4.5. Therefore, the first-order loss rates for OH and HO₂ can be estimated as:

 $k_{OH}^{loss} = 3.8 \cdot 10^8 \cdot [WSOC]$

 $k_{HO2}^{loss} = 1.5 \cdot 10^8 \cdot [Fe(III)]$ (iron-containing; FeBulk and FeN<100)

 $k_{HO2}^{loss} = 8.3 \cdot 10^{5} [HO_2] + 9.7 \cdot 10^{7} [O_2^{-}]$ (iron-free, FeN<100)

The resulting q values are summarized in Table S6.

		Cloud		Aeroso	Aerosol	
	OH	[WSOC]	q	[WSOC]	q	
All droplets (particles)		$1.3 \cdot 10^{-4}$	50	2.6	105	
	HO ₂	[Fe(III)]	q	[Fe(III)]	q	
FeBulk		$8.2\cdot 10^{-8}$	0.8	$1.6\cdot 10^{-3}$	1.6	
FeN<100, Fe-containing		$1.7 \cdot 10^{-5}$	11	0.33	24	
		[HO ₂]	q	[HO ₂]	q	
FeN<100, Fe-free		$2.4 \cdot 10^{-8}$	0.24	$2.2\cdot 10^{-7}$	0.01	

Table S6. Diffuso-reactive parameter q (Equation S.1) of OH and HO₂ radicals in cloud droplets and aerosol particles (pH = 4.5); the concentrations of the reactants of the main loss reactions (WSOC, Fe(III), HO₂) are given in M.

For OH, the diffuso-reactive parameters are 50 and 105 in clouds and aerosol particles, respectively. However, it has been discussed in our previous study that iron concentrations on the order of micromolar (clouds) and molar (aerosol particles) are sufficient to make the Fenton reaction compensating for the rapid OH loss (Table 1 in Ervens (2015)).

Generally, the q values of HO₂ are smaller than those for OH with a maximum of 24 in iron-containing particles. Similar to the OH formation, also HO₂ is efficiently formed in the aqueous phase, with highest rates in iron-containing particles (FeN>100). Therefore, also for the HO₂ radical (including its anion), no significant concentration gradients occur between droplet (particle) surface and center. In iron-free droplets and particles, q is less than unity, i.e., even without HO₂ formation in the aqueous phase no concentration gradients exist.

S3 Contribution of gas phase diffusion to the reactive uptake parameter γ

For the derivation of γ based on lab studies, it is assumed that γ solely depends on the molecular speed and the droplet surface (e.g., Pöschl et al. (2007)). Figure S8 shows the calculated γ values using Equation 7 (identical to Fig. 8 in the main manuscript), together with results using the simpler version of this equation, Equation S.3, that does not include a term to account for gas phase diffusion.

$$k^{\rm loss} = \gamma \frac{\omega S}{4} \tag{S.2}$$

and accordingly

$$\gamma = \frac{S}{k^{\text{loss}}} \tag{S.3}$$

The comparison of the γ values demonstrates that the reactive uptake of the OH radical into cloud droplets is significantly controlled by gas phase diffusion; neglecting this effect would lead to an overestimate of the reactive uptake coefficient by a factor of ~3 ($\gamma_{OH} \sim 0.002$ vs $\gamma_{OH} \sim 0.006$). The difference in the γ_{HO2} values calculated by Equations 7 and S.3 is negligible for cloud droplets with a pH = 3 whereas it is approximately a factor of 2 at pH = 6. The reason for this trend is the larger k^{loss} rate at higher pH since the O_2^- radical anion reacts faster than the undissociated HO₂ radical.

The difference in the γ values for both radicals is much smaller for aerosol particles, i.e., γ_{OH} is overestimated by ~10% if gas phase diffusion is neglected (0.038 vs 0.045 in Figure S8c). The values for the HO₂ radical, γ_{HO2} , are nearly indistinguishable using both equations (Equation 7 and S.3, Figure S8d). Also under aerosol conditions, the pH value asnd $F_{N,Fe}$ have a much greater influence on γ_{HO2} than gas phase diffusion. This analysis demonstrates that gas phase diffusion should be taken into account for the reactive uptake of the radical into cloud droplets as suggested previously ((Jacob, 2000)), whereas the role for uptake onto aerosol particles is of minor importance.



Figure S1. Same as Figure 2 (cloud case) but for a, b) pH = 3 and c, d) pH = 6 (lower part)



Figure S2. Same as Figure 3 (aerosol case) but for a, b) pH = 3 and c, d) pH = 6 (lower part)



Figure S3. Gas phase concentrations of (a, d) H_2O_2 [ppb], (b,e) OH [molec cm⁻³], (c,f) HO₂ [molec cm⁻³]. Upper panels: Cloud simulations; lower panels: Aerosol simulations. The grey vertical line in all panels denotes the time of t = 400 s, at which most of the analyses are performed.



Figure S4. Relative contributions of chemical and phase transfer rates to the total sources and losses of the three ROS at t = 2000 s. The total rates [mol g_{air}^{-1} s⁻¹] are shown in boxes at the upper right of each panel. For the FeN<100 approach, the contribution in iron-free and iron-containing droplets (particles) are displayed as open and dashed bars; those for the FeBulk approach in solid filled bars. Simulations were performed at constant pH values of pH = 3 (red), 4.5 (black). and 6 (blue) for cloud conditions: a) H₂O₂, b) OH, c) HO₂, and aerosol conditions: d) H₂O₂, e) OH, f) HO₂. The chemical aqueous phase source (S) and loss (L) reactions are listed between the panels.



Figure S5. Bulk aqueous phase concentrations of H_2O_2 , OH, and HO_2 for the cloud (a - c) and aerosol (d - f) cases as a function of $F_{N,Fe}$ using the model parameters listed in Table 1. Solid lines: $m_{Fe} = 10$ ng m⁻³ (identical to Figure 6); dashed lines: $m_{Fe} = 50$ ng m⁻³.



Figure S6. Comparison of aqueous phase concentrations in aerosol particles using the physical Henry's law constant for H_2O_2 ($K_{H,H2O2} = 1.02 \cdot 10^5$ M atm⁻¹) for a) H_2O_2 , b) OH, c) HO₂, and the effective Henry's law constant ($K_{H,H2O2} = 2.7 \cdot 10^8$ M atm⁻¹) as determined based on measurements of gas and particle H_2O_2 concentrations, d) H_2O_2 , e) OH, f) HO₂,



Figure S7. Predicted Fe(II)/Fe(total) ratios at pH = 3, 4.5 and 6 and the conditions as given in Table 1. a) Cloud, b) Aerosol, c) Aerosol with enhanced partitioning of H₂O₂ ($K_{H,H2O2} = 2.7 \cdot 10^8$ M atm⁻¹; Section 3.3.2). Solid lines are for $m_{Fe} = 10$ ng m⁻³; dashed lines are for $m_{Fe} = 50$ ng m⁻³



Figure S8. Reactive uptake coefficients for (a, c) OH and (b, d) HO₂. Left panels: cloud conditions; right panels: aerosol conditions. The solid lines denote γ values based on Equation (7); dashed lines denote γ values based on Equation (S.3). The difference between the two values represents the effect of gas phase diffusion.



Figure S9. ROS aqueous phase concentrations for a-c) cloud case and d-f) aerosol case for droplet and particle diameters that differ by a factor of 0.5 and 2, respectively, from those of the base case.

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