

# The Chemical Mechanism of SCAV

KPP version: 2.2.3\_rs3

SCAV version: 2.4.0

Date: June 8, 2022

Batch file: SC\_no-iodine\_no-mercury.bat

Integrator: rosenbrock\_mz

Gas equation file: gas.eqn

Replacement file:

Selected reactions:

“(Sc && !I && !Hg)”

Number of aerosol phases: 1

Number of species in selected mechanism:

Gas phase: 32

Aqueous phase: 56

All species: 88

Number of reactions in selected mechanism:

Gas phase (Gnnn): 0

Aqueous phase (Annn): 53

Henry (Hnnn): 62

Photolysis (Jnnn): 0

Aqueous phase photolysis (PHnnn): 1

Heterogeneous (HETnnn): 0

Equilibria (EQnn): 34

Isotope exchange (IEXnnn): 0

Tagging equations (TAGnnn): 0

Dummy (Dnn): 0

All equations: 150

Table 1: Gas phase reactions

#	labels	reaction	rate coefficient	reference
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## General notes

### Three-body reactions

Rate coefficients for three-body reactions are defined via the function  $\mathbf{k\_3rd}(T, M, k_0^{300}, n, k_{\text{inf}}^{300}, m, f_c)$ . In the code, the temperature  $T$  is called `temp` and the concentration of “air molecules”  $M$  is called `cair`. Using the auxiliary variables  $k_0(T)$ ,  $k_{\text{inf}}(T)$ , and  $k_{\text{ratio}}$ ,  $\mathbf{k\_3rd}$  is defined as:

$$k_0(T) = k_0^{300} \times \left(\frac{300\text{K}}{T}\right)^n \quad (1)$$

$$k_{\text{inf}}(T) = k_{\text{inf}}^{300} \times \left(\frac{300\text{K}}{T}\right)^m \quad (2)$$

$$k_{\text{ratio}} = \frac{k_0(T)M}{k_{\text{inf}}(T)} \quad (3)$$

$$\mathbf{k\_3rd} = \frac{k_0(T)M}{1 + k_{\text{ratio}}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{\text{ratio}}))^2}\right)} \quad (4)$$

A similar function, called `k_3rd_iupac` here, is used by Wallington et al. (2018) for three-body reactions. It has the same function parameters as `k_3rd` and it is defined as:

$$k_0(T) = k_0^{300} \times \left(\frac{300\text{K}}{T}\right)^n \quad (5)$$

$$k_{\text{inf}}(T) = k_{\text{inf}}^{300} \times \left(\frac{300\text{K}}{T}\right)^m \quad (6)$$

$$k_{\text{ratio}} = \frac{k_0(T)M}{k_{\text{inf}}(T)} \quad (7)$$

$$N = 0.75 - 1.27 \times \log_{10}(f_c) \quad (8)$$

$$\mathbf{k\_3rd\_iupac} = \frac{k_0(T)M}{1 + k_{\text{ratio}}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{\text{ratio}})/N)^2}\right)} \quad (9)$$

## Structure-Activity Relationships (SAR)

Some unmeasured rate coefficients are estimated with structure-activity relationships, using the following parameters and substituent factors:

$k$ for H-abstraction by OH in $\text{cm}^{-3}\text{s}^{-1}$	
<code>k_p</code>	$4.49 \times 10^{-18} \times (T/\text{K})^2 \exp(-320 \text{K}/T)$
<code>k_s</code>	$4.50 \times 10^{-18} \times (T/\text{K})^2 \exp(253 \text{K}/T)$
<code>k_t</code>	$2.12 \times 10^{-18} \times (T/\text{K})^2 \exp(696 \text{K}/T)$
<code>k_ROHRO</code>	$2.1 \times 10^{-18} \times (T/\text{K})^2 \exp(-85 \text{K}/T)$
<code>k_CO2H</code>	$0.7 \times k_{\text{CH}_3\text{CO}_2\text{H}+\text{OH}}$
<code>k_ROOHRO</code>	$0.6 \times k_{\text{CH}_3\text{OOH}+\text{OH}}$
<code>f_alk</code>	1.23
<code>f_sOH</code>	3.44
<code>f_tOH</code>	2.68
<code>f_sOOH</code>	8.
<code>f_tOOH</code>	8.
<code>f_ONO2</code>	0.04
<code>f_CH2ONO2</code>	0.20
<code>f_cpan</code>	0.25
<code>f_allyl</code>	3.6
<code>f_CHO</code>	0.55
<code>f_CO2H</code>	1.67
<code>f_CO</code>	0.73
<code>f_O</code>	8.15
<code>f_pCH2OH</code>	1.29
<code>f_tCH2OH</code>	0.53

