

The Chemical Mechanism of SCAV

used in the MADE-IN simulations

Table 1: Heterogeneous reactions

#	labels	reaction	rate coefficient	reference
H1001f	TrAraMblScScm	$O_3 \rightarrow O_3(aq)$	$k_{\text{exf}}(\text{KPP_O3})$	see note
H1001b	TrAraMblScScm	$O_3(aq) \rightarrow O_3$	$k_{\text{exb}}(\text{KPP_O3})$	see note
H2102f	TrAraMblScScm	$H_2O_2 \rightarrow H_2O_2(aq)$	$k_{\text{exf}}(\text{KPP_H2O2})$	see note
H2102b	TrAraMblScScm	$H_2O_2(aq) \rightarrow H_2O_2$	$k_{\text{exb}}(\text{KPP_H2O2})$	see note
H3200f	TrAraNMblScScm	$NH_3 \rightarrow NH_3(aq)$	$k_{\text{exf}}(\text{KPP_NH3})$	see note
H3200b	TrAraNMblScScm	$NH_3(aq) \rightarrow NH_3$	$k_{\text{exb}}(\text{KPP_NH3})$	see note
H3201	TrAraMblNScScm	$N_2O_5 \rightarrow HNO_3(aq) + HNO_3(aq)$	$k_{\text{exf_N2O5}*C}(\text{KPP_H2O_1})$	Behnke et al. (1994), Behnke et al. (1997)
H3203f	TrAraMblNScScm	$HNO_3 \rightarrow HNO_3(aq)$	$k_{\text{exf}}(\text{KPP_HNO3})$	see note
H3203b	TrAraMblNScScm	$HNO_3(aq) \rightarrow HNO_3$	$k_{\text{exb}}(\text{KPP_HNO3})$	see note
H4100f	TrAraMblScScm	$CO_2 \rightarrow CO_2(aq)$	$k_{\text{exf}}(\text{KPP_CO2})$	see note
H4100b	TrAraMblScScm	$CO_2(aq) \rightarrow CO_2$	$k_{\text{exb}}(\text{KPP_CO2})$	see note
H4101f	TrAraScScm	$HCHO \rightarrow HCHO(aq)$	$k_{\text{exf}}(\text{KPP_HCHO})$	see note
H4101b	TrAraScScm	$HCHO(aq) \rightarrow HCHO$	$k_{\text{exb}}(\text{KPP_HCHO})$	see note
H4103f	TrAraScScm	$HCOOH \rightarrow HCOOH(aq)$	$k_{\text{exf}}(\text{KPP_HCOOH})$	see note
H4103b	TrAraScScm	$HCOOH(aq) \rightarrow HCOOH$	$k_{\text{exb}}(\text{KPP_HCOOH})$	see note
H4104f	TrAraScScm	$CH_3OOH \rightarrow CH_3OOH(aq)$	$k_{\text{exf}}(\text{KPP_CH3OOH})$	see note
H4104b	TrAraScScm	$CH_3OOH(aq) \rightarrow CH_3OOH$	$k_{\text{exb}}(\text{KPP_CH3OOH})$	see note
H9100f	TrAraSMblScScm	$SO_2 \rightarrow SO_2(aq)$	$k_{\text{exf}}(\text{KPP_SO2})$	see note
H9100b	TrAraSMblScScm	$SO_2(aq) \rightarrow SO_2$	$k_{\text{exb}}(\text{KPP_SO2})$	see note
H9200	TrAraSMblScScm	$H_2SO_4 \rightarrow H_2SO_4(aq)$	$k_{\text{exf}}(\text{KPP_H2SO4})$	see note

*Notes:

The forward (k_{exf}) and backward (k_{exb}) rate coefficients are calculated in the file `messy_scav_base.f90` using the accommodation coefficients in subroutine `scav_alpha` and Henry's law constants in subroutine `scav_henry`.

k_{mt} = mass transfer coefficient

lwc = liquid water content of aerosol mode

$f_{het}(X, Y) = k_{\text{mt}}(X) \times lwc \times f(Y)[Y]/Het_T$, with $f(H_2O) = 1$, $f(Cl^-) = 5.0E2$, and $f(Br^-) = 3.0E5$, $[Y]$ = concentration of Y; $Het_T = [H_2O] + f(Cl^-)[Cl^-] + f(Br^-)[Br^-]$

H6301, H6302, H7601: The total uptake is determined by $k_{\text{mt}}(ClNO_3)$. The relative rates are assumed to be the same as for N_2O_5 (H3201, H6300, H7300).

