

Observation and modelling of OH and HO₂
concentrations in the Pearl River Delta 2006:
A missing OH source in a VOC rich atmosphere

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Online supplementary materials

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This file includes:

- Supporting text
 - List of reactions of RACM-MIM-GK
 - List of reactions used in the sensitivity model runs M1 – M6
 - Comparison to the model results shown by Hofzumahaus et al. (2009)
 - RO₂ analysis for M0 and M0 + OHobs model runs
- Supporting tables: Table S1, S2, S3, S4, S5, S6, S7
- Supporting figures: Fig. S1, S2

RACM-MIM-GK

Details of the RACM-MIM-GK are shown in Table S1. The notation of the compounds refers to Stockwell et al. (1997), Geiger et al. (2003) and Karl et al. (2006). Bimolecular and termolecular (at a given atmospheric pressure) rate constants are given in units of cm^3s^{-1} and photolysis reactions in units of s^{-1} , if not otherwise noted.

Table S1: List of reactions in RACM-MIM-GK (M0).

#	reaction	rate constant ^a	reference
1	2 ACO ₃ →2 MO ₂	ARRH(2.8e-12,-530.0)	Stockwell et al. (1997)
2	2 HO ₂ →H ₂ O ₂ + O ₂	2.3e-13×exp(600/T) + 1.7e-33 ×exp(1000/T)×M	Stockwell et al. (1997)
3	2 ISOP→1.18 CAR ₄ + HCHO + HO ₂ + 0.58 MACR + 0.24 MVK	2.0e-12	Karl et al. (2006)
4	2 MACP→0.5 CO + HACE + 0.5 HCHO + HO ₂ + MGLY	2.00e-12	Geiger et al. (2003)
5	2 MO ₂ →1.33 HCHO + 0.66 HO ₂	ARRH(9.1e-14,-416.0)	Stockwell et al. (1997)
6	2 NO + O ₂ →2 NO ₂	ARRH(3.3e-39,-530.0)	Stockwell et al. (1997)
7	2 NO ₃ →2 NO ₂ + O ₂	ARRH(8.5e-13,2450.0)	Stockwell et al. (1997)
8	2 OLND→1.21 ALD + 0.504 HCHO + 0.285 KET + NO ₂ + ONIT	ARRH(2.96e-14,-1000.0)	Stockwell et al. (1997)
9	2 OLNN→HO ₂ + 2 ONIT	ARRH(7.0e-14,-1000.0)	Stockwell et al. (1997)
10	2 XO ₂ →	ARRH(7.13e-17,-2950.0)	Stockwell et al. (1997)
11	ACO ₃ + AIP→ALD + HO ₂ + KET + MO ₂	ARRH(7.4e-13,-765.0)	Stockwell et al. (1997)
12	ACO ₃ + CSLP→GLY + HO ₂ + MGLY + MO ₂	ARRH(7.4e-13,-765.0)	Stockwell et al. (1997)
13	ACO ₃ + ETEP→0.6 ALD + 0.8 HCHO + 0.5 HO ₂ + 0.5 MO ₂ + 0.5 ORA ₂	ARRH(9.48e-13,-765.0)	Stockwell et al. (1997)
14	ACO ₃ + ETHP→ALD + 0.5 HO ₂ + 0.5 MO ₂ + 0.5 ORA ₂	ARRH(1.03e-12,-211.0)	Stockwell et al. (1997)
15	ACO ₃ + HC ₃ P→0.724 ALD + 0.006 ETHP + 0.1 GLY + 0.091 HCHO + 0.488 HO ₂ + 0.127 KET + 0.004 MGLY + 0.508 MO ₂ + 0.499 ORA ₂ + 0.071 XO ₂	ARRH(6.9e-13,-460.0)	Stockwell et al. (1997)
16	ACO ₃ + HC ₅ P→0.677 ALD + 0.018 ETHP + 0.076 HCHO + 0.438 HO ₂ + 0.33 KET + 0.554 MO ₂ + 0.495 ORA ₂ + 0.237 XO ₂	ARRH(5.59e-13,-522.0)	Stockwell et al. (1997)
17	ACO ₃ + HC ₈ P→0.497 ALD + 0.015 ETHP + 0.489 HO ₂ + 0.581 KET + 0.507 MO ₂ + 0.495 ORA ₂ + 0.318 XO ₂	ARRH(2.47e-13,-683.0)	Stockwell et al. (1997)
18	ACO ₃ + HO ₂ →O ₃ + ORA ₂	ARRH(3.86e-16,-2640.0)	Stockwell et al. (1997)
19	ACO ₃ + HO ₂ →PAA	ARRH(1.15e-12,-550.0)	Stockwell et al. (1997)
20	ACO ₃ + KETP→0.12 ACO ₃ + 0.35 ALD + 0.38 HO ₂ + 0.11 KET + 0.54 MGLY + 0.5 MO ₂ + 0.5 ORA ₂ + 0.08 XO ₂	ARRH(7.51e-13,-565.0)	Stockwell et al. (1997)
21	ACO ₃ + LIMP→0.4 HCHO + HO ₂ + 0.6 MACR + MO ₂ + 0.4 OLI	ARRH(7.4e-13,-765.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

22	ACO3 + MO2 → HCHO + HO2 + MO2	ARRH(3.21e-11,440.0)	Stockwell et al. (1997)
23	ACO3 + MO2 → HCHO + ORA2	ARRH(2.68e-16,-2510.0)	Stockwell et al. (1997)
24	ACO3 + NO → MO2 + NO2	2.0e-11	Stockwell et al. (1997)
25	ACO3 + NO2 → PAN	TROE(9.7e-29,5.6,9.3e-12,1.5)	Stockwell et al. (1997)
26	ACO3 + NO3 → MO2 + NO2	4.0e-12	Stockwell et al. (1997)
27	ACO3 + OLIP → 0.941 ALD + 0.51 HO2 + 0.569 KET + 0.51 MO2 + 0.49 ORA2	ARRH(5.09e-13,-765.0)	Stockwell et al. (1997)
28	ACO3 + OLND → 0.65 ALD + 0.207 HCHO + 0.167 KET + 0.516 MO2 + 0.516 NO2 + 0.484 ONIT + 0.484 ORA2	ARRH(5.37e-13,-765.0)	Stockwell et al. (1997)
29	ACO3 + OLNN → 0.5 HO2 + 0.5 MO2 + ONIT + 0.5 ORA2	ARRH(8.85e-13,-765.0)	Stockwell et al. (1997)
30	ACO3 + OLTP → 0.859 ALD + 0.501 HCHO + 0.501 HO2 + 0.141 KET + 0.501 MO2 + 0.499 ORA2	ARRH(8.11e-13,-765.0)	Stockwell et al. (1997)
31	ACO3 + TCO3 → ACO3 + HCHO + MO2	ARRH(2.8e-12,-530.0)	Stockwell et al. (1997)
32	ACO3 + TOLP → DCB + 0.65 GLY + HO2 + 0.35 MGLY + MO2	ARRH(7.4e-13,-765.0)	Stockwell et al. (1997)
33	ACO3 + XO2 → MO2	ARRH(3.4e-14,-1560.0)	Stockwell et al. (1997)
34	ACO3 + XYLP → DCB + 0.37 GLY + HO2 + 0.63 MGLY + MO2	ARRH(7.4e-13,-765.0)	Stockwell et al. (1997)
35	ADDC + NO2 → CSL + HNO2	3.6e-11	Stockwell et al. (1997)
36	ADDC + O2 → 0.02 CSL + 0.98 CSLP + 0.02 HO2	ARRH(1.66e-17,-1044.0)	Stockwell et al. (1997)
37	ADDC + O3 → CSL + OH	5.0e-11	Stockwell et al. (1997)
38	ADDT + NO2 → CSL + HNO2	3.6e-11	Stockwell et al. (1997)
39	ADDT + O2 → 0.02 CSL + 0.02 HO2 + 0.98 TOLP	ARRH(1.66e-17,-1044.0)	Stockwell et al. (1997)
40	ADDT + O3 → CSL + OH	5.0e-11	Stockwell et al. (1997)
41	ADDX + NO2 → CSL + HNO2	3.6e-11	Stockwell et al. (1997)
42	ADDX + O2 → 0.02 CSL + 0.02 HO2 + 0.98 XYLP	ARRH(1.66e-17,-1044.0)	Stockwell et al. (1997)
43	ADDX + O3 → CSL + OH	1.0e-11	Stockwell et al. (1997)
44	ALD + hν → CO + HO2 + MO2	PHTFKT(7.344e-06,1.202,-0.417)	MCMv3.1 ^b
45	ALD + NO3 → ACO3 + HNO3	ARRH(1.4e-12,1900.0)	Stockwell et al. (1997)
46	ALD + OH → ACO3 + H2O	ARRH(5.5e-12,-331.0)	Stockwell et al. (1997)
47	API + NO3 → 0.9 OLNND + 0.1 OLNND	ARRH(1.19e-12,-490.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

