

The Chemical Mechanism of MECCA

KPP version: 2.2.1_rs3

MECCA version: 2.5k

Date: April 15, 2011.

Number of aerosol phases: 0

Number of species in selected mechanism:

Gas phase: 80

Aqueous phase: 0

All species: 80

Number of reactions in selected mechanism:

Gas phase (Gmm): 37

Aqueous phase (Amn): 0

Henry (Hmn): 0

Photolysis (Jmn): 14

Heterogeneous (HETmn): 0

Equilibria (EQmn): 0

Dummy (Dmn): 0

All equations: 51

This document is available as electronic supplement to our article “Simulation of the diurnal variations of the oxygen isotope anomaly ($\Delta^{17}\text{O}$) of reactive atmospheric species” by Morin et al. in Atmos. Chem. Phys. (2011), see:

<http://www.atmos-chem-phys.org>

Table 1: Gas phase reactions

#	labels	reaction	rate coefficient	reference
G1000	StTrG	$O_2 + O(^1D) \rightarrow O(^3P) + O_2$	$3.3E-11*EXP(55./temp)$	Sander et al. (2006)
G1001	StTrG	$O_2 + O(^3P) \rightarrow O_3$	$6.E-34*((temp/300.)**(-2.4))*cair$	Sander et al. (2006)
G2100	StTrG	$H + O_2 \rightarrow HO_2$	$k_3rd(temp, cair, 4.4E-32, 1.3, 4.7E-11, 0.2, 0.6)$	Sander et al. (2006)
G2104	StTrG	$OH + O_3 \rightarrow HO_2 + O_2$	$1.7E-12*EXP(-940./temp)$	Sander et al. (2006)
G2105	StTrG	$OH + H_2 \rightarrow H_2O + H$	$2.8E-12*EXP(-1800./temp)$	Sander et al. (2006)
G2107	StTrG	$HO_2 + O_3 \rightarrow OH + 2 O_2$	$1.E-14*EXP(-490./temp)$	Sander et al. (2006)
G2109	StTrG	$HO_2 + OH \rightarrow H_2O + O_2$	$4.8E-11*EXP(250./temp)$	Sander et al. (2006)
G2110	StTrG	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	k_HO2_HO2	Christensen et al. (2002), Kircher and Sander (1984)*
G2111	StTrG	$H_2O + O(^1D) \rightarrow 2 OH$	$1.63E-10*EXP(60./temp)$	Sander et al. (2006)
G2112	StTrG	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$1.8E-12$	Sander et al. (2006)
G3101	StTrG	$N_2 + O(^1D) \rightarrow O(^3P) + N_2$	$2.15E-11*EXP(110./temp)$	Sander et al. (2006)
G3103	StTrGN	$NO + O_3 \rightarrow NO_2 + O_2$	$3.E-12*EXP(-1500./temp)$	Sander et al. (2006)
G3106	StTrGN	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2E-13*EXP(-2450./temp)$	Sander et al. (2006)
G3108	StTrGN	$NO_3 + NO \rightarrow 2 NO_2$	$1.5E-11*EXP(170./temp)$	Sander et al. (2006)
G3109	StTrGN	$NO_3 + NO_2 \rightarrow N_2O_5$	k_NO3_NO2	Sander et al. (2006)*
G3110	StTrGN	$N_2O_5 \rightarrow NO_2 + NO_3$	$k_NO3_NO2/(2.7E-27*EXP(11000./temp))$	Sander et al. (2006)*
G3200	TrGN	$NO + OH \rightarrow HONO$	$k_3rd(temp, cair, 7.0E-31, 2.6, 3.6E-11, 0.1, 0.6)$	Sander et al. (2006)
G3201	StTrGN	$NO + HO_2 \rightarrow NO_2 + OH$	$3.5E-12*EXP(250./temp)$	Sander et al. (2006)
G3202	StTrGN	$NO_2 + OH \rightarrow HNO_3$	$k_3rd(temp, cair, 1.8E-30, 3.0, 2.8E-11, 0., 0.6)$	Sander et al. (2006)
G3203	StTrGN	$NO_2 + HO_2 \rightarrow HNO_4$	k_NO2_HO2	Sander et al. (2006)*
G3204	TrGN	$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2$	$3.5E-12$	Sander et al. (2006)
G3205	TrGN	$HONO + OH \rightarrow NO_2 + H_2O$	$1.8E-11*EXP(-390./temp)$	Sander et al. (2006)
G3206	StTrGN	$HNO_3 + OH \rightarrow H_2O + NO_3$	k_HNO3_OH	Sander et al. (2006)*
G3207	StTrGN	$HNO_4 \rightarrow NO_2 + HO_2$	$k_NO2_HO2/(2.1E-27*EXP(10900./temp))$	Sander et al. (2006)*
G3208	StTrGN	$HNO_4 + OH \rightarrow NO_2 + H_2O$	$1.3E-12*EXP(380./temp)$	Sander et al. (2006)
G4101	StTrG	$CH_4 + OH \rightarrow CH_3O_2 + H_2O$	$1.85E-20*EXP(2.82*log(temp)-987./temp)$	Atkinson (2003)*
G4102	TrG	$CH_3OH + OH \rightarrow HCHO + HO_2$	$2.9E-12*EXP(-345./temp)$	Sander et al. (2006)
G4103	StTrG	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	$4.1E-13*EXP(750./temp)$	Sander et al. (2006)*
G4104	StTrGN	$CH_3O_2 + NO \rightarrow HCHO + NO_2 + HO_2$	$2.8E-12*EXP(300./temp)$	Sander et al. (2006)
G4105	TrGN	$CH_3O_2 + NO_3 \rightarrow HCHO + HO_2 + NO_2$	$1.3E-12$	Atkinson et al. (1999)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4106a	StTrG	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2 \text{HCHO} + 2 \text{HO}_2$	$9.5\text{E-}14 * \text{EXP}(390./\text{temp}) / (1.+1./26.2 * \text{EXP}(1130./\text{temp}))$	Sander et al. (2006)
G4106b	StTrG	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2$	$9.5\text{E-}14 * \text{EXP}(390./\text{temp}) / (1.+26.2 * \text{EXP}(-1130./\text{temp}))$	Sander et al. (2006)
G4107	StTrG	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow .7 \text{CH}_3\text{O}_2 + .3 \text{HCHO} + .3 \text{OH} + \text{H}_2\text{O}$	k_CH300H_OH	Sander et al. (2006)*
G4108	StTrG	$\text{HCHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{HO}_2$	$9.52\text{E-}18 * \text{EXP}(2.03 * \log(\text{temp}) + 636./\text{temp})$	Sivakumaran et al. (2003)
G4109	TrGN	$\text{HCHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CO} + \text{HO}_2$	$3.4\text{E-}13 * \text{EXP}(-1900./\text{temp})$	Sander et al. (2006)*
G4110	StTrG	$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	$1.57\text{E-}13 + \text{cair} * 3.54\text{E-}33$	McCabe et al. (2001)
G4111	TrG	$\text{HCOOH} + \text{OH} \rightarrow \text{HO}_2$	$4.0\text{E-}13$	Sander et al. (2006)