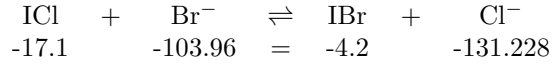
H7301, H7302, H7602: The total uptake is determined by $k_{\text{mt}}(BrNO_3)$. The relative rates are assumed to be the same as for N_2O_5 (H3201, H6300, H7300).

Table 2: Acid-base and other equilibria

#	labels	reaction	$K_0[M^{m-n}]$	$-\Delta H/R[K]$	reference
EQ21	TrAraMblScScm	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.0E-16	-6716	Chameides (1984)
EQ30	TrAraMblNScScm	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	5.88E-10	-2391	Chameides (1984)
EQ32	TrAraMblNScScm	$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	15	8700	Davis and de Bruin (1964)
EQ40	TrAraMblScScm	$\text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	4.3E-7	-913	Chameides (1984)
EQ41	TrAraScScm	$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$	1.8E-4		Weast (1980)
EQ90	TrAraSMblScScm	$\text{SO}_2 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	1.7E-2	2090	Chameides (1984)
EQ91	TrAraSMblScScm	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	6.0E-8	1120	Chameides (1984)
EQ92	TrAraSMblScScm	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.2E-2	2720	Seinfeld and Pandis (1998)
EQ93	TrAraSMblScScm	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	1.0E3		Seinfeld and Pandis (1998)

*Notes:

EQ82 and EQ83: Thermodynamic calculations on the IBr/ICl equilibrium according to the data tables from Wagman et al. (1982):



$$\frac{\Delta G}{[\text{kJ/mol}]} = -4.2 - 131.228 - (-17.1 - 103.96) = -14.368$$

$$K = \frac{[\text{IBr}] \times [\text{Cl}^-]}{[\text{ICl}] \times [\text{Br}^-]} = \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left(\frac{14368}{8.314 \times 298}\right) = 330$$

This means we have equal amounts of IBr and ICl when the $[\text{Cl}^-]/[\text{Br}^-]$ ratio equals 330.

Table 3: Aqueous phase reactions

#	labels	reaction	k_0 [$M^{1-n}s^{-1}$]	$-E_a/R[K]$	reference
A9101	TrAraSMblScScm	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-}$	1.5E9	-5300	Hoffmann (1986)
A9206	TrAraSMblScScm	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+$	3.7E5	-5500	Hoffmann (1986)
A9209	TrAraSMblScScm	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+$	5.2E6	-3650	Martin and Damschen (1981)

A6102: Jacobi (1996) found an upper limit of **6E9** and cite an upper limit from another study of **2E9**. Here, we set the rate coefficient to **1E9**.

A6301: There is also an earlier study by Exner et al. (1992) which found a smaller rate coefficient but did not consider the back reaction.

A7400: assumed to be the same as for $Br_2^- + H_2O_2$.

A9106: see also: (Huie and Neta, 1987; Warneck, 1991). If this reaction produces a lot of SO_4^- , it will have an effect. However, we currently assume only the stable $S_2O_8^{2-}$ as product.

A9205: D. Sedlak, pers. comm. (1993)

A9208: D. Sedlak, pers. comm. (1993)

A9105: The rate coefficient for the sum of the paths (leading to either HSO_5^- or SO_4^{2-}) is from Huie and Neta (1987), the ratio 0.28/0.72 is from Deister and Warneck (1990).

A9605: assumed to be the same as for $SO_3^{2-} + HOCl$.

A9705: assumed to be the same as for $SO_3^{2-} + HOBr$.

Table 4: Photolysis reactions

#	labels	reaction	rate coefficient	reference
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*Notes: J-values are calculated with an external module and then supplied to the SCAV chemistry

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