Supplementary Material for the paper

The influence of natural and anthropogenic secondary sources on the glyoxal global distribution

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Table 1. Photolysis reactions in TM4-ECPL and related references

#	*reaction*			*refs.*
*	O_3 + *hv*	→	O(^3P) + O_2	1
j1	O_3 + *hv*	→	O(^1D) + O_2	1
j2	H_2O_2 + *hv*	→	2OH	1
j3	NO_2 + *hv*	→	NO + O	1
j4	NO_3 + *hv*	→	NO_2 + O	1
j5	NO_3 + *hv*	→	NO + O_2	1
j6	$HONO_2$ + *hv*	→	NO_2 + OH	1
j7	HO_2NO_2 + *hv*	→	NO_2 + HO_2	1
j8	N_2O_5 + *hv*	→	NO_2 + NO_3	1
j9	CH_3OOH + *hv* + O_2	→	HCHO + HO_2 + OH	1
j10	CH_3ONO_2 + *hv* + O_2	→	HCHO + HO_2 + NO_2	1
j11	HCHO + *hv*	→	CO + H_2	1
j12	HCHO + *hv* + $2O_2$	→	CO + $2HO_2$	1
j13	C_2H_5OOH + *hv* + O_2	→	CH_3CHO + HO_2 + OH	2
j14	$C_2H_5ONO_2$ + *hv* + O_2	→	CH_3CHO + HO_2 + NO_2	1
j15	CH_3CHO + *hv* + $2O_2$	→	CH_3O_2 + CO + HO_2	1
j16	$CH_3C(O)O_2NO_2$ + *hv*	→	CH_3COO_2 + NO_2	1
j17	CH_3COO_2H + *hv* + O_2	→	CH_3O_2 + CO_2 + OH	2
j18	$C_3H_7O_2$*prim* + *hv* + O_2	→	1-C_2H_5CHO + HO_2 + OH	2
j19	$C_3H_7ONO_2$*prim* + *hv*	→	1-C_2H_5CHO + HO_2 + NO_2	4
j19	C_2H_5CHO*prim* + *hv* + O_2	→	$C_2H_5O_2$ + CO + HO_2	7
j20	$C_3H_7O_2$*sec* + *hv* + O_2	→	CH_3COCH_3 + HO_2 + OH	2
j21	$C_3H_7ONO_2$*sec* + *hv*	→	CH_3COCH_3 + HO_2 + NO_2	4
j22	CH_3COCH_3 + *hv* + $2O_2$	→	CH_3COO_2 + CH_3O_2	5
j23	CH_3COCHO + *hv* + $2O_2$	→	0.3*(CH_3O_2 + 2CO + HO_2)+ 0.7*(CH_3COO_2 + CO + HO_2)	1
j24	CH_3COCH_2OOH + *hv* + O_2	→	CH3COCHO + OH + HO_2	2
j25	$HOCH_2CH_2OOH$ + *hv* + O_2	→	OH + *e*(2HCHO + HO_2) + *f*(HOCH2CHO + HO_2)	2, 8
j26	$HOCH_2CH_2$ONO2 + *hv* + O_2	→	NO_2 + *e*(HCHO + HO2) + *f* ($HOCH_2CHO$ + HO2)	1, 8
j27	$HOCH_2CHO$ + *hv* + $2O_2$	→	HCHO + CO + $2HO_2$	1
j28	CHOCHO + *hv*	→	2CO + $2HO_2$	1
j29	$C_4H_9ONO_2$ + *hv* +O_2	→	NO_2 + 0.67($CH_3CH_2COCH_3$ + HO_2) + 0.33($C_2H_5O_2$ +CH_3CHO)	4
j30	C_4H_9OOH + *hv* + O_2	→	OH + 0.67($CH_3CH_2COCH_3$+ HO_2) + 0.33($C_2H_5O_2$ +CH_3CHO)	2
j31	$CH_3CH_2COCH_3$ + *hv* + $2O_2$	→	CH_3COO_2 + $C_2H_5O_2$	5
j32	$CH_3CHONO_2COCH_3$ + *hv* + O_2	→	CH_3CHO + CH_3COO_2 + NO_2	4
j33	$CH_3CHOOHCOCH_3$ + *hv* + O_2	→	CH_3CHO + CH_3COO_2 + OH	2
j34	$CH_3COCOCH_3$ + *hv* + $2O_2$	→	$2CH_3COO_2$	6
j35	ISOOH + *hv* + O_2	→	HCHO + OH + HO_2 + 0.64MVK + 0.36MACR	2
j36	NITRATES + *hv* + O_2	→	HCHO + HO_2 + NO_2 + 0.64MVK + 0.36MACR	4
j37	MVKOOH + *hv* + O_2	→	CH_3COO_2 + HOCH2CHO + OH	2
j38	MACROOH + *hv* + O_2	→	CH_3COCH_2OH + CO + OH + HO2	2
j39	$CH_2ONO_2CH_2OOH$ + *hv*	→	OH + NO_2 + 2HCHO	2
j40	$CH_2ONO_2CH_2OOH$ + *hv*	→	CH_3CHO + HCHO + NO_2 + OH	2
j41	$CH_3COCOOH$ + *hv*	→	CH_3CHO + CO_2	2
j43	MACR + *hv*	→	$0.67HO_2$ + $0.33MACRO_2$ + $0.67CH_2O$ + $0.67CH_3COO_2$ +0.33OH	1
j44	MVK + *hv*	→	$0.3CH_3CO_3$ + $0.7C_3H_6$ + 0.7CO + $0.3CH_3O_2$	1

* not explicitely accounted in the model; it is solved in the EBI code.