*Notes:

Rate coefficients for three-body reactions are defined via the function `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_{ratio} , `k_3rd` is defined as:

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

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

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

$$\text{k_3rd} = \frac{k_0(T)M}{1 + k_{\text{ratio}}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{\text{ratio}}))^2}\right)} \quad (4)$$

A similar function, called `k_3rd_iupac` here, is used by Atkinson et al. (2005) for three-body reactions. It has

the same function parameters as `k_3rd` and it is defined as:

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

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

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

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

$$\text{k_3rd_iupac} = \frac{k_0(T)M}{1 + k_{\text{ratio}}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{\text{ratio}})/N)^2}\right)} \quad (9)$$

G2110: The rate coefficient is: `k_HO2_HO2 = (1.5E-12*EXP(19./temp)+1.7E-33*EXP(1000./temp)*cair)*(1.+1.4E-21*EXP(2200./temp)*C(ind_H2O))`. The value for the first (pressure-independent) part is from Christensen et al. (2002), the water term from Kircher and Sander (1984).

G3109: The rate coefficient is: `k_NO3_NO2 = k_3rd(temp, cair, 2.E-30, 4.4, 1.4E-12, 0.7, 0.6)`.

G3110: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G3203: The rate coefficient is: `k_NO2_HO2 = k_3rd(temp, cair, 1.8E-31, 3.2, 4.7E-12, 1.4, 0.6)`.