48	API + O ₃ →0.65ALD + 0.14CO + 0.2ETHP + 0.02H ₂ O ₂ + 0.1HO ₂ + 0.53KET + 0.42KETP + 0.85OH	ARRH(1.01e-15,736.0)	Stockwell et al. (1997)
49	API + OH→APIP	ARRH(1.21e-11,-444.0)	Stockwell et al. (1997)
50	APIP + HO ₂ →OP2	1.5e-11	Stockwell et al. (1997)
51	APIP + MO ₂ →ALD + HCHO + 2HO ₂ + KET	ARRH(3.56e-14,-708.0)	Stockwell et al. (1997)
52	APIP + NO→0.8ALD + 0.8HO ₂ + 0.8KET + 0.8NO ₂ + 0.2ONIT	4.0e-12	Stockwell et al. (1997)
53	APIP + NO ₃ →ALD + HO ₂ + KET + NO ₂	1.2e-12	Stockwell et al. (1997)
54	CAR4 + hν→ACO ₃ + CO + HCHO + HO ₂	PHTFKT(1.140e-05,0.396,-0.298)	Karl et al. (2006)
55	CAR4 + O ₃ →0.1ACO ₃ + 0.22CO + 0.32HO ₂ + 0.9MGLY + 0.19OH + 0.45ORA1	2.4e-17	Karl et al. (2006)
56	CAR4 + OH→MACP	4.52e-11	Karl et al. (2006)
57	CH4 + OH→H ₂ O + MO ₂	T2ARR(7.44e-18,1361.0)	Stockwell et al. (1997)
58	CO + OH→CO ₂ + HO ₂	1.5e-13×(1 + 2.439e-20×M)	Stockwell et al. (1997)
59	CSL + NO ₃ →HNO ₃ + PHO	2.2e-11	Stockwell et al. (1997)
60	CSL + OH→0.85ADDC + 0.05HO ₂ + 0.1PHO + 0.05XO ₂	6.0e-11	Stockwell et al. (1997)
61	CSLP + HO ₂ →OP2	ARRH(3.75e-13,-980.0)	Stockwell et al. (1997)
62	CSLP + MO ₂ →GLY + HCHO + 2HO ₂ + MGLY	ARRH(3.56e-14,-708.0)	Stockwell et al. (1997)
63	CSLP + NO→GLY + HO ₂ + MGLY + NO ₂	4.0e-12	Stockwell et al. (1997)
64	CSLP + NO ₃ →GLY + HO ₂ + MGLY + NO ₂	1.2e-12	Stockwell et al. (1997)
65	DCB + hν→HO ₂ + TCO ₃	4.33e-4/7.5e-3×j(NO ₂)	Stockwell et al. (1997)
66	DCB + NO ₃ →0.25ALD + 0.25GLY + 0.5HNO ₃ + 0.5HO ₂ + 0.03KET + 0.25MGLY + 0.5NO ₂ + 0.5TCO ₃ + 0.5XO ₂	ARRH(2.87e-13,1000.0)	Stockwell et al. (1997)
67	DCB + O ₃ →0.28ACO ₃ + 0.16ALD + 0.66CO + 0.5GLY + 0.29HO ₂ + 0.62MGLY + 0.21OH + 0.11ORA1 + 0.21ORA2 + 0.11PAA	2.0e-18	Stockwell et al. (1997)
68	DCB + OH→0.15GLY + 0.5HO ₂ + 0.15MGLY + 0.5TCO ₃ + 0.35UDD + 0.5XO ₂	ARRH(2.8e-11,-175.0)	Stockwell et al. (1997)
69	DIEN + NO ₃ →0.9MACR + 0.1OLND + 0.9OLNN	1.0e-13	Stockwell et al. (1997)
70	DIEN + O ₃ →0.15ACO ₃ + 0.36CO + 0.05H ₂ + 0.001H ₂ O ₂ + 0.9HCHO + 0.3HO ₂ + 0.02KETP + 0.39MACR + 0.03MO ₂ + 0.09O + 0.28OH + 0.35OLT + 0.15ORA1 + 0.13XO ₂	ARRH(1.34e-14,2283.0)	Stockwell et al. (1997)
71	DIEN + OH→ISOP	ARRH(1.48e-11,-448.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