$k$ for OH-addition to double bonds in $\text{cm}^{-3}\text{s}^{-1}$	
<code>k_adp</code>	$4.5 \times 10^{-12} \times (T/300 \text{K})^{-0.85}$
<code>k_ads</code>	$1/4 \times (1.1 \times 10^{-11} \times \exp(485 \text{K}/T) + 1.0 \times 10^{-11} \times \exp(553 \text{K}/T))$
<code>k_adt</code>	$1.922 \times 10^{-11} \times \exp(450 \text{K}/T) - k_{\text{ads}}$
<code>k_adsecprim</code>	$3.0 \times 10^{-11}$
<code>k_adtertprim</code>	$5.7 \times 10^{-11}$
<code>a_PAN</code>	0.56
<code>a_CHO</code>	0.31
<code>a_COCH3</code>	0.76
<code>a_CH2OH</code>	1.7
<code>a_CH2OOH</code>	1.7
<code>a_COH</code>	2.2
<code>a_COOH</code>	2.2
<code>a_CO2H</code>	0.25
<code>a_CH2ONO2</code>	0.64

### RO<sub>2</sub> self and cross reactions

The self and cross reactions of organic peroxy radicals are treated according to the permutation reaction formalism as implemented in the MCM (Rickard and Pascoe, 2009), as described by Jenkin et al. (1997). Every organic peroxy radical reacts in a pseudo-first-order reaction with a rate constant that is expressed as  $k^{1\text{st}} = 2 \times \sqrt{k_{\text{self}} \times \mathbf{k\_CH302}} \times [\text{RO}_2]$  where  $k_{\text{self}}$  = second-order rate coefficient of the self reaction of the organic peroxy radical,  $\mathbf{k\_CH302}$  = second-order rate coefficient of the self reaction of  $\text{CH}_3\text{O}_2$ , and  $[\text{RO}_2]$  = sum of the concentrations of all organic peroxy radicals.

### Specific notes

Table 2: Photolysis reactions

#	labels	reaction	rate coefficient	reference
J (gas)				
PH (aqueous)				
PH2100_1	TrAraScJ	$\text{H}_2\text{O}_2(\text{aq}) + h\nu \rightarrow 2 \text{OH}(\text{aq})$	$1.0 * j_x(\text{ip\_H2O2}) * 2.33$	██████

## General notes

$j$ -values are calculated with an external module (e.g., JVAL) and then supplied to the SCAV chemistry.

Values that originate from the Master Chemical Mechanism (MCM) by Rickard and Pascoe (2009) are translated according in the following way:

$j(11) \rightarrow j_x(\text{ip\_COH2})$

$j(12) \rightarrow j_x(\text{ip\_CHOH})$

$j(15) \rightarrow j_x(\text{ip\_HOCH2CHO})$

$j(18) \rightarrow j_x(\text{ip\_MACR})$

$j(22) \rightarrow j_x(\text{ip\_ACETOL})$

$j(23)+j(24) \rightarrow j_x(\text{ip\_MVK})$

$j(31)+j(32)+j(33) \rightarrow j_x(\text{ip\_GLYOX})$

$j(34) \rightarrow j_x(\text{ip\_MGLYOX})$

$j(41) \rightarrow j_x(\text{ip\_CH300H})$

$j(53) \rightarrow j(\text{isopropyl nitrate})$

$j(54) \rightarrow j(\text{isopropyl nitrate})$

$j(55) \rightarrow j(\text{isopropyl nitrate})$

$j(56)+j(57) \rightarrow j_x(\text{ip\_NOA})$

## Specific notes

Table 3: Reversible (Henry’s law) equilibria and irreversible (“heterogenous”) uptake