G3206: The rate coefficient is: `k_HNO3_OH = 2.4E-14 * EXP(460./temp) + 1./ (1./ (6.5E-34 * EXP(1335./temp)*cair) + 1./ (2.7E-17 * EXP(2199./temp)))`

G3207: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G4103: Sander et al. (2006) recommend a zero product yield for HCHO.

G4107: The rate coefficient is: `k_CH3OOH_OH = 3.8E-12*EXP(200./temp)`.

G4109: The same temperature dependence assumed as for CH₃CHO+NO₃.

Table 2: Photolysis reactions

#	labels	reaction	rate coefficient	reference
J1000	StTrGJ	$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	jx(ip_02)	see note
J1001a	StTrGJ	$O_3 + h\nu \rightarrow O(^1D)$	jx(ip_01D)	see note
J1001b	StTrGJ	$O_3 + h\nu \rightarrow O(^3P)$	jx(ip_03P)	see note
J2101	StTrGJ	$H_2O_2 + h\nu \rightarrow 2 OH$	jx(ip_H202)	see note
J3101	StTrGNJ	$NO_2 + h\nu \rightarrow NO + O(^3P)$	jx(ip_N02)	see note
J3103a	StTrGNJ	$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$	jx(ip_N020)	see note
J3103b	StTrGNJ	$NO_3 + h\nu \rightarrow NO$	jx(ip_N002)	see note
J3104a	StTrGNJ	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	jx(ip_N205)	see note
J3200	TrGJ	$HONO + h\nu \rightarrow NO + OH$	jx(ip_HONO)	see note
J3201	StTrGNJ	$HNO_3 + h\nu \rightarrow NO_2 + OH$	jx(ip_HN03)	see note
J3202	StTrGNJ	$HNO_4 + h\nu \rightarrow .667 NO_2 + .667 HO_2 + .333 NO_3 + .333 OH$	jx(ip_HN04)	see note
J4100	StTrGJ	$CH_3OOH + h\nu \rightarrow HCHO + OH + HO_2$	jx(ip_CH300H)	see note
J4101a	StTrGJ	$HCHO + h\nu \rightarrow H_2 + CO$	jx(ip_COH2)	see note
J4101b	StTrGJ	$HCHO + h\nu \rightarrow H + CO + HO_2$	jx(ip_CH0H)	see note

*Notes:

J-values are calculated with an external module and then supplied to the MECCA chemistry

References

- Atkinson, R.: Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, *Atmos. Chem. Phys.*, 3, 2233–2307, 2003.
- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Rossi, M. J., and Troe, J.: Summary of evaluated kinetic and photochemical data for atmospheric chemistry: Web version August 1999, <http://www.iupac-kinetic.ch.cam.ac.uk/>, 1999.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, Jr., R. F., Hynes, R. G., Jenkin, M. E., Kerr, J. A., Rossi, M. J., and Troe, J.: Summary of evaluated kinetic and photochemical data for atmospheric chemistry: Web version March 2005, <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2005.
- Christensen, L. E., Okumura, M., Sander, S. P., Salawitch, R. J., Toon, G. C., Sen, B., Blavier, J.-F., and Jucks, K. W.: Kinetics of $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$: Implications for stratospheric H_2O_2 , *Geophys. Res. Lett.*, 29, doi:10.1029/2001GL014525, 2002.
- Kircher, C. C. and Sander, S. P.: Kinetics and mechanism of HO_2 and DO_2 disproportionations, *J. Phys. Chem.*, 88, 2082–2091, 1984.
- McCabe, D. C., Gierczak, T., Talukdar, R. K., and Ravishankara, A. R.: Kinetics of the reaction $\text{OH} + \text{CO}$ under atmospheric conditions, *Geophys. Res. Lett.*, 28, 3135–3138, 2001.
- Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Moortgat, G. K., Keller-Rudek, H., Wine, P. H., Ravishankara, A. R., Kolb, C. E., Molina, M. J., Finlayson-Pitts, B. J., Huie, R. E., and Orkin, V. L.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, CA, 2006.
- Sivakumaran, V., Hölscher, D., Dillon, T. J., and Crowley, J. N.: Reaction between OH and HCHO: temperature dependent rate coefficients (202–399 K) and product pathways (298 K), *Phys. Chem. Chem. Phys.*, 5, 4821–4827, 2003.