72	ETE + NO ₃ →0.2OLND + 0.8OLNN	T2ARR(4.88e-18,2282.0)	Stockwell et al. (1997)
73	ETE + O ₃ →0.43 CO + 0.13 H ₂ + HCHO + 0.26 HO ₂ + 0.12 OH + 0.37 ORA1	ARRH(9.14e-15,2580.0)	Stockwell et al. (1997)
74	ETE + OH→E ₁ TEP	ARRH(1.96e-12,-438.0)	Stockwell et al. (1997)
75	E ₁ TEP + HO ₂ →OP ₂	ARRH(1.9e-13,-1300.0)	Stockwell et al. (1997)
76	E ₁ TEP + MO ₂ →0.35 ALD + 1.55 HCHO + HO ₂	ARRH(1.71e-13,-708.0)	Stockwell et al. (1997)
77	E ₁ TEP + NO→0.2ALD + 1.6 HCHO + HO ₂ + NO ₂	9.0e-12	Stockwell et al. (1997)
78	E ₁ TEP + NO ₃ →0.2ALD + 1.6 HCHO + HO ₂ + NO ₂	1.2e-12	Stockwell et al. (1997)
79	ETH + OH→E ₁ THP + H ₂ O	T2ARR(1.51e-17,492.0)	Stockwell et al. (1997)
80	E ₁ THP + HO ₂ →OP ₂	ARRH(7.5e-13,-700.0)	Stockwell et al. (1997)
81	E ₁ THP + MO ₂ →0.75 ALD + 0.75 HCHO + HO ₂	ARRH(1.18e-13,-158.0)	Stockwell et al. (1997)
82	E ₁ THP + NO→ALD + HO ₂ + NO ₂	8.7e-12	Stockwell et al. (1997)
83	E ₁ THP + NO ₃ →ALD + HO ₂ + NO ₂	1.2e-12	Stockwell et al. (1997)
84	GLY + hν→1.55 CO + 0.15 H ₂ + 0.45 HCHO + 0.8 HO ₂	PHTFKT(3.802e-05,0.644,-0.312)	Stockwell et al. (1997)
85	GLY + hν→1.87 CO + 0.87 H ₂ + 0.13 HCHO	PHTFKT(6.845e-05,0.130,-0.201)	MCMv3.1 ^b
86	GLY + NO ₃ →2 CO + HNO ₃ + HO ₂	ARRH(2.9e-12,1900.0)	Stockwell et al. (1997)
87	GLY + OH→2 CO + H ₂ O + HO ₂	1.14e-11	Stockwell et al. (1997)
88	H ₂ + OH→H ₂ O + HO ₂	ARRH(5.5e-12,2000.0)	Stockwell et al. (1997)
89	H ₂ O + 2 HO ₂ →H ₂ O + H ₂ O ₂ + O ₂	3.22e-34×exp(2800/T) + 2.38e-34×exp(3200/T)×1e-20×M	Stockwell et al. (1997)
90	H ₂ O + O ₁ D→2 OH	2.2e-10	Stockwell et al. (1997)
91	H ₂ O ₂ + hν→2 OH	j(H ₂ O ₂)	SR ^c
92	H ₂ O ₂ + OH→H ₂ O + HO ₂	ARRH(2.9e-12,160.0)	Stockwell et al. (1997)
93	HACE + OH→HO ₂ + MGLY	3.00e-12	Geiger et al. (2003)
94	HC ₃ + OH→0.335 ALD + 0.036 CO + 0.036 GLY + H ₂ O + 0.583 HC ₃ P + 0.01 HCHO + 0.381 HO ₂ + 0.036 OH + 0.036 ORA1	ARRH(5.26e-12,260.0)	Stockwell et al. (1997)
95	HC ₃ P + HO ₂ →OP ₂	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
96	HC ₃ P + MO ₂ →0.58 ALD + 0.119 GLY + 0.81 HCHO + 0.018 KET + 0.005 MGLY + 0.007 MO ₂ + 0.992 OH + 0.085 XO ₂	ARRH(9.46e-14,-431.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

97	HC3P + NO → 0.233 ALD + 0.048 ETHP + 0.063 GLY + 0.047 HCHO + 0.742 HO2 + 0.623 KET + 0.15 MO2 + 0.941 NO2 + 0.059 ONIT + 0.048 XO2	4.0e-12	Stockwell et al. (1997)
98	HC3P + NO3 → 0.243 ALD + 0.053 ETHP + 0.063 GLY + 0.048 HCHO + 0.792 HO2 + 0.67 KET + 0.155 MO2 + NO2 + 0.051 XO2	1.2e-12	Stockwell et al. (1997)
99	HC5 + OH → H2O + 0.75 HC5P + 0.25 HO2 + 0.25 KET	ARRH(8.02e-12,155.0)	Stockwell et al. (1997)
100	HC5P + HO2 → OP2	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
101	HC5P + MO2 → 0.523 ALD + 0.014 ETHP + 0.829 HCHO + 0.946 HO2 + 0.24 KET + 0.049 MO2 + 0.245 XO2	ARRH(1.0e-13,-467.0)	Stockwell et al. (1997)
102	HC5P + NO → 0.211 ALD + 0.245 ETHP + 0.021 HCHO + 0.599 HO2 + 0.722 KET + 0.031 MO2 + 0.876 NO2 + 0.124 ONIT + 0.334 XO2	4.0e-12	Stockwell et al. (1997)
103	HC5P + NO3 → 0.239 ALD + 0.262 ETHP + 0.021 HCHO + 0.699 HO2 + 0.828 KET + 0.04 MO2 + NO2 + 0.391 XO2	1.2e-12	Stockwell et al. (1997)
104	HC8 + OH → 0.025 ALD + H2O + 0.951 HC8P + 0.024 HKET + 0.049 HO2	ARRH(1.64e-11,125.0)	Stockwell et al. (1997)
105	HC8P + HO2 → OP2	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
106	HC8P + MO2 → 0.411 ALD + 0.013 ETHP + 0.753 HCHO + 0.993 HO2 + 0.419 KET + 0.322 XO2	ARRH(4.34e-14,-633.0)	Stockwell et al. (1997)
107	HC8P + NO → 0.15 ALD + 0.133 ETHP + 0.606 HO2 + 0.642 KET + 0.739 NO2 + 0.261 ONIT + 0.416 XO2	4.0e-12	Stockwell et al. (1997)
108	HC8P + NO3 → 0.187 ALD + 0.155 ETHP + 0.845 HO2 + 0.88 KET + NO2 + 0.587 XO2	1.2e-12	Stockwell et al. (1997)
109	HCHO + hν → CO + 2 HO2	j _r (HCHO)	SR ^c
110	HCHO + hν → CO + H2	j _m (HCHO)	SR ^c
111	HCHO + NO3 → CO + HNO3 + HO2	ARRH(3.4e-13,1900.0)	Stockwell et al. (1997)
112	HCHO + OH → CO + H2O + HO2	1.0e-11	Stockwell et al. (1997)
113	HKET + hν → ACO3 + HCHO + HO2	PHTFKT(7.649e-06,0.682,-0.279)	MCMv3.1 ^b
114	HKET + OH → H2O + HO2 + MGly	3.0e-12	Stockwell et al. (1997)
115	HNO2 + hν → NO + OH	j(HONO)	SR ^c
116	HNO2 + OH → H2O + NO2	ARRH(1.8e-11,390.0)	Stockwell et al. (1997)
117	HNO3 + hν → NO2 + OH	PHTFKT(9.312e-07,1.230,-0.307)	MCMv3.1 ^b