References

1. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Web Version February, http://www.iupac-kinetic.ch.cam.ac.uk/ summary/ IUPACsumm_web_Feb2006.pdf, 2006

2. j = j13

3. j = 1.7 x j22

4. j = j10

5. j= 3 x 10^{-4} x j3

6. j = 0.285 x j3

7. j = (2.58 x 10^{-4} + 1.2 x 10^{-5}) x j3

8. R1 = 2.7 x 10^{14}exp(-6350/T)

   R2 = 6.3 x 10^{-14}exp(-550/T)

   e = R1/(R1 + R2 x [O_2]) , f = 1 – e

   T= temperature, lumping as in

   Poisson, N., Kanakidou, M., and Crutzen, P. J.: Impact of Non Methane Hydrocarbons on tropospheric chemistry and particular the oxidizing power of the global troposphere: 3-Dimensional Modelling results, J. Atmos. Chem., 36, 157-230, 2000.

Table 2. Thermal reactions in TM4-ECPL as related references.

#	*reaction*			*rate coefficient*	*Refs*
*	$O(^1D)+ M$	→	$O(^3P) + M$	4×10^{-11}	1
*	$O(^3P) + O_2 + M$	→	$O_3 + M$	6.0×10^{-34} (T /300)$^{-2.6}$ (O_2) 5.6×10^{-34} (T /300)$^{-2.6}$ (N_2)	1
*	$O(^1D)+ H_2O$	→	2 OH	2.2×10^{-10}	1
k1	$O_3 + OH$	→	$HO_2 + O_2$	1.7×10^{-12}exp(-940/T)	1
k2	$HO_2 + O_3$	→	$OH + O_2$	2.03×10^{-16} (T/300)$^{4.57}$ exp(693/T)	1
k3	$HO_2 + OH$	→	$H_2O + O_2$	4.8×10^{-11}exp(250/T)	1
k4	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	1.9×10^{-33} [N2] exp(980/T)	1
k5	$H_2O_2 + OH$	→	$H_2O + HO_2$	2.9×10^{-12}exp(-160/T)	1
k6	$HO_2 + NO$	→	$NO_2 + HO$	3.6×10^{-12}exp(270/T)	1
k7	$NO + O_3$	→	$NO_2 + O_2$	1.4×10^{-12}exp(-1310/T)	1
k8	$NO + NO_3$	→	$2NO_2$	1.8×10^{-11}exp(110/T)	1
k9	$NO_2 + O_3$	→	$NO_3 + O_2$	1.4×10^{-13}exp(-2470/T)	1
k10	$NO_2 + OH + M$	→	$HONO_2 + M$	3.3×10^{-30}(T/300)$^{-3.0}$[N_2] 4.1×10^{-11} Fc = 0.4	1
k11	$NO_2 + NO_3 + M$	→	$N_2O_5 + M$	3.6×10^{-30}(T/300)$^{-4.1}$[N2] 1.9×10^{-12}(*T*/300)$^{0.2}$ *F*c = 0.35	1
k12	$NO_2 + HO_2 + M$	→	$HO_2NO_2 + M$	1.8×10^{-31}(T/300)$^{-3.2}$[N_2] 4.7×10^{-12} *F*c = 0.6	1
k13	$HO_2 + NO_3$	→	$OH + NO_2 + O_2$	4.0×10^{-12}	1
k14	$HONO_2 + OH$	→	$H_2O + NO_3$	1.5×10^{-13}	1
k15	$HO_2NO_2 + HO$	→	$H_2O + O_2 + NO_2$	3.2×10^{-13}exp(690/*T*)	1
k16	$HO_2NO_2 + M$	→	$HO_2 + NO_2 + M$	4.1×10^{-5}exp(-10650/T)[N2] 4.8×10^{15}exp(-11170/*T*) *F*c = 0.6	1
k17	$N_2O_5 + M$	→	$NO_2 + NO_3 + M$	1.3 x 10-3(T/300)$^{-3.5}$exp(-11000/T)[N2] 9.7×10^{14}(*T*/300)$^{0.1}$exp(-11080/*T*) *F*c = 0.35	1
k18	$CH_4 + OH$	→	$H_2O + CH_3O_2$	1.85×10^{-12} exp(-1690/T)	1
k19	$CH_3O_2 + NO$	→	$HCHO + HO_2 + NO_2$	2.3×10^{-12}exp(360/*T*)	1
k10	$CH_3O_2 + NO_3$	→	$HCHO + HO_2 + NO_2$	1.3×10^{-12}	1
k21	$CH_3O_2 + HO_2$	→	$CH_3OOH + O_2$	3.8×10^{-13}exp(780/T)	1
k22	$CH_3O_2 + CH_3O_2$	→	k22a(2HCHO + $2HO_2 + O_2$) +(1-k22a)($CH_3OH + HCHO + O_2$)	k22 = 7.4×10^{-13}exp(-520/T) k22a=5.4exp(0.870/T)	1
k23	$CH_3OOH + OH$	→	$CH_3O_2 + H_2O$	1.9 x 10-12	1
k24	$CH_3OOH + OH$	→	$H_2O + HCHO + OH$	3.6 x 10-12	1
k25	$CH_3ONO_2 + OH$	→	$HCHO + NO_2 + H_2O$	4.0×10^{-13}exp(-845/*T*)	1
k26	$HCHO + OH$	→	$H_2O + CO + HO_2$	5.4×10^{-12}exp(135/T)	1
k27	$CH_3OH + OH$	→	$H_2O + HCHO + HO_2$	2.85 x 10-12exp(-345/*T*)	1
k28	$CO + OH$	→	$HO_2 + CO_2$	1.44×10^{-13}(1 +[N2] / 4×10^{19})	1
k29	$C_2H_6 + OH + O_2$	→	$H_2O + C_2H_5O_2$	6.9×10^{-12}exp(-1000/T)	1
k30	$C_2H_5O_2 + NO + O_2$	→	(1 -RTC2) x [$CH_3CHO + HO_2 + NO_2$] + RTC2 x $C_2H_5ONO_2$	k30 = 2.6 x 10-12 exp(380/T) R1= 1.94×10^{-22} [AIR]exp(0.972) R2 = 0.826(T/300)$^{-8.1}$	2