#	labels	reaction	rate coefficient	reference
H1000f_1	TrAlSc	$O_2 \rightarrow O_2(aq)$	$k_{\text{exf}}(\text{ind}_{O2})$	see general notes*
H1000b_1	TrAlSc	$O_2(aq) \rightarrow O_2$	$k_{\text{exb}}(\text{ind}_{O2})$	see general notes*
H1001f_1	TrAlMblScSem	$O_3 \rightarrow O_3(aq)$	$k_{\text{exf}}(\text{ind}_{O3})$	see general notes*
H1001b_1	TrAlMblScSem	$O_3(aq) \rightarrow O_3$	$k_{\text{exb}}(\text{ind}_{O3})$	see general notes*
H2100f_1	TrAlSc	$OH \rightarrow OH(aq)$	$k_{\text{exf}}(\text{ind}_{OH})$	see general notes*
H2100b_1	TrAlSc	$OH(aq) \rightarrow OH$	$k_{\text{exb}}(\text{ind}_{OH})$	see general notes*
H2101f_1	TrAlSc	$HO_2 \rightarrow HO_2(aq)$	$k_{\text{exf}}(\text{ind}_{HO2})$	see general notes*
H2101b_1	TrAlSc	$HO_2(aq) \rightarrow HO_2$	$k_{\text{exb}}(\text{ind}_{HO2})$	see general notes*
H2102f_1	TrAlMblScSem	$H_2O_2 \rightarrow H_2O_2(aq)$	$k_{\text{exf}}(\text{ind}_{H2O2})$	see general notes*
H2102b_1	TrAlMblScSem	$H_2O_2(aq) \rightarrow H_2O_2$	$k_{\text{exb}}(\text{ind}_{H2O2})$	see general notes*
H3100f_1	TrAraScN	$NO \rightarrow NO(aq)$	$k_{\text{exf}}(\text{ind}_{NO})$	see general notes*
H3100b_1	TrAraScN	$NO(aq) \rightarrow NO$	$k_{\text{exb}}(\text{ind}_{NO})$	see general notes*
H3101f_1	TrAlScN	$NO_2 \rightarrow NO_2(aq)$	$k_{\text{exf}}(\text{ind}_{NO2})$	see general notes*
H3101b_1	TrAlScN	$NO_2(aq) \rightarrow NO_2$	$k_{\text{exb}}(\text{ind}_{NO2})$	see general notes*
H3102f_1	TrAlScN	$NO_3 \rightarrow NO_3(aq)$	$k_{\text{exf}}(\text{ind}_{NO3})$	see general notes*
H3102b_1	TrAlScN	$NO_3(aq) \rightarrow NO_3$	$k_{\text{exb}}(\text{ind}_{NO3})$	see general notes*
H3200f_1	TrAlMblScSemN	$NH_3 \rightarrow NH_3(aq)$	$k_{\text{exf}}(\text{ind}_{NH3})$	see general notes*
H3200b_1	TrAlMblScSemN	$NH_3(aq) \rightarrow NH_3$	$k_{\text{exb}}(\text{ind}_{NH3})$	see general notes*
H3201_1	TrAlMblScSemN	$N_2O_5 \rightarrow HNO_3(aq) + HNO_3(aq)$	$k_{\text{exf}}\text{N205}*\text{C}(\text{ind}_{H2O\_1})$	Behnke et al. (1994), Behnke et al. (1997)
H3202f_1	TrAlScN	$HONO \rightarrow HONO(aq)$	$k_{\text{exf}}(\text{ind}_{HONO})$	see general notes*
H3202b_1	TrAlScN	$HONO(aq) \rightarrow HONO$	$k_{\text{exb}}(\text{ind}_{HONO})$	see general notes*
H3203f_1	TrAlMblScSemN	$HNO_3 \rightarrow HNO_3(aq)$	$k_{\text{exf}}(\text{ind}_{HNO3})$	see general notes*
H3203b_1	TrAlMblScSemN	$HNO_3(aq) \rightarrow HNO_3$	$k_{\text{exb}}(\text{ind}_{HNO3})$	see general notes*
H3204f_1	TrAlScN	$HNO_4 \rightarrow HNO_4(aq)$	$k_{\text{exf}}(\text{ind}_{HNO4})$	see general notes*
H3204b_1	TrAlScN	$HNO_4(aq) \rightarrow HNO_4$	$k_{\text{exb}}(\text{ind}_{HNO4})$	see general notes*
H4100f_1	TrAlMblScSem	$CO_2 \rightarrow CO_2(aq)$	$k_{\text{exf}}(\text{ind}_{CO2})$	see general notes*
H4100b_1	TrAlMblScSem	$CO_2(aq) \rightarrow CO_2$	$k_{\text{exb}}(\text{ind}_{CO2})$	see general notes*
H4101f_1	TrAlScSem	$HCHO \rightarrow HCHO(aq)$	$k_{\text{exf}}(\text{ind}_{HCHO})$	see general notes*
H4101b_1	TrAlScSem	$HCHO(aq) \rightarrow HCHO$	$k_{\text{exb}}(\text{ind}_{HCHO})$	see general notes*
H4102f_1	TrAlSc	$CH_3O_2 \rightarrow CH_3OO(aq)$	$k_{\text{exf}}(\text{ind}_{CH3O2})$	see general notes*
H4102b_1	TrAlSc	$CH_3OO(aq) \rightarrow CH_3O_2$	$k_{\text{exb}}(\text{ind}_{CH3O2})$	see general notes*
H4103f_1	TrAlScSem	$HCOOH \rightarrow HCOOH(aq)$	$k_{\text{exf}}(\text{ind}_{HCOOH})$	see general notes*
H4103b_1	TrAlScSem	$HCOOH(aq) \rightarrow HCOOH$	$k_{\text{exb}}(\text{ind}_{HCOOH})$	see general notes*