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

118	$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$2.4\text{e-}14 \times \exp(460/T)$ $6.5\text{e-}34 \times \exp(1335/T) \times M / (1$ $+ (6.5\text{e-}34 \times \exp(1335/T) \times M) /$ $(2.7\text{e-}17 \times \exp(2199/T)))$ $3.17\text{e-}6 / 7.5\text{e-}3 \times j(\text{NO}_2)$	+ Sander et al. (2000)
119	$\text{HNO}_4 + \text{h}\nu \rightarrow 0.65\text{HO}_2 + 0.65\text{NO}_2 + 0.35\text{NO}_3 + 0.35\text{OH}$	ARRH(1.3e-12,-380.0)	Stockwell et al. (1997)
120	$\text{HNO}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	ETROE(2.1e-27,10900.0, 1.8e-31,3.2,4.7e-12,1.4)	Stockwell et al. (1997)
121	$\text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	ARRH(2.05e-13,-1360.0)	Stockwell et al. (1997)
122	$\text{HO}_2 + \text{ISOP} \rightarrow \text{ISHP}$	ARRH(1.15e-13,-1300.0)	Geiger et al. (2003)
123	$\text{HO}_2 + \text{KETP} \rightarrow \text{OP}_2$	1.5e-11	Stockwell et al. (1997)
124	$\text{HO}_2 + \text{LIMP} \rightarrow \text{OP}_2$	ARRH(1.82e-13,-1300.0)	Stockwell et al. (1997)
125	$\text{HO}_2 + \text{MACP} \rightarrow \text{MAHP}$	ARRH(3.8e-13,-800.0)	Geiger et al. (2003)
126	$\text{HO}_2 + \text{MO}_2 \rightarrow \text{OP}_1$	ARRH(3.7e-12,-250.0)	Stockwell et al. (1997)
127	$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	TROE(1.8e-31,3.2,4.7e-12,1.4)	Stockwell et al. (1997)
128	$\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_4$	3.5e-12	Stockwell et al. (1997)
129	$\text{HO}_2 + \text{NO}_3 \rightarrow 0.3\text{HNO}_3 + 0.7\text{NO}_2 + \text{O}_2 + 0.7\text{OH}$	ARRH(2.0e-14,680.0)	Sander et al. (2000)
130	$\text{HO}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH}$	ARRH(4.8e-11,-250.0)	Stockwell et al. (1997)
131	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
132	$\text{HO}_2 + \text{OLIP} \rightarrow \text{OP}_2$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
133	$\text{HO}_2 + \text{OLND} \rightarrow \text{ONIT}$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
134	$\text{HO}_2 + \text{OLNN} \rightarrow \text{ONIT}$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
135	$\text{HO}_2 + \text{OLTP} \rightarrow \text{OP}_2$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
136	$\text{HO}_2 + \text{PHO} \rightarrow \text{CSL}$	1.0e-11	Stockwell et al. (1997)
137	$\text{HO}_2 + \text{TCO}_3 \rightarrow \text{O}_3 + \text{ORA}_2$	ARRH(3.86e-16,-2640.0)	Stockwell et al. (1997)
138	$\text{HO}_2 + \text{TCO}_3 \rightarrow \text{OP}_2$	ARRH(1.15e-12,-550.0)	Stockwell et al. (1997)
139	$\text{HO}_2 + \text{TOLP} \rightarrow \text{OP}_2$	ARRH(3.75e-13,-980.0)	Stockwell et al. (1997)
140	$\text{HO}_2 + \text{XO}_2 \rightarrow \text{OP}_2$	ARRH(1.66e-13,-1300.0)	Stockwell et al. (1997)
141	$\text{HO}_2 + \text{XYLP} \rightarrow \text{OP}_2$	ARRH(3.75e-13,-980.0)	Stockwell et al. (1997)
142	$\text{h}\nu + \text{KET} \rightarrow \text{ACO}_3 + \text{ETHP}$	PHTFKT(5.804e-06,1.092, -0.377)	Stockwell et al. (1997) MCMv3.1 ^b

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

143	$h\nu + \text{MACR} \rightarrow \text{ACO3} + \text{CO} + \text{HCHO} + \text{HO2}$	PHTFKT(1.140e-05,0.396, -0.298)	Geiger et al. (2003)
144	$h\nu + \text{MGly} \rightarrow \text{ACO3} + \text{CO} + \text{HO2}$	PHTFKT(1.537e-04,0.170, -0.208)	MCMv3.1 ^b
145	$h\nu + \text{MVK} \rightarrow \text{ACO3} + \text{CO} + \text{HCHO} + \text{HO2}$	PHTFKT(1.140e-05,0.396, -0.298)	MCMv3.1 ^b
146	$h\nu + \text{NO2} \rightarrow \text{NO} + \text{O}$	j(NO ₂)	SR ^c
147	$h\nu + \text{NO3} \rightarrow \text{NO} + \text{O2}$	PHTFKT(2.485e-02,0.168, -0.108)	MCMv3.1 ^b
148	$h\nu + \text{NO3} \rightarrow \text{NO2} + \text{O}$	PHTFKT(1.747e-01,0.155, -0.125)	MCMv3.1 ^b
149	$h\nu + \text{O3} \rightarrow \text{O} + \text{O2}$	PHTFKT(4.775e-04,0.298, -0.080)	MCMv3.1 ^b
150	$h\nu + \text{O3} \rightarrow \text{O1D} + \text{O2}$	j(O ¹ D)	SR ^c
151	$h\nu + \text{ONIT} \rightarrow 0.2\text{ALD} + \text{HO2} + 0.8\text{KET} + \text{NO2}$	PHTFKT(2.485e-06,1.196, -0.328)	MCMv3.1 ^b
152	$h\nu + \text{OP1} \rightarrow \text{HCHO} + \text{HO2} + \text{OH}$	PHTFKT(7.649e-06,0.682, -0.279)	MCMv3.1 ^b
153	$h\nu + \text{OP2} \rightarrow \text{ALD} + \text{HO2} + \text{OH}$	PHTFKT(7.649e-06,0.682, -0.279)	MCMv3.1 ^b
154	$h\nu + \text{PAA} \rightarrow \text{MO2} + \text{OH}$	PHTFKT(7.649e-06,0.682, -0.279)	MCMv3.1 ^b
155	$\text{ISHP} + \text{OH} \rightarrow \text{CAR4} + \text{OH}$	1.00e-10	Karl et al. (2006)
156	$\text{ISO} + \text{NO3} \rightarrow \text{ISON}$	ARRH(3.03e-12,446.0)	Geiger et al. (2003)
157	$\text{ISO} + \text{O3} \rightarrow 0.1\text{ACO3} + 0.36\text{CO} + 0.09\text{H2O2} + 0.9\text{HCHO} + 0.25\text{HO2} + 0.1\text{MACP} + 0.39\text{MACR} + 0.08\text{MO2} + 0.26\text{MVK} + 0.25\text{OH} + 0.08\text{ORA1}$	ARRH(7.86e-15,1913.0)	Karl et al. (2006)
158	$\text{ISO} + \text{OH} \rightarrow \text{ISOP}$	ARRH(2.54e-11,-410.0)	Geiger et al. (2003)
159	$\text{ISON} + \text{OH} \rightarrow \text{HACE} + \text{NALD}$	1.30e-11	Geiger et al. (2003)
160	$\text{ISOP} + \text{NO} \rightarrow 0.34\text{CAR4} + 0.63\text{HCHO} + \text{HO2} + 0.22\text{MACR} + 0.34\text{MVK} + \text{NO2}$	ARRH(2.43e-12,-360.0)	Karl et al. (2006)
161	$\text{ISOP} + \text{NO} \rightarrow \text{ISON}$	ARRH(1.12e-13,-360.0)	Geiger et al. (2003)
162	$\text{KET} + \text{OH} \rightarrow \text{H2O} + \text{KETP}$	T2ARR(5.68e-18,-92.0)	Stockwell et al. (1997)
163	$\text{KETP} + \text{MO2} \rightarrow 0.12\text{ACO3} + 0.3\text{ALD} + 0.75\text{HCHO} + 0.3\text{HKET} + 0.88\text{HO2} + 0.4\text{MGly} + 0.08\text{XO2}$	ARRH(6.91e-13,-508.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