				$A = 1/(1+\log(R1/R2)^2)$ $RTC2 = 0.4R1/(1+R1/R2)0.411^A$	
k31	$C_2H_5O_2 + HO_2$	→	$C_2H_5OOH + O_2$	$3.8 \times 10^{-13}\exp(900/T)$	1
k32	$C_2H_5O_2 + CH_3O_2$	→	(1 - k32a)(CH_3CHO +HCHO +$2HO_2$ -O2) + k32a(CH_3CHO +CH_3OH +O_2)	R1=0.45 k32a = 0.5((1-k22a)+(1-R1))	2
k33	$C_2H_5OOH + OH$	→	$C_2H_5O_2 + H_2O$	k33 = $2.6 \times 10^{-12}\exp(190/T)$	2
k34	$C_2H_5OOH + OH$	→	$CH_3CHO + OH + H_2O$	k34 = $4.5 \times 10^{-18}\, T^2 \exp(1069/T)$	2
k35	$C_2H_5ONO_2 + OH$	→	$CH_3CHO + NO_2 + H_2O$	k35 = $6.7 \times 10^{-13}\exp(-395/T)$	1
k36	CH_3CHO+ HO + O_2	→	$CH_3COO_2 + HO_2$	$4.4 \times 10^{-12}\exp(365/T)$	1
k37	$CH_3COO_2 + HO_2$	→	$CH_3COOOH + O_2$	$5.2 \times 10^{-13}\exp(980/T)$	1
k38	$CH3COO_2 + HO_2$	→	$CH_3COOH + O_3$	$1.04 \times 10^{-13}\exp(983/T)$	2
k39	$CH3COO_2 + NO + O_2$	→	$CH_3O_2 + CO_2 + NO_2$	$7.5 \times 10^{-12}\exp(290/T)$	1
k40	$CH_3COO_2 + NO_2 + M$	→	$CH_3CO_3NO_2 + M$	$2.7 \times 10^{-28}(T/300)^{-7.1}[N_2]$ $1.2 \times 10^{-11}(T/300)^{-0.9}$ $Fc = 0.3$	1
k41	$CH_3COO_2 + CH_3O_2$	→	$HCHO + HO_2 + CH_3O_2 + CO_2$	9.9×10^{-12}	1
k42	$CH_3COO_2 + CH_3O_2$	→	$CH_3COOH + HCHO + O_2$	1.1×10^{-12}	1
k43	$CH_3COO_2 + CH_3COO_2$ $+ O_2$	→	$2(CH_3O_2 + CO_2)$	$2.9 \times 10^{-12}\exp(500/T)$	1
k44	$CH_3COO_2NO_2 + OH$	→	$HCHO + CO_2 + NO_2 + H_2O$	3×10^{-14}	1
k45	$CH_3COO_2NO_2$	→	$CH_3COO_2 + NO_2$	$4.9 \times 10^{-3}\exp(-12100/T)[N2]$ 5.4 x 1016exp(-13830/T) $Fc = 0.3$	1
k46	$CH_3COO_2NO_2$	→	$CH_3ONO_2 + CO_2$	$2.1 * 10^{12} \exp(-12525/T)$	2
k47	$CH_3COO_2H + OH$	→	$CH_3COO_2 + H_2O$	like k36	2
k48	$CH_3COOH + OH + O_2$	→	$CH_3O_2 + CO_2 + H_2O$	$4.2 \times 10^{-14}\exp(855/T)$	1
k49	$C_3H_8 + OH + O_2$	→	(0.3)$C_3H_7O_2$prim + (0.7) $C_3H_7O_2$sec + H_2O	$7.6 \times 10^{-12}\exp(-585/T)$	1
k50	$C_3H_7O_2$prim + NO + O_2	→	(1 - RTC3P) x [$C_2H_5CHO + HO_2 + NO_2$] + RTC3P x $C_3H_7ONO_2$prim	$2.9 \times 10^{-12}\exp(350/T)$	1
k51	$C_3H_7O_2$sec + NO + O_2	→	(1 - RTC3S) x [$CH_3COCH_3 + HO_2 + NO_2$] + RTC3S x $C_3H_7ONO_2$sec	$2.7 \times 10^{-12}\exp(360/T)$	1
k52	$C_3H_7O_2$prim+ HO_2	→	C_3H_7OOHprim + O_2	k52 = $3.4 \times 10^{-15} * \exp(100/T)$	1
k53	$C_3H_7O_2$prim + CH_3O_2	→	(1 – k32a)(C_2H_5CHO +HCHO +$_2HO_2$ +O_2) + k32a(C_2H_5CHOprim + CH_3OH +O_2	R1=2.5×10^{-13} k56 = $2(R1*k25)^{0.5}$	2
k54	C_3H_7OOHprim + OH	→	$C_3H_7O_2$prim + H_2O	like k33	
k55	C_3H_7OOHprim + OH	→	C_2H_5CHO prim + OH + H_2O	like k34	
k56	$C_3H_7ONO_2$prim + OH	→	C_2H_5CHO prim + NO_2 + H_2O	5.8×10^{-13}	1
k57	$C_2H_5CHO + OH$	→	1/2 ($3CH_3COO_2 + H_2O + HO_2$)	k57 = $5.1 \times 10^{-12}\exp(405/T)$	1
k58	$C_2H_5CHO + NO_3 + O_2$	→	$HNO_3 + CH_3CH_2O_2 + CO$	6.5×10^{-15}	1
k59	$C_3H_7O_2$sec + HO_2	→	C_3H_7OOHsec + O_2	$6.2 \times 10^{-13} \exp(-230/T)$	1
k60	$C_3H_7O_2$sec + CH_3O_2	→	(1 – k60a)(CH_3COCH_3 + HCHO +$2HO_2$ + O_2) +k60a(CH_3COCH_3 + CH_3OH +O_2)	R1 = 5×10^{-15} k60a = 0.5((1-k22a) + (1-0.45)) k60 = $2((R1k_{25})^{0.5}$	2
k61	C_3H_7OOHsec + OH	→	$C_3H_7O_2$sec + H_2O	like k33	2
k62	C_3H_7OOHsec + OH	→	$CH_3COCH_3 + OH + H_2O$	$2.12 * 10^{-18} * T^2\exp(688/T)$	2
k63	$C_3H_7ONO_2$sec + OH	→	$CH_3COCH_3 + NO_2$ + H2O	$6.2 \times 10^{-13}\exp(-230/T)$	1
k64	$CH_3COCH_3 + OH + O_2$	→	$CH_3COCH_2O_2$ + H2O	{$8.8 \times 10^{-12}\exp(-1320/T)$ + $1.7 \times 10^{-14}\exp(420/T)$}	1
k65	$CH_3COCH_2O_2$ + NO + O_2	→	$CH_3COCHO + NO_2 + HO_2$	like k50	2