Table 3: Reversible (Henry’s law) equilibria and irreversible (“heterogenous”) uptake

#	labels	reaction	rate coefficient	reference
H4104f_1	TrAlScScm	$\text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{OOH}(\text{aq})$	$k_{\text{exf}}(\text{ind\_CH300H})$	see general notes*
H4104b_1	TrAlScScm	$\text{CH}_3\text{OOH}(\text{aq}) \rightarrow \text{CH}_3\text{OOH}$	$k_{\text{exb}}(\text{ind\_CH300H})$	see general notes*
H4105f_1	TrAraSc	$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}(\text{aq})$	$k_{\text{exf}}(\text{ind\_CH30H})$	see general notes*
H4105b_1	TrAraSc	$\text{CH}_3\text{OH}(\text{aq}) \rightarrow \text{CH}_3\text{OH}$	$k_{\text{exb}}(\text{ind\_CH30H})$	see general notes*
H4200f_1	TrAraScScmC	$\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH}(\text{aq})$	$k_{\text{exf}}(\text{ind\_CH3C02H})$	see general notes*
H4200b_1	TrAraScScmC	$\text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{COOH}$	$k_{\text{exb}}(\text{ind\_CH3C02H})$	see general notes*
H4201f_1	TrAraScC	$\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CHO}(\text{aq})$	$k_{\text{exf}}(\text{ind\_CH3CHO})$	see general notes*
H4201b_1	TrAraScC	$\text{CH}_3\text{CHO}(\text{aq}) \rightarrow \text{CH}_3\text{CHO}$	$k_{\text{exb}}(\text{ind\_CH3CHO})$	see general notes*
H4202f_1	TrAraScCN	$\text{PAN} \rightarrow \text{PAN}(\text{aq})$	$k_{\text{exf}}(\text{ind\_PAN})$	see general notes*
H4202b_1	TrAraScCN	$\text{PAN}(\text{aq}) \rightarrow \text{PAN}$	$k_{\text{exb}}(\text{ind\_PAN})$	see general notes*
H4300f_1	TrAraScC	$\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{COCH}_3(\text{aq})$	$k_{\text{exf}}(\text{ind\_CH3COCH3})$	see general notes*
H4300b_1	TrAraScC	$\text{CH}_3\text{COCH}_3(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_3$	$k_{\text{exb}}(\text{ind\_CH3COCH3})$	see general notes*
H6000f_1	TrAlMblScCl	$\text{Cl}_2 \rightarrow \text{Cl}_2(\text{aq})$	$k_{\text{exf}}(\text{ind\_Cl2})$	see general notes*
H6000b_1	TrAlMblScCl	$\text{Cl}_2(\text{aq}) \rightarrow \text{Cl}_2$	$k_{\text{exb}}(\text{ind\_Cl2})$	see general notes*
H6200f_1	TrAlMblScScmCl	$\text{HCl} \rightarrow \text{HCl}(\text{aq})$	$k_{\text{exf}}(\text{ind\_HCl})$	see general notes*
H6200b_1	TrAlMblScScmCl	$\text{HCl}(\text{aq}) \rightarrow \text{HCl}$	$k_{\text{exb}}(\text{ind\_HCl})$	see general notes*