164	KETP + NO → 0.23 ACO3 + 0.46 ALD + 0.77 HO2 + 0.54 MGLY + NO2 + 0.16 XO2	4.0e-12	Stockwell et al. (1997)
165	KETP + NO3 → 0.23 ACO3 + 0.46 ALD + 0.77 HO2 + 0.54 MGLY + NO2 + 0.16 XO2	1.2e-12	Stockwell et al. (1997)
166	LIM + NO3 → 0.87 OLND + 0.13 OLNN	1.22e-11	Stockwell et al. (1997)
167	LIM + O3 → 0.14 CO + 0.16 ETHP + 0.02 H2O2 + 0.04 HCHO + 0.1 HO2 + 0.42 KETP + 0.79 MACR + 0.85 OH + 0.46 OLT + 0.01 ORA1 + 0.07 ORA2	2.0e-16	Stockwell et al. (1997)
168	LIM + OH → LIMP	1.7e-10	Stockwell et al. (1997)
169	LIMP + MO2 → 1.4 HCHO + 2 HO2 + 0.6 MACR + 0.4 OLI	ARRH(3.56e-14,-708.0)	Stockwell et al. (1997)
170	LIMP + NO → 0.25 HCHO + 0.65 HO2 + 0.4 MACR + 0.65 NO2 + 0.25 OLI + 0.35 ONIT	4.0e-12	Stockwell et al. (1997)
171	LIMP + NO3 → 0.4 HCHO + HO2 + 0.6 MACR + NO2 + 0.4 OLI	1.2e-12	Stockwell et al. (1997)
172	MACP + NO → 0.25 ACO3 + 0.25 CO + 0.25 HACE + 0.75 HCHO + 0.75 HO2 + 0.5 MGLY + NO2	ARRH(2.54e-12,-360.0)	Geiger et al. (2003)
173	MACP + NO2 → MPAN	TROE(9.70e-29,5.6, 9.30e-12,1.5)	Geiger et al. (2003)
174	MACR + O3 → 0.1 ACO3 + 0.22 CO + 0.32 HO2 + 0.9 MGLY + 0.19 OH + 0.45 ORA1	ARRH(1.36e-15,2112)	Geiger et al. (2003)
175	MACR + OH → MACP	ARRH(1.86e-11,-175)	Geiger et al. (2003)
176	MAHP + OH → MACP	3.00e-11	Geiger et al. (2003)
177	MGLY + NO3 → ACO3 + CO + HNO3	ARRH(1.4e-12,1900.0)	Stockwell et al. (1997)
178	MGLY + OH → ACO3 + CO + H2O	1.72e-11	Stockwell et al. (1997)
179	MO2 + NO → HCHO + HO2 + NO2	ARRH(4.2e-12,-180.0)	Stockwell et al. (1997)
180	MO2 + NO3 → HCHO + HO2 + NO2	1.2e-12	Stockwell et al. (1997)
181	MO2 + OLIP → 0.932 ALD + 0.755 HCHO + HO2 + 0.313 KET	ARRH(9.18e-14,-708.0)	Stockwell et al. (1997)
182	MO2 + OLND → 0.64 ALD + 0.96 HCHO + 0.5 HO2 + 0.149 KET + 0.5 NO2 + 0.5 ONIT	ARRH(9.68e-14,-708.0)	Stockwell et al. (1997)
183	MO2 + OLNN → 0.75 HCHO + HO2 + ONIT	ARRH(1.6e-13,-708.0)	Stockwell et al. (1997)
184	MO2 + OLTP → 0.669 ALD + 1.25 HCHO + HO2 + 0.081 KET	ARRH(1.46e-13,-708.0)	Stockwell et al. (1997)
185	MO2 + TCO3 → ACO3 + 2 HCHO + HO2	ARRH(3.21e-11,440.0)	Stockwell et al. (1997)
186	MO2 + TCO3 → HCHO + ORA2	ARRH(2.68e-16,-2510.0)	Stockwell et al. (1997)
187	MO2 + TOLP → DCB + 0.65 GLY + HCHO + HO2 + 0.35 MGLY	ARRH(3.56e-14,-708.0)	Stockwell et al. (1997)
188	MO2 + XO2 → HCHO + HO2	ARRH(5.99e-15,-1510.0)	Stockwell et al. (1997)
189	MO2 + XYLP → DCB + 0.37 GLY + HCHO + HO2 + 0.63 MGLY	ARRH(3.56e-14,-708.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

190	MPAN + OH → HACE + NO2	3.60e-12	Geiger et al. (2003)
191	MPAN → MACP + NO2	ETROE(8.60e-29,13954, 9.70e-29,5.6,9.30e-12,1.5)	Geiger et al. (2003)
192	MVK + O3 → 0.1 ACO3 + 0.22 CO + 0.32 HO2 + 0.9 MGLY + 0.19 OH + 0.45 ORA1	ARRH(7.51e-16,1521)	MCMv3.1 ^b
193	MVK + OH → MACP	ARRH(4.13e-12,-452)	MCMv3.1 ^b
194	N2 + O1D → N2 + O	ARRH(1.8e-11,-110.0)	Stockwell et al. (1997)
195	N2O5 → NO2 + NO3	ETROE(3.0e-27,10991.0, 2.0e-30,4.4,1.4e-12,0.7)	Sander et al. (2000)
196	NALD + OH → CO + HCHO + NO2	ARRH(5.60e-12,-270.0)	Geiger et al. (2003)
197	NO + NO3 → 2NO2	ARRH(1.5e-11,-170.0)	Stockwell et al. (1997)
198	NO + O → NO2	TROE(9.0e-32,1.5,3.0e-11,0.0)	Stockwell et al. (1997)
199	NO + O3 → NO2 + O2	ARRH(3.0e-12,1500.0)	Sander et al. (2000)
200	NO + OH → HNO2	TROE(7.0e-31,2.6,1.5e-11,0.5)	Stockwell et al. (1997)
201	NO + OLIP → 1.71 ALD + HO2 + 0.29 KET + NO2	4.0e-12	Stockwell et al. (1997)
202	NO + OLND → 1.24 ALD + 0.287 HCHO + 0.464 KET + 2 NO2	4.0e-12	Stockwell et al. (1997)
203	NO + OLNN → HO2 + NO2 + ONIT	4.0e-12	Stockwell et al. (1997)
204	NO + OLTP → 0.94 ALD + HCHO + HO2 + 0.06 KET + NO2	4.0e-12	Stockwell et al. (1997)
205	NO + TCO3 → ACO3 + HCHO + NO2	2.0e-11	Stockwell et al. (1997)
206	NO + TOLP → 0.5 DCB + 1.2 GLY + 0.95 HO2 + 0.65 MGLY + 0.95 NO2 + 0.05 ONIT	4.0e-12	Stockwell et al. (1997)
207	NO + XO2 → NO2	4.0e-12	Stockwell et al. (1997)
208	NO + XYLP → 0.95 DCB + 0.35 GLY + 0.95 HO2 + 0.6 MGLY + 0.95 NO2 + 0.05 ONIT	4.0e-12	Stockwell et al. (1997)
209	NO2 + NO3 → N2O5	TROE(2.0e-30,4.4,1.4e-12,0.7)	Sander et al. (2000)
210	NO2 + NO3 → NO + NO2 + O2	ARRH(4.5e-14,1260.0)	Stockwell et al. (1997)
211	NO2 + O → NO + O2	ARRH(5.6e-12,-180.0)	Sander et al. (2000)
212	NO2 + O → NO3	TROE(9.0e-32,2.0,2.2e-11,0.0)	Stockwell et al. (1997)
213	NO2 + O3 → NO3 + O2	ARRH(1.2e-13,2450.0)	Stockwell et al. (1997)
214	NO2 + OH → HNO3	TROE(2.4e-30,3.1,1.7e-11,2.1)	Sander et al. (2000)
215	NO2 + PHO → 0.1 CSL + ONIT	2.0e-11	Stockwell et al. (1997)
216	NO2 + TCO3 → TPAN	TROE(9.7e-29,5.6,9.3e-12,1.5)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