k66	$CH_3COCH_2O_2 + HO_2$	→	$CH_3COCH_2OOH + O_2$	like k52	2
k67	$CH_3COCHO + OH + O_2$	→	$CH_3COO_2 + CO + H_2O$	1.5×10^{-11}	1
k68	$CH_3COCH_2OOH + OH$	→	$CH_3COCH_2O_2 + H_2O$	like k33	2
k69	$C_2H_4 + OH + O_2 + M$	→	$HOCH_2CH_2O_2 + M$	$k_0=8.6 \times 10^{-29}(T/300)^{-3.1}[N_2]$ $k_\infty=9 \times 10^{-12}(T/300)^{-0.85}$ Fc = 0.48	1
k70	$C_2H_4 + O_3 + 2O_2$	→	(0.0044)CHOCHO + (1.37)HCHO + (0.43)CO + (0.26)HO_2 + (0.12)OH + (0.002)H_2O_2 + (0.13)H_2 + (0.31)H_2O + (0.2)CO_2	$9.1 \times 10^{-15}\exp(-2580/T)$	1
k71	$HOCH_2CH_2O_2 + NO +$ O_2	→	(1-RTC2) x [NO_2 +e(2HCHO + HO_2) + f(HOCH2CHO + HO_2)]+ RTC2 x $HOCH_2CH_2ONO_2$	R1 = $2.7 \times 10^{14}\exp(-6350/T)$ R2 = $6.3 \times 10^{-14}\exp(-550/T)$ e = R1/(R1 + R2 x [O_2]) , f = 1 - e k71 = 9×10^{-12}	1
k72	$HOCH_2CH_2O_2 + HO_2$	→	$HOCH_2CH_2OOH + O_2$	1.2×10^{-11}	1
k73	$HOCH_2CH_2O_2 + CH_3O_2$	→	(1 - k32a)($HOCH_2CHO$ +HCHO +2HO_2 +O_2) +k32a($HOCH_2CHO$ +CH_3OH +O_2)	like k32	2
k74	$HOCH_2CH_2OOH + OH$	→	$HOCH_2CH_2O_2 + H_2O$	like k33	2
k75	$HOCH_2CH_2OOH + OH$	→	$HOCH_2CHO + OH + H_2O$	like k34	2
k76	$HOCH_2CH_2ONO_2 + OH$	→	$HOCH_2CHO + NO_2 + H_2O$	like k35	2
k77	$HOCH_2CHO + OH$	→	CO_2 + HCHO	8.8×10^{-12}	1
k79	$HOCH_2CHO + OH + O_2$	→	CHOCHO + $HO_2 + H_2O$	2.2×10^{-12}	1
k80	CHOCHO + OH + O_2	→	2CO + $HO_2 + H_2O$	$2.8 \times 10^{-12}\exp(340/T)$	3
k81	CHOCHO + $NO_3 + O_2$		$HNO_3 + HO_2$ +2CO	$1. \times 10^{-15}$	4
k82	$C_3H_6 + OH + O_2$	→	$HOC_3H_6O_2$	$8 \times 10^{-27}(T/300)^{-3.5}[N_2]$ $3.0 \times 10^{-11}(T/300)^{-1.0}$ Fc = 0.5	1
k83	$C_3H_6 + O_3 + 2O_2$	→	0.5(HCHO + 0.15CH_3COOH + 0.71CH_3O_2 + 0.68CO + 0.54OH + 0.17HO_2) +	$5.5 \times 10^{-15}\exp(-1880/T)$	1
k84	$HOC_3H_6O_2$ + NO	→	(1 - 0.35RTC3P - 0.65RTC3S) x [CH_3CHO + HCHO + HO_2 + NO_2 + O_2] + 0.35RTC3P x $C_3H_7ONO_2$prim + 0.65RTC3S x $C_3H_7ONO_2$sec	like k30	2
k85	$HOC_3H_6O_2 + HO_2$	→	$HOC_3H_6OOH + O_2$	like k52	2
k86	$HOC_3H_6O_2 + CH_3O_2$	→	(1 - k60a)(CH_3CHO + 2HCHO +2HO_2 + O_2) + k60a(CH_3COCH_2OH + CH_3OH + O_2)	like k53	2
k87	HOC_3H_6OOH + OH	→	$HOC_3H_6O_2 + H_2O$	2×10^{-11}	2
k88	C_4H_{10} + OH + O_2	→	$C_4H_9O_2 + H_2O$	$9.1 \times 10^{-12}\exp(-405/T)$	
k89	$C_4H_9O_2$ + NO	→	(1 - RTC4S) x [NO_2 + 0.67($CH_3CH_2COCH_3$ + HO_2) + 0.33($C_2H_5O_2$ + CH_3CHO + O_2] + RTC4S x $C_4H_9ONO_2$)	like k30 R1=1.94×10^{-22} [AIR] exp(0.9740 R2=$0.826(T/300)^{-8.1}$ A=$1/(1 + \log(R1/R2)^2)$ RTC4P=$0.4R1/(1+R1/R2)0.411^A$ RTC4S=$0.45{*}k33{*}R1/(1+R1/R2)0.411^A$	1
k90	$C_4H_9O_2 + HO_2$	→	$C_4H_9OOH + O_2$	like k52	2
k91	$C_4H_9O_2 + CH_3O_2$	→	(1 – k60a)[HCHO +HO_2 +0.67($CH_3CH_2C(O)CH_3$ +HO_2 +O_2) + 0.33(CH_3CHO +$CH_3CH_2O_2$ +O2)] +k60a($CH_3CH_2COCH_3$ +CH_3OH +O_2)	like k60	2
k92	$C_4H_9ONO_2$sec + OH	→	$CH_3CH_2COCH_3$ +NO_2 +H_2O	1.71×10^{-12}	2
k93	C_4H_9OOH + OH	→	$C_4H_9O_2 + H_2O$	like k33	2