H6201f_1	TrAlMblScCl	$\text{HOCl} \rightarrow \text{HOCl}(\text{aq})$	$k_{\text{exf}}(\text{ind\_HOCl})$	see general notes*
H6201b_1	TrAlMblScCl	$\text{HOCl}(\text{aq}) \rightarrow \text{HOCl}$	$k_{\text{exb}}(\text{ind\_HOCl})$	see general notes*
H7000f_1	TrAlMblScBr	$\text{Br}_2 \rightarrow \text{Br}_2(\text{aq})$	$k_{\text{exf}}(\text{ind\_Br2})$	see general notes*
H7000b_1	TrAlMblScBr	$\text{Br}_2(\text{aq}) \rightarrow \text{Br}_2$	$k_{\text{exb}}(\text{ind\_Br2})$	see general notes*
H7200f_1	TrAlMblScScmBr	$\text{HBr} \rightarrow \text{HBr}(\text{aq})$	$k_{\text{exf}}(\text{ind\_HBr})$	see general notes*
H7200b_1	TrAlMblScScmBr	$\text{HBr}(\text{aq}) \rightarrow \text{HBr}$	$k_{\text{exb}}(\text{ind\_HBr})$	see general notes*
H7201f_1	TrAlMblScBr	$\text{HOBr} \rightarrow \text{HOBr}(\text{aq})$	$k_{\text{exf}}(\text{ind\_HOBr})$	see general notes*
H7201b_1	TrAlMblScBr	$\text{HOBr}(\text{aq}) \rightarrow \text{HOBr}$	$k_{\text{exb}}(\text{ind\_HOBr})$	see general notes*
H7600f_1	TrAlMblScBrCl	$\text{BrCl} \rightarrow \text{BrCl}(\text{aq})$	$k_{\text{exf}}(\text{ind\_BrCl})$	see general notes*
H7600b_1	TrAlMblScBrCl	$\text{BrCl}(\text{aq}) \rightarrow \text{BrCl}$	$k_{\text{exb}}(\text{ind\_BrCl})$	see general notes*
H9100f_1	TrAlMblScScmS	$\text{SO}_2 \rightarrow \text{SO}_2(\text{aq})$	$k_{\text{exf}}(\text{ind\_S02})$	see general notes*
H9100b_1	TrAlMblScScmS	$\text{SO}_2(\text{aq}) \rightarrow \text{SO}_2$	$k_{\text{exb}}(\text{ind\_S02})$	see general notes*
H9200_1	TrAlMblScScmS	$\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{SO}_4(\text{aq})$	$\text{xnom7sul f} * k_{\text{exf}}(\text{ind\_H2S04})$	see general notes*

## General notes

The forward ( $k_{\text{exf}}$ ) and backward ( $k_{\text{exb}}$ ) rate coefficients are calculated in sub-

routine `scav_aero_calc_k_ex` in the file `messy_scav_aero.f90` using accommodation coefficients and Henry’s law constants from chemprop (see `chemprop.pdf`). For uptake of X (X =  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_3$ , or  $\text{BrNO}_3$ ) and subsequent reaction with  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  in H3201, H6300, H6301, H6302, H7300, H7301, H7302, H7601,

and H7602, we define:

$$k_{\text{exf}}(\text{X}) = \frac{k_{\text{mt}}(\text{X}) \times \text{LWC}}{[\text{H}_2\text{O}] + 5 \times 10^2 [\text{Cl}^-] + 3 \times 10^5 [\text{Br}^-]}$$