217	$\text{NO}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{NO}_2$	2.2e-11	Stockwell et al. (1997)
218	$\text{NO}_3 + \text{OLI} \rightarrow 0.89 \text{OLND} + 0.11 \text{OLNN}$	ARRH(8.64e-13,-450.0)	Stockwell et al. (1997)
219	$\text{NO}_3 + \text{OLIP} \rightarrow 1.71 \text{ALD} + \text{HO}_2 + 0.29 \text{KET} + \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
220	$\text{NO}_3 + \text{OLND} \rightarrow 1.24 \text{ALD} + 0.28 \text{HCHO} + 0.469 \text{KET} + 2 \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
221	$\text{NO}_3 + \text{OLNN} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{ONIT}$	1.2e-12	Stockwell et al. (1997)
222	$\text{NO}_3 + \text{OLT} \rightarrow 0.57 \text{OLND} + 0.43 \text{OLNN}$	ARRH(1.79e-13,450.0)	Stockwell et al. (1997)
223	$\text{NO}_3 + \text{OLT} \rightarrow 0.94 \text{ALD} + \text{HCHO} + \text{HO}_2 + 0.06 \text{KET} + \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
224	$\text{NO}_3 + \text{TCO}_3 \rightarrow \text{ACO}_3 + \text{HCHO} + \text{NO}_2$	4.0e-12	Stockwell et al. (1997)
225	$\text{NO}_3 + \text{TOLP} \rightarrow 0.5 \text{DCB} + 1.3 \text{GLY} + \text{HO}_2 + 0.7 \text{MGLY} + \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
226	$\text{NO}_3 + \text{TPAN} \rightarrow 0.4 \text{HCHO} + 0.4 \text{NO}_2 + 0.6 \text{NO}_3 + 0.6 \text{ONIT} + 0.4 \text{PAN} + \text{XO}_2$	ARRH(2.2e-14,500.0)	Stockwell et al. (1997)
227	$\text{NO}_3 + \text{XO}_2 \rightarrow \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
228	$\text{NO}_3 + \text{XYLP} \rightarrow \text{DCB} + 0.74 \text{GLY} + \text{HO}_2 + 1.26 \text{MGLY} + \text{NO}_2$	1.2e-12	Stockwell et al. (1997)
229	$\text{O} + \text{O}_2 \rightarrow \text{O}_3$	$6.0\text{e-}34 \times \text{M} \times (\text{T}/300)^{(-2.4)}$	Sander et al. (2000)
230	$\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$	ARRH(8.0e-12,2060.0)	Stockwell et al. (1997)
231	$\text{O}_1\text{D} + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	ARRH(3.2e-11,-70.0)	Stockwell et al. (1997)
232	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	ARRH(1.5e-12,880.0)	Sander et al. (2000)
233	$\text{O}_3 + \text{OLI} \rightarrow 0.99 \text{ALD} + 0.07 \text{CH}_4 + 0.3 \text{CO} + 0.06 \text{ETH} + 0.18 \text{ETHP} + 0.011 \text{H}_2\text{O}_2 + 0.02 \text{HCHO} + 0.22 \text{HO}_2 + 0.16 \text{KET} + 0.12 \text{KETP} + 0.23 \text{MO}_2 + 0.63 \text{OH} + 0.14 \text{ORA}_2$	ARRH(4.4e-15,845.0)	Stockwell et al. (1997)
234	$\text{O}_3 + \text{OLT} \rightarrow 0.44 \text{ALD} + 0.06 \text{CH}_4 + 0.37 \text{CO} + 0.03 \text{ETH} + 0.1 \text{ETHP} + 0.05 \text{H}_2 + 0.006 \text{H}_2\text{O}_2 + 0.64 \text{HCHO} + 0.25 \text{HO}_2 + 0.03 \text{KET} + 0.03 \text{KETP} + 0.19 \text{MO}_2 + 0.4 \text{OH} + 0.14 \text{ORA}_1 + 0.1 \text{ORA}_2$	ARRH(4.33e-15,1800.0)	Stockwell et al. (1997)
235	$\text{O}_3 + \text{TPAN} \rightarrow 0.7 \text{ACO}_3 + 0.13 \text{CO} + 0.04 \text{H}_2 + 0.7 \text{HCHO} + 0.08 \text{HO}_2 + 0.7 \text{NO}_2 + 0.036 \text{OH} + 0.11 \text{ORA}_1 + 0.3 \text{PAN}$	ARRH(2.46e-15,1700.0)	Stockwell et al. (1997)
236	$\text{OH} + \text{OLI} \rightarrow \text{OLIP}$	ARRH(1.33e-11,-500.0)	Stockwell et al. (1997)
237	$\text{OH} + \text{OLT} \rightarrow \text{OLTP}$	ARRH(5.72e-12,-500.0)	Stockwell et al. (1997)
238	$\text{OH} + \text{ONIT} \rightarrow \text{H}_2\text{O} + \text{HC}_3\text{P} + \text{NO}_2$	ARRH(5.31e-12,260.0)	Stockwell et al. (1997)
239	$\text{OH} + \text{OP}_1 \rightarrow 0.35 \text{HCHO} + 0.65 \text{MO}_2 + 0.35 \text{OH}$	ARRH(2.93e-12,-190.0)	Stockwell et al. (1997)
240	$\text{OH} + \text{OP}_2 \rightarrow 0.08 \text{ALD} + 0.44 \text{HC}_3\text{P} + 0.41 \text{KET} + 0.49 \text{OH} + 0.07 \text{XO}_2$	ARRH(3.4e-12,-190.0)	Stockwell et al. (1997)
241	$\text{OH} + \text{PAA} \rightarrow 0.65 \text{ACO}_3 + 0.35 \text{HCHO} + 0.35 \text{HO}_2 + 0.35 \text{XO}_2$	ARRH(2.93e-12,-190.0)	Stockwell et al. (1997)

Table S1: List of reactions in RACM-MIM-GK (M0)
(continued).

242	OH + PAN → H ₂ O + HCHO + NO ₃ + XO ₂	4.0e-14	Stockwell et al. (1997)
243	OH + SO ₂ → HO ₂ + SULF	TROE(3.0e-31,3.3,1.5e-12,0.0)	Stockwell et al. (1997)
244	OH + TOL → 0.9 ADDT + 0.1 HO ₂ + 0.1 XO ₂	ARRH(1.81e-12,-355.0)	Stockwell et al. (1997)
245	OH + TPAN → 0.4 HCHO + 0.6 HKET + 0.4 HO ₂ + 0.6 NO ₃ + 0.4 PAN + XO ₂	ARRH(3.25e-13,-500.0)	Stockwell et al. (1997)
246	OH + UDD → 0.88 ALD + HO ₂ + 0.12 KET	2.7e-10	Stockwell et al. (1997)
247	OH + XYL → 0.9 ADDX + 0.1 HO ₂ + 0.1 XO ₂	ARRH(7.3e-12,-355.0)	Stockwell et al. (1997)
248	OLND + OLNN → 0.64 ALD + 0.202 HCHO + 0.5 HO ₂ + 0.149 KET + 0.5 NO ₂ + 1.5 ONIT	ARRH(4.25e-14,-1000.0)	Stockwell et al. (1997)
249	PAN → ACO ₃ + NO ₂	ETROE(8.6e-29,13954.0, 9.7e-29,5.6,9.3e-12,1.5)	Stockwell et al. (1997)
250	TPAN → NO ₂ + TCO ₃	ETROE(8.6e-29,13954.0, 9.7e-29,5.6,9.3e-12,1.5)	Stockwell et al. (1997)

^a Function definitions (M : number density, T : absolute temperature in units of K)