k94	C_4H_9OOH + OH	→	$CH_3CH_2COCH_3$ + OH + H_2O	$2.12 \times 10^{-18} * T^2 \exp(1131/T)$	2
k95	$CH_3CH_2COCH_3$ + OH + $0.5O_2$	→	$CH_3CHO_2COCH_3$	$1.3 \times 10^{-12} \exp(-25/T)$	1
k96	$CH_3CHO_2COCH_3$ + NO + O_2	→	(1 - RTC4S) x [CH_3CHO + CH_3COO_2 + NO_2] + RTC4S x $CH_3CHONO_2COCH_3$	like k30	2
k97	$CH_3CHO_2COCH_3$ + HO_2	→	$CH_3CHOOHCOCH_3$ + O_2	like k52	2
k98	$CH_3CHONO_2COCH_3$ + OH	→	$CH_3COCOCH_3$ + NO_2 + H_2O	9.20×10^{-13}	2
k99	$CH_3CHOOHCOCH_3$ + OH	→	$CH_3CHO_2COCH_3$ + H_2O	like k33	2
k100	$CH_3CHOOHCOCH_3$ + OH	→	$CH_3COCOCH_3$ + OH + H_2O	$2.12*10^{-18} * T^2 \exp(983/T)$	2
k101	ISOPRENE + OH →	→	0.99 $ISOPO_2$ + 0.03 CHOCHO	$2.7 \times 10^{-11} \exp(390/T)$	1
k102	$ISOPO_2$ + NO + O_2	→	(1 - RTC5S) x [HCHO + HO_2 + NO_2 + 0.64 MVK + 0.36 MACR] + RTC5S x NITRATES	k102 = 0.45 * k30 R1=1.94×10^{-22} [AIR] exp(0.95*5) R2=$0.826(T/300)^{-8.1}$ A=$1/(1 + \log(R1/R2)^2)$ RTC5P=$0.4R1/(1+R1/R2)0.411^A$ RTC5S=$0.45*k30*R1/(1+R1/R2)0.411^A$	2
k103	$ISOPO_2$ + HO_2	→	ISOOH + O_2	like k52	2
k104	$ISOPO_2$ + CH_3O_2 + O2	→	(1 − k60a)(2(HCHO + HO_2) + 0.64 MVK + 0.36 MACR) + k60a(0.64 MVK + 0.36 MACR + $2O_2$ + HCHO + CH_3OH)	like k60	2
k105	ISOOH + OH	→	RO_2 + H_2O	like k85	2
k106	ISOOH + OH + $2O_2$	→	$ISOPO_2$ + H_2O	2×10^{-11}	2
k107	RO_2 + NO	→	HOCH2CHO + CH_3COCHO + HO_2 + NO_2	like k30	2
k108	RO_2 + HO_2	→	CH_3COCHO + HOCH2CHO + H_2O	like k52	2
k109	NITRATES + OH + O_2	→	CH_3COCHO + HOCH2CHO + H_2O + NO_2	R1= $1.9 \times 10^{-11} \exp(450/T)$ R2= $9.5 \times 10^{-12} \exp(504/T)$ k=0.49k80+ 0.28R2 + 0.23R1	2
k110	MVK + O_3	→	0.38 CH_3COCHO + 0.2088 CH_3COO_2 + 0.26 $CH_3COCOOH$ + 0.26 CO + 0.0432 CH_3COOH + 0.108 CH_3CHO + 0.62 HCHO + 048 CO_2 + 0.54 HO_2 + 0.1008 OH + 0.048 H_2 + 0.116 H_2O	$8.5 \times 10^{-16} \exp(-1520/T)$	2
k111	MVK + OH	→	$MVKO_2$	$2.6 \times 10^{-12} \exp(610/T)$	1
k112	$MVKO_2$ + NO + O2	→	CH_3COO2 + HOCH2CHO + NO_2	like k30	1
k113	$MVKO_2$ + HO_2	→	MVKOOH + O2	like k52	2
k114	MVKOOH + OH	→	$MVKO_2$ + H_2O	like k106	2
k115	MVKOOH + OH + 3O2	→	CH_3COO_2 + 2CO + OH + $2HO_2$ + H2O	R1 = $2.12 \times 10^{-18} T^2 \exp(1045/T)$ R2 = $4.5 \times 10^{-18} T^2 \exp(1032/T)$ k115 = R1 + R2	2
k116	MACR + O_3 + $1.476O_2$	→	0.2 CH3COCHO + 1.6 HCHO + 1.658 CO + 0.142 CO_2 + 1.116 HO_2 + 0.72 OH + 0.058 H_2O + 0.024 H_2	$1.4 \times 10^{-15} \exp(-2100/T)$	1
k117	MACR + OH	→	$MACRO_2$	$8.0 \times 10^{-12} \exp(380/T)$	1
k118	$MACRO_2$ + NO + O_2	→	CH_3COCH_2OH + CO + NO_2 + HO_2	like k30	2
k119	$MACRO_2$ + HO_2	→	MACROOH + O_2	like k52	2
k120	MACROOH + OH	→	$MACRO_2$	like k33	2
k121	MACROOH + OH + O_2	→	CH_3COCHO + CO + 2 HO_2 + OH + H_2O	$4.5*10^{-18} * T^2 \exp(1032/T)$	2
k122	MACROOH + OH	→	CH_3COCH_2OH + CO + OH + H_2O	like k57	2