Here,  $k_{\text{mt}}$  = mass transfer coefficient, and LWC = liquid water content of the aerosol. The total uptake rate

of X is only determined by  $k_{\text{mt}}$ . The factors only affect the branching between hydrolysis and the halide reactions. The factor  $5 \times 10^2$  was chosen such that the chloride reaction dominates over hydrolysis at about  $[\text{Cl}^-] > 0.1 \text{ M}$  (see Fig. 3 in Behnke et al. (1997)), i.e. when the ratio  $[\text{H}_2\text{O}]/[\text{Cl}^-]$  is less than  $5 \times 10^2$ . The ratio

$5 \times 10^2 / 3 \times 10^5$  was chosen such that the reactions with chloride and bromide are roughly equal for sea water composition (Behnke et al., 1994). These ratios were measured for uptake of  $\text{N}_2\text{O}_5$ . Here, they are also used for  $\text{ClNO}_3$  and  $\text{BrNO}_3$ .

Table 4: Heterogeneous reactions

#	labels	reaction	rate coefficient	reference
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## General notes

Heterogeneous reaction rates are calculated with an external module (e.g., SCAV\_KHET) and then supplied to the SCAV chemistry (see [www.messy-interface.org](http://www.messy-interface.org) for details)

Table 5: Acid-base and other equilibria

#	labels	reaction	$K_0[M^{m-n}]$	$-\Delta H/R[K]$	reference
EQ20_1	TrAlSc	$\text{HO}_2 \rightleftharpoons \text{O}_2^- + \text{H}^+$	1.6E-5		Weinstein-Lloyd and Schwartz (1991)
EQ21_1	TrAlMblScScm	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.0E-16	-6716	Chameides (1984)
EQ30_1	TrAlMblScScmN	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	5.88E-10	-2391	Chameides (1984)
EQ31_1	TrAlScN	$\text{HONO} \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	5.1E-4	-1260	Schwartz and White (1981)
EQ32_1	TrAlMblScScmN	$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	15	8700	Davis and de Bruin (1964)
EQ33_1	TrAlScN	$\text{HNO}_4 \rightleftharpoons \text{NO}_4^- + \text{H}^+$	1.E-5		Warneck (1999)
EQ40_1	TrAlMblScScm	$\text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	4.3E-7	-913	Chameides (1984)*
EQ41_1	TrAlScScm	$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$	1.8E-4		Weast (1980)
EQ42_1	TrAraScScmC	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.754E-5		Fisher and Barnes (1972)*
EQ61_1	TrAlMblScScmCl	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	1.7E6	6896	Marsh and McElroy (1985)
EQ62_1	TrAlScCl	$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	3.2E-8		Lax (1969)
EQ71_1	TrAlMblScScmBr	$\text{HBr} \rightleftharpoons \text{H}^+ + \text{Br}^-$	1.0E9		Lax (1969)
EQ72_1	TrAlScBr	$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{BrO}^-$	2.3E-9	-3091	Kelley and Tartar (1956)*
EQ90_1	TrAlMblScScmS	$\text{SO}_2 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	1.7E-2	2090	Chameides (1984)
EQ91_1	TrAlMblScScmS	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	6.0E-8	1120	Chameides (1984)
EQ92_1	TrAlMblScScmS	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.2E-2	2720	Seinfeld and Pandis (1998)
EQ93_1	TrAlMblScScmS	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	1.0E3		Seinfeld and Pandis (1998)

## Specific notes

EQ40\_1: For  $pK_a(\text{CO}_2)$ , see also Dickson and Millero (1987).

EQ42\_1: The  $pK_a$  has a minimum near 25 °C, the temperature dependence is therefore small.

EQ72\_1: For  $pK_a(\text{HOBr})$ , see also Keller-Rudek et al. (1992).