ARRH : $k = \text{ARRH}(A, B) = A \times e^{-B/T}$;

T₂ARR : $k = \text{T2ARR}(C, D) = C \times T^2 \times e^{-D/T}$;

TROE : $k = \text{TROE}(k_0^{300}, n, k_\infty^{300}, m) = \left(\frac{k_0(T)[M]}{k_\infty(T)[M]} \right) \times 0.6^{\{1 + [\log_{10}(\frac{k_0(T)[M]}{k_\infty(T)})]^2\}^{-1}}$, $k_0(T) = k_0^{300} \times (\frac{T}{300})^{-n}$, $k_\infty(T) = k_\infty^{300} \times (\frac{T}{300})^{-m}$;

ETROE : $k = \text{ETROE}(A, B, k_0^{300}, n, k_\infty^{300}, m) = \{A \times e^{-B/T}\}^{-1} \times \left(\frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)[M]}} \right) \times 0.6^{\{1 + [\log_{10}(\frac{k_0(T)[M]}{k_\infty(T)})]^2\}^{-1}}$;

PHTFKT : $j = \text{PHTFKT}(I, m, n) = I \times (\cos\theta)^m \times e^{(n \times \sec\theta)}$ × f , $f = j(\text{NO}_2) / (I_{j(\text{NO}_2)} \times (\cos\theta)^{m_{j(\text{NO}_2)}} \times e^{(n_{j(\text{NO}_2)} \times \sec\theta)})$;

θ is the solar zenith angle and $j(\text{NO}_2)$ is the measured photolysis frequency of NO₂.

ARRH, T₂ARR, TROE and ETROE are adapted from Stockwell et al. (1997).

PHTFKT is adapted from MCMv3.1 (Jenkin et al., 2003; Saunders et al., 2003), but further scaled by measured $j(\text{NO}_2)$.

^b The photolysis frequency is calculated by the function PHTFKT (see above footnote).

^c The photolysis frequency is calculated from actinic flux spectra measured by a spectroradiometer (SR).

List of reactions used in the sensitivity model runs M1 – M6

Scenario M1 A mechanistic reactant X is included in M0 to account for additional reactivity which converts RO₂ to RO and HO₂ to OH. The rate constants are assumed to be the same as for the corresponding NO reactions (Table S2). The oxidation product XO is assumed to be an end product so that it does not have any further impact.

Table S2: Generic reactions added in scenario M1 to the base model M0.

#	reaction	rate constant	reference
251	HO ₂ + X → OH + XO	$3.7 \times 10^{-12} \times \exp((-1.) \times (-250.0)\text{K}/T)$	this study
252	ACO ₃ + X → MO ₂ + XO	2.0×10^{-11}	this study
253	APIP + X → 0.8ALD + 0.8HO ₂ + 0.8KET + 0.2ONIT + 0.8XO	4.0×10^{-12}	this study
254	CSLP + X → GLY + HO ₂ + MGLY + XO	4.0×10^{-12}	this study
255	E _{TEP} + X → 0.2ALD + 1.6HCHO + HO ₂ + XO	9.0×10^{-12}	this study
256	E _{THP} + X → ALD + HO ₂ + XO	8.7×10^{-12}	this study
257	HC _{3P} + X → 0.233ALD + 0.048ETHP + 0.063GLY + 0.047HCHO + 0.742HO ₂ + 0.623KET + 0.15MO ₂ + 0.059ONIT + 0.941XO + 0.048XO ₂	4.0×10^{-12}	this study
258	HC _{5P} + X → 0.211ALD + 0.245ETHP + 0.021HCHO + 0.599HO ₂ + 0.722KET + 0.031MO ₂ + 0.124ONIT + 0.876XO + 0.334XO ₂	4.0×10^{-12}	this study
259	HC _{8P} + X → 0.15ALD + 0.133ETHP + 0.606HO ₂ + 0.642KET + 0.261ONIT + 0.739XO + 0.416XO ₂	4.0×10^{-12}	this study
260	ISOP + X → 0.34CAR4 + HCHO + HO ₂ + 0.22MACR + 0.34MVK + XO	$2.43 \times 10^{-12} \times \exp((-1.) \times (-360.0)\text{K}/T)$	this study
261	KETP + X → 0.23ACO ₃ + 0.46ALD + 0.77HO ₂ + 0.54MGLY + XO + 0.16XO ₂	4.0×10^{-12}	this study
262	LIMP + X → 0.25HCHO + 0.65HO ₂ + 0.4MACR + 0.25OLLI + 0.35ONIT + 0.65XO	4.0×10^{-12}	this study
263	MACP + X → 0.25ACO ₃ + 0.25CO + 0.25HACE + 0.75HCHO + 0.75HO ₂ + 0.5MGLY + XO	$2.54 \times 10^{-12} \times \exp((-1.) \times (-360.0)\text{K}/T)$	this study
264	MO ₂ + X → HCHO + HO ₂ + XO	$4.2 \times 10^{-12} \times \exp((-1.) \times (-180.0)\text{K}/T)$	this study
265	OLIP + X → 1.71ALD + HO ₂ + 0.29KET + XO	4.0×10^{-12}	this study
266	OLND + X → 1.24ALD + 0.287HCHO + 0.464KET + 2XO	4.0×10^{-12}	this study
267	OLNN + X → HO ₂ + ONIT + XO	4.0×10^{-12}	this study
268	OLTP + X → 0.94ALD + HCHO + HO ₂ + 0.06KET + XO	4.0×10^{-12}	this study

Table S2: (continued).

269	$\text{TCO}_3 + \text{X} \rightarrow \text{ACO}_3 + \text{HCHO} + \text{XO}$	2.0×10^{-11}	this study
270	$\text{TOLP} + \text{X} \rightarrow 0.5 \text{DCB} + 1.2 \text{GLY} + 0.95 \text{HO}_2 + 0.65 \text{MGLY} + 0.05 \text{ONIT} + 0.95 \text{XO}$	4.0×10^{-12}	this study
271	$\text{X} + \text{XYLP} \rightarrow 0.95 \text{DCB} + 0.35 \text{GLY} + 0.95 \text{HO}_2 + 0.6 \text{MGLY} + 0.05 \text{ONIT} + 0.95 \text{XO}$	4.0×10^{-12}	this study

Scenario M2 A mechanistic reactant Y is included in M0 to account for additional reactivity which converts HO_2 to OH. The rate constants are assumed to be the same as for the corresponding NO reaction. For that purpose, only one reaction as simple as $\text{HO}_2 + \text{Y} \rightarrow \text{OH} + \text{YO}$ has been added to the base model M0. The oxidation product YO is assumed to be an end product so that it does not have any further impact.

Scenario M3 OH-forming channels in the reactions of acyl peroxy + HO_2 and β -keto peroxy + HO_2 are added to M0 (see Table S3). The corresponding peroxide forming reactions ($\text{ACO}_3 + \text{HO}_2 \rightarrow \text{PAA}$, $\text{KETP} + \text{HO}_2 \rightarrow \text{OP2}$, $\text{MACP} + \text{HO}_2 \rightarrow \text{MAHP}$, $\text{TCO}_3 + \text{HO}_2 \rightarrow \text{OP2}$) are removed.

Table S3: Reactions added in scenario M3 to the base model M0.