k123	$CH_3COCH_2OH + OH$	→	$CH_3COCHO + HO_2 + H_2O$	3.0×10^{-12}	1
k124	ISOPRENE + O_3	→	0.425 MACR + 0.18 MVK + 0.12 CH_2CCH_3COOH + 0.12 $CH_3COCOOH$ + 0.84 HCHO + 0.3 CO + 0.24 CO_2 + 0.24 HCOOH + $0.04C_3H_6$ + 0.34OH + $0.025H_2$ + $0.19H_2O$	1.03×10^{-14}exp(-1995/T)	1
k125	HCOOH + OH + O_2	→	$CO_2 + HO_2 + H_2O$	4.5×10^{-13}	2
k126	$C_4H_{10} + NO_3 + O_2$	→	$C_4H_9O_2 + HNO_3$	2.8×10^{-12} exp(-3280/T)	1
k127	HCHO + NO_3 + O_2	→	$HNO_3 + HO_2$ +CO	5.6×10^{-16}	1
k128	$CH_3CHO + NO_3 + O_2$	→	$HNO_3 + CH_3O_2$ + CO	1.4×10^{-12}exp(-1860/T)	1
k129	$CH_3OH + NO_3 + O_2$	→	HNO_3 + HCHO +HO_2	9.4×10^{-13}exp(-2650/T)	1
k130	$C_2H_4 + NO_3$	→	CH_2ONOCH_2OO	3.3×10^{-12}exp(-2880/T)	1
k131	$CH_2ONO_2CH_2OO$ + NO	→	$2NO_2$ + 2HCHO	like k30	1
k132	$CH_2ONO_2CH_2OO$ + NO	→	$2NO_2 + CH_3CHO$ + HCHO	like k30	
k133	$CH_2ONO_2CH_2OO + HO_2$	→	$CH_2ONO_2CH_2O_2H + O_2$	0.4 *3.5 x 10^{-15} exp(1000/T)	
k134	$CH_2ONO_2CH_2OO + HO_2$	→	$CH_2ONO_2CH_2O_2H + O_2$	0.6 *3.5 x 10^{-15} exp(1000/T)	
k135	$CH_2ONO_2CH_2O_2H$ + OH	→	NO_2 + HCHO +CO +$2HO_2$ + OH	like k34	
k136	$CH_2ONO_2CH_2O_2H$ + OH	→	$CH_2ONO_2CH_2OO + H_2O$	like k33	
K137	$C_3H_6 + NO_3$	→	$CH_3CHONO_2CH_2OO$	4.6×10^{-13}exp(-1155/T)	1
k138	ISOPRENE + NO_3	→	NITRATES	3.15×10^{-12} exp(-450/T)	1
k139	MACR + NO_3	→	HNO_3 + $MACRO_2$	3.4×10^{-15}	1
k140	$CH_3O_2 + HO_2$	→	$0.5CH_2O + 0.5CH_3O_2H$	3.8×10^{-13}exp(780/*T*)	1
k141	$CH_3COCOOH$ + OH	→	$CH_3C(O)OO + CO_2 + H_2O$	4.9×10^{-14}exp(276/*T*)	7
k142	DMS + OH	→	$0.995CH_3O_2$ + HCHO + $0.995SO_2$ + 0.005MSAg	1.13×10^{-11}exp(-253/*T*)	1
k144	DMS + OH	→	DMSO	$1.0 \times 10^{-39}[O_2]$ exp(5820/*T*) / {1 + 5.0 x $10^{-30}[O_2]$ exp(6280/*T*)}	1
k144	DMS + NO_3	→	$CH_3O_2 + HNO_3$ + HCHO + SO_2	1.9×10^{-13}exp(520/*T*)	1
k145	DMSO + OH	→	MSIA	8.7×10^{-11}	11
k146	MSIA + OH	→	$CH_3O_2 + SO_2$	$1. \times 10^{-10}$	11
k147	DMSO	→	MSAp	$1. \times 10^{-10}$	11
k148	MSIA	→	MSAp	$1. \times 10^{-10}$	11
k149	MSAg	→	MSAp	4.5×10^{-5}	11
k150	SO_2 + OH	→	$HO_2 + SO_4$ + 2ACID	$4.5 \times 10^{-31}(T/300)^{-3.9}[N_2]$ 1.3×10^{-12} $(T/300)^{-0.7}$ *F*c = 0.525	1
k151	ACID + NH_3	→	NH_4		9
k152	NH_3 + OH	→	NH_2	3.5×10^{-12}exp(-925/*T*)	1
k153	NH_2 + NO	→	Products	$1.6 \times 10^{-11}(T/298)^{-1.4}$	1
k154	$NH_2 + NO_2$	→	Products	$2.0 \times 10^{-11}(T/298)^{-1.3}$	1
k155	$NH_2 + HO_2$	→	Products	3.4×10^{-11}	10
k156	$NH_2 + O_2$	→	Products	6×10^{-21}	1
k157	$NH_2 + O_3$	→	Products	4.3×10^{-12}exp(-930/*T*)	10
k158	a-PINENE + O_3	→	$TERO_2$	6.3×10^{-16} exp(-580/T)	1
k159	a-PINENE + OH	→	$TERO_2$	1.2×10^{-11} exp(440/T)	1
k160	a-PINENE + NO_3	→	$TERO_2 + HNO_3$	1.2×10^{-12} exp(490/T)	1