Table 6: Aqueous phase reactions

#	labels	reaction	$k_0 [M^{1-n}s^{-1}]$	$-E_a/R[K]$	reference
A1000_1	TrAlSc	$O_3 + O_2^- \rightarrow OH + OH^-$	1.5E9		Sehested et al. (1983)
A2100_1	TrAlSc	$OH + O_2^- \rightarrow OH^-$	1.0E10		Sehested et al. (1968)
A2101_1	TrAlSc	$OH + OH \rightarrow H_2O_2$	5.5E9		Buxton et al. (1988)
A2102_1	TrAlSc	$HO_2 + O_2^- \rightarrow H_2O_2 + OH^-$	1.0E8	-900	Christensen and Sehested (1988)
A2103_1	TrAlSc	$HO_2 + OH \rightarrow H_2O$	7.1E9		Sehested et al. (1968)
A2104_1	TrAlSc	$HO_2 + HO_2 \rightarrow H_2O_2$	9.7E5	-2500	Christensen and Sehested (1988)
A2105_1	TrAlSc	$H_2O_2 + OH \rightarrow HO_2$	2.7E7	-1684	Christensen et al. (1982)
A3100_1	TrAlScN	$NO_2^- + O_3 \rightarrow NO_3^-$	5.0E5	-6950	Damschen and Martin (1983)
A3101_1	TrAlScN	$NO_2 + NO_2 \rightarrow HNO_3 + HONO$	1.0E8		Lee and Schwartz (1981)
A3102_1	TrAlScN	$NO_4^- \rightarrow NO_2^-$	8.0E1		Warneck (1999)
A3200_1	TrAlScN	$NO_2 + HO_2 \rightarrow HNO_4$	1.8E9		Warneck (1999)
A3201_1	TrAlScN	$NO_2^- + OH \rightarrow NO_2 + OH^-$	1.0E10		Wingenter et al. (1999)
A3202_1	TrAlScN	$NO_3 + OH^- \rightarrow NO_3^- + OH$	8.2E7	-2700	Exner et al. (1992)
A3203_1	TrAlScN	$HONO + OH \rightarrow NO_2$	1.0E10		Barker et al. (1970)
A3204_1	TrAlScN	$HONO + H_2O_2 + H^+ \rightarrow HNO_3 + H^+$	4.6E3	-6800	Damschen and Martin (1983)
A4100_1	TrAlSc	$CO_3^- + O_2^- \rightarrow HCO_3^- + OH^-$	6.5E8		Ross et al. (1992)
A4101_1	TrAlSc	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	4.3E5		Ross et al. (1992)
A4102_1	TrAlSc	$HCOO^- + CO_3^- \rightarrow 2 HCO_3^- + HO_2$	1.5E5		Ross et al. (1992)
A4103_1	TrAlSc	$HCOO^- + OH \rightarrow OH^- + HO_2 + CO_2$	3.1E9	-1240	Chin and Wine (1994)
A4104_1	TrAlSc	$HCO_3^- + OH \rightarrow CO_3^-$	8.5E6		Ross et al. (1992)
A4105_1	TrAlSc	$HCHO + OH \rightarrow HCOOH + HO_2$	7.7E8	-1020	Chin and Wine (1994)
A4106_1	TrAlSc	$HCOOH + OH \rightarrow HO_2 + CO_2$	1.1E8	-991	Chin and Wine (1994)
A4107_1	TrAlSc	$CH_3OO + O_2^- \rightarrow CH_3OOH + OH^-$	5.0E7		Jacob (1986)
A4108_1	TrAlSc	$CH_3OO + HO_2 \rightarrow CH_3OOH$	4.3E5		Jacob (1986)
A4109_1	TrAlSc	$CH_3OH + OH \rightarrow HCHO + HO_2$	9.7E8		Buxton et al. (1988)
A4110a_1	TrAlSc	$CH_3OOH + OH \rightarrow CH_3OO$	2.7E7	-1715	Jacob (1986)
A4110b_1	TrAlSc	$CH_3OOH + OH \rightarrow HCHO + OH$	1.1E7	-1715	Jacob (1986)
A9100_1	TrAlScS	$SO_3^- + O_2 \rightarrow SO_5^-$	1.5E9		Huie and Neta (1987)
A9101_1	TrAlMblScScmS	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-}$	1.5E9	-5300	Hoffmann (1986)
A9102_1	TrAlScS	$SO_4^- + O_2^- \rightarrow SO_4^{2-}$	3.5E9		Jiang et al. (1992)
A9103_1	TrAlScS	$SO_4^- + SO_3^{2-} \rightarrow SO_3^- + SO_4^{2-}$	4.6E8		Huie and Neta (1987)
A9104_1	TrAlScS	$SO_5^- + O_2^- \rightarrow HSO_5^- + OH^-$	2.3E8		Buxton et al. (1996)
A9200_1	TrAlScS	$SO_3^{2-} + OH \rightarrow SO_3^- + OH^-$	5.5E9		Buxton et al. (1988)
A9201_1	TrAlScS	$SO_4^- + OH \rightarrow HSO_5^-$	1.0E9		Jiang et al. (1992)

Table 6: Aqueous phase reactions (...continued)

#	labels	reaction	$k_0 [M^{1-n} s^{-1}]$	$-E_a/R[K]$	reference
A9202_1	TrAlScS	$SO_4^- + HO_2 \rightarrow SO_4^{2-} + H^+$	3.5E9		Jiang et al. (1992)
A9203_1	TrAlScS	$SO_4^- + H_2O \rightarrow SO_4^{2-} + H^+ + OH$	1.1E1	-1110	Herrmann et al. (1995)
A9204_1	TrAlScS	$SO_4^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2$	1.2E7		Wine et al. (1989)
A9205_1	TrAlScS	$HSO_3^- + O_2 \rightarrow SO_4^{2-} + OH$	3.0E3		see note*
A9206_1	TrAlMblScScmS	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+$	3.7E5	-5500	Hoffmann (1986)
A9207_1	TrAlScS	$HSO_3^- + OH \rightarrow SO_3^-$	4.5E9		Buxton et al. (1988)
A9208_1	TrAlScS	$HSO_3^- + HO_2 \rightarrow SO_4^{2-} + OH + H^+$	3.0E3		see note*
A9209_1	TrAlMblScScmS	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+$	5.2E6	-3650	Martin and Damschen (1981)
A9210_1	TrAlScS	$HSO_3^- + SO_4^- \rightarrow SO_3^- + SO_4^{2-} + H^+$	8.0E8		Huie and Neta (1987)
A9212_1	TrAlScS	$HSO_3^- + HSO_5^- + H^+ \rightarrow 2 HSO_4^- + H^+$	7.1E6		Betterton and Hoffmann (1988)
A9301_1	TrAlScNS	$SO_4^- + NO_3^- \rightarrow SO_4^{2-} + NO_3$	5.0E4		Exner et al. (1992)
A9302_1	TrAlScNS	$SO_4^{2-} + NO_3 \rightarrow NO_3^- + SO_4^-$	1.0E5		Løgager et al. (1993)
A9304_1	TrAlScNS	$HSO_3^- + NO_3 \rightarrow SO_3^- + NO_3^- + H^+$	1.4E9	-2000	Exner et al. (1992)
A9305_1	TrAlScNS	$HSO_3^- + HNO_4 \rightarrow HSO_4^- + NO_3^- + H^+$	3.1E5		Warneck (1999)
A9400_1	TrAlScS	$SO_3^{2-} + HCHO \rightarrow CH_2OHSO_3^- + OH^-$	1.4E4		Boyce and Hoffmann (1984)*
A9401_1	TrAlScS	$SO_3^{2-} + CH_3OOH + H^+ \rightarrow SO_4^{2-} + H^+ + CH_3OH$	1.6E7	-3800	Lind et al. (1987)
A9402_1	TrAlScS	$HSO_3^- + HCHO \rightarrow CH_2OHSO_3^-$	4.3E-1		Boyce and Hoffmann (1984)*
A9403_1	TrAlScS	$HSO_3^- + CH_3OOH + H^+ \rightarrow HSO_4^- + H^+ + CH_3OH$	1.6E7	-3800	Lind et al. (1987)
A9404_1	TrAlScS	$CH_2OHSO_3^- + OH^- \rightarrow SO_3^{2-} + HCHO$	3.6E3		Seinfeld and Pandis (1998)

## Specific notes

A9205\_1: D. Sedlak, pers. comm. (1993).

A9208\_1: D. Sedlak, pers. comm. (1993).

A9400\_1: Product  $2.48 \times 10^7 \times 5.5 \times 10^{-4}$  considering the hydrated form of HCHO.

A9402\_1: Product  $790 \times 5.5 \times 10^{-4}$  considering the hydrated form of HCHO.

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