k161	b-PINENE + O_3	→	TERO2 +b1*HCHO + b2*HCHO	1.5 x 10^{-17}	5
k162	b-PINENE + OH	→	$TERO_2$	2.38 x 10^{-11} exp(357/T)	5
k163	b-PINENE + NO_3	→	$TERO_2$ + HNO_3	1.6 x 10^{-10} exp(-1248/T)	5
k164	BENZENE + OH	→	0.64*(6/8)$AROO_2$ + 0.36CHOCHO	2.47 x 10^{-12} exp(-207/T)	6
k165	TOLUENE + O_3	→	(7/8)*$AROO_2$ + c2*MGLY	2.34 x 10^{-12} exp(-6694/T)	5
k166	TOLUENE + OH	→	0.65* (7/8)$AROO_2$ + 0.36CHOCHO+ c2*MGLY	5.69 x 10^{-12}	5
k167	TOLUENE + NO_3	→	(7/8)*$AROO_2$ + HNO_3	6.8 x 10^{-17}	5
k168	XYLENE + O_3	→	AROO2 + d2 (MGLY + 1/4$C_4H_9O_2$)	(2.4 x 10^{-13}exp(−5586/T)+5.37 x 10^{-13} exp(−6039/T)+1.91 x 10^{-13} exp(−5586/T))/3	5
k169	XYLENE + OH	→	0.68AROO2 + 0.32CHOCHO + d2 (MGLY + 1/4$C_4H_9O_2$)	1.72 x 10^{-11}	5
k170	XYLENE + NO_3	→	AROO2 + HNO_3	3.54 x 10^{-16}	5
k171	$TERO_2$ + NO +O_2	→	[(X-a1-a2) +(X-b1-b2)]*[(1 - RTC5S) *(HCHO + HO_2+ NO_2 + 0.64 MVK + 0.36MACR] + RTC5S * NITRATES]	like k30	
k172	$TERO_2$ + HO_2	→	[(X-a1-a2) +(X-b1-b2)]*[ISOOH + O_2]	like k31	
k173	$TERO_2$ + CH_3O_2 + O_2	→	[(X-a1-a2) +(X-b1-b2)]*[(1 − k60a) (2(HCHO + HO_2) +	like k60	
k174	$TERO_2$ +$TERO_2$	→	Products	like k53	
k175	$AROO_2$ + NO	→	[(X-c1-c2) +(X-d1-d2)]*[(1-RTC4S) *[NO_2 + 0.67($CH_3CH_2COCH_3$ + HO_2) + 0.33($C_2H_5O_2$ + CH_3CHO + O_2] + RTC4S *$C_4H_9ONO_2$)	like 30	
k176	$AROO_2$ + HO_2	→	[(X-c1-c2) +(X-d1-d2)]*[C_4H_9OOH+O2]	like 52	
k177	$AROO_2$ + CH_3O_2	→	[(X-c1-c2) +(X-d1-d2)]*[(1 - k60a) [HCHO+HO_2+0.67($CH_3CH_2C(O)CH_3$+HO_2 +O_2)	like 60	
k178	$AROO_2$ + $AROO_2$	→	Products	like 53	
k179	C_2H_2 + OH	→	0.635(CHOCHO + OH) + 0.365(HCOOH + CO + HO_2)	5 x 10^{-30}(T/300)$^{-1.5}$[N_2] 1 x 10^{-12} Fc=0.37	1
k180	CH_3COO_2 + $CH_3COCH_2O_2$	→	CH_3COOH + CH_3COCHO + O_2	2.5 x 10^{-12}	1
k181	CH_3COO_2 + $CH_3COCH_2O_2$	→	CH_3O_2 + CH_3COCH_2OH + CO_2	2.5 x 10^{-12}	1
k182	$C_2H_5O_2$ + CH_3COO_2	→	C_2H_5O(CH_3CHO+HO_2) + CH_3O_2 + CO_2	0.5 * 4.4 x 10^{-13}exp(1070/T)	1
k183	$C_2H_5O_2$ + CH_3COO_2	→	CH_3CHO + CH_3COOH + O_2	0.5 * 4.4 x 10^{-13}exp(1070/T)	1
k184	$ISOPO_2$ + NO_3	→	HO_2 + NO_2 + HCHO + 0.36MACR + 0.64MVK	2.3 10^{-12}	7
k185	RO_2 + NO_3	→	HO_2 + $HOCH_2CHO$ + CH_3COCHO + NO_2	2.3 10^{-12}	7
k186	$TERO_2$ + NO_3	→	HO_2 + NO_2 + 2(HCHO +0.36MACR + 0.64MVK)	2.3 10^{-12}	7

* not explicitely accounted in the model; it is solved in the EBI code.

For three bodies reactions: $$k = \frac{ko}{1+\frac{ko}{k\infty}} x Fc^{\frac{1}{1+\log(\frac{ko}{k\infty})^2}}$$

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Table 3. Emissions used in TM4. Units are Tg(Species) y^{-1}. NOx and NH_3 are in Tg(N) y^{-1}. DMS, SO_2 and SO_4 is in Tg(S) y^{-1}

Species	***Tg y^{-1}***	***Reference***
NOx	53	POET 2000
NH_3	52	EDGAR v2.0
SO_2	90	EDGAR v2.0
SO_4	2	EDGAR v2.0
DMS	19	Spiro. et al. (1992)
CO	1111	POET 2000
HCHO	4	POET 2000
CH_3OH	243	POET 2000
HCOOH	20.4[(1)]	Kesselmeier and Staudt (1999); Keene and Galloway (1988)
C_2H_6	12	POET 2000
C_2H_4	17	POET 2000
C_2H_2	7	EDGAR v2.0
CH_3COOH	9[(1)]	Kesselmeier and Staudt (1999); Keene and Galloway (1988)
CH_3CHO	8	POET 2000
Carboxylic Acids (as 50% HCOOH + 50% CH_3COOH)	19[(2)]	EDGAR v2.0
C_3H_8	12	POET 2000
$CH_3C(O)CH_3$	27	POET 2000
C_3H_6	7	POET 2000
C_4H_{10}	75[(3)]	POET 2000
$CH_3C(O)CH_2CH_3$	14	POET 2000
Isoprene	506[(4)]	POET 2000
Benzene	7	POET 2000
Toluene	14	POET 2000
Xylene	12	POET 2000
Monoterpenes (as 50% a-Pinene + 50% b- Pinene)	238	POET 2000

(1) Natural emissions
(2) Anthopogenic emissions
(3) including higher alkanes
(4) including 1Tg y^{-1} from oceans

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