#	reaction	rate constant	reference ^a
19m	$\text{ACO}_3 + \text{HO}_2 \rightarrow 0.5 \text{OH} + \text{PAA}$	$1.15 \times 10^{-12} \times \exp((-1.) \times (-550.0) \text{K}/T)$	this study
123m	$\text{HO}_2 + \text{KETP} \rightarrow 0.15 \text{OH} + \text{OP2}$	$1.15 \times 10^{-13} \times \exp((-1.) \times (-1300.0) \text{K}/T)$	this study
125m	$\text{HO}_2 + \text{MACP} \rightarrow \text{MAHP} + 0.5 \text{OH}$	$1.82 \times 10^{-13} \times \exp((-1.) \times (-1300.0) \text{K}/T)$	this study
138m	$\text{HO}_2 + \text{TCO}_3 \rightarrow 0.5 \text{OH} + \text{OP2}$	$1.15 \times 10^{-12} \times \exp((-1.) \times (-550.0) \text{K}/T)$	this study

^a Based on recent laboratory studies (Dillon and Crowley, 2008; Jenkin et al., 2007) and the adoption of MIM2 by Taraborrelli et al. (2009).

Scenario M4 The isoprene epoxide chemistry proposed by Paulot et al. (2009) is included into mechanism M3 (Table S4). While Paulot et al. (2009) have only considered the reactions without NO, the chemistry with NO is adopted from Stavrou et al. (2010). In addition, reaction 155 in Table S1 is removed since it is replaced by reactions 272 and 273.

Table S4: Reactions added in scenario M4 to mechanism M3.

#	reaction	rate constant	reference
272	ISHP + OH \rightarrow IEPOX ^a + OH	$1.9 \times 10^{-11} \times \exp((-1.)) \times (-390)\text{K}/T$	Paulot et al. (2009)
273	ISHP + OH \rightarrow 0.3 CAR4 + 0.7 ISOP + 0.3 OH	$0.38 \times 10^{-11} \times \exp((-1.)) \times (-200)\text{K}/T$	Paulot et al. (2009)
274	IEPOX + OH \rightarrow IEPOXO2 ^b	$5.78 \times 10^{-11} \times \exp((-1.)) \times (400)\text{K}/T$	Paulot et al. (2009)
275	IEPOXO2 + NO \rightarrow IEPOXO ^c + NO ₂	$2.54 \times 10^{-12} \times \exp((-1.)) \times (-360.0)\text{K}/T$	Stavrou et al. (2010)
276	HO ₂ + IEPOXO2 \rightarrow IEPOXO + OH + O ₂	$0.074 \times 10^{-11} \times \exp((-1.)) \times (-700)\text{K}/T$	Paulot et al. (2009)
277	IEPOXO \rightarrow 0.275 ALD + 0.251 CO + 0.275 GLY + 0.375 HCHO + 0.725 HKET + 0.825 HO ₂ + 0.275 MGLY + 0.125 OH + 0.074 ORA1	$1e6 [s^{-1}]^d$	

^a IEPOX: isoprene epoxide.

^b IEPOXO2: peroxy radical of isoprene epoxide.

^c IEPOXO : alkoxy radical of isoprene epoxide.

^d Assuming IEPOXO would follow prompt unimolecular decomposition (KDEC reaction rate from MCMv3.1) since it is a kind of β -hydroxyalkoxy radical.

Scenario M5 The LIM0 mechanism is additionally included into mechanism M4 (Table S5). The notation for LIM0 has been adapted from Taraborrelli et al. (2009). The isoprene peroxy radicals ISOPBO2 and ISOPDO2 are lumped as ISOP, and the reaction rate constants of the four unimolecular reaction channels of isoprene peroxy radicals in LIM0 are scaled according to the yields of ISOPBO2 and ISOPDO2 from isoprene oxidation. Regarding the photolysis frequency of HPALDs, Peeters and Mueller (2010) assumed the absorption cross section of HPALDs to be the same as that of MACR (O=C-C(C)=C), but to have a quantum yield of unity. Since the quantum yield of MACR photolysis is about 0.01 (Gierczak et al., 1997), we upscaled the MACR photolysis frequency by a factor of 100 to provide an estimate of the HPALDs photolysis frequency.

Table S5: Reactions added in scenario M5 to mechanism M4.

#	reaction	rate constant	reference
278	ISOP \rightarrow HCHO + MACR + OH	$0.30 \times 2.08 \times 10^{11} \times \exp((-1.) \times (8993) \text{K}/T)$	Peeters and Mueller (2010)
279	ISOP \rightarrow HCHO + MVK + OH	$0.60 \times 2.08 \times 10^{11} \times \exp((-1.) \times (8993) \text{K}/T)$	Peeters and Mueller (2010)
280	ISOP \rightarrow HO ₂ + HPALD1 ^a	$0.60 \times 4.06 \times 10^9 \times \exp((-1.) \times (7302) \text{K}/T)$	Peeters and Mueller (2010)
281	ISOP \rightarrow HO ₂ + HPALD2 ^b	$0.30 \times 8.5 \times 10^9 \times \exp((-1.) \times (7432) \text{K}/T)$	Peeters and Mueller (2010)
282	HPALD1 + $h\nu \rightarrow$ 0.5 GLYALD ^c + HCHO + HO ₂ + 0.5 HYAC ^d + 0.5 MGLY + $m^e \times$ OH	PHTFKT(1.14e-03, 0.396, -0.298)	Peeters and Mueller (2010)
283	HPALD1 + OH \rightarrow OH	4.6×10^{-11}	Peeters and Mueller (2010)
284	HPALD2 + $h\nu \rightarrow$ 0.5 GLYALD + HCHO + HO ₂ + 0.5 HYAC + 0.5 GLY + $m \times$ OH	PHTFKT(1.14e-03, 0.396, -0.298)	Peeters and Mueller (2010)
285	HPALD2 + OH \rightarrow OH	4.6×10^{-11}	Peeters and Mueller (2010)
286	GLYALD + OH \rightarrow 0.5 CO + 0.34 CO ₂ + 0.17 GLY + 0.67 HCHO + 0.75 HO ₂ + 0.25 OH + 0.17 ORA1	4.8×10^{-12}	Peeters and Mueller (2010)
287	HYAC + OH \rightarrow 0.05 CO + 0.2 CO ₂ + 0.825 HO ₂ + 0.75 MGLY + 0.125 MO2 + 0.1 OH + 0.125 ORA1 + 0.125 ORA2	3.0×10^{-12}	Peeters and Mueller (2010)

^a HPALD1: 4-hydroperoxy-2-methyl-but-2-enals.

^b HPALD2: 4-hydroperoxy-3-methyl-but-2-enals.

^c GLYALD: glycolaldehyde.

^d HYAC: hydroxyacetone.

^e m could vary between 1 and 3 due to the calculation of Peeters and Mueller (2010).

^f A definition of PHTFKT is given in Table S1.

Scenario M6 An OH-forming reaction between isoprene hydroperoxy radicals and HO₂ as postulated by Lelieveld et al. (2008) has been additionally included into mechanism M3. The reaction is listed in Table S6 and replaces the original reaction 122 in RACM-MIM-GK (M0).

Table S6: Reaction added in scenario M6 to mechanism M3.

#	reaction	rate constant	reference
122m	$\text{HO}_2 + \text{ISOP} \rightarrow \text{ISHP} + n^a \times \text{OH}$	$2.5 \times 10^{-13} \exp((-1.) \times (-1360)\text{K}/T)$	Lelieveld et al. (2008)

^a $n = 2$ or 4

Comparison to the model results shown by Hofzumahaus et al. (2009)

The comparison of the model results between the model calculations constrained by averaged diurnal profiles (expression (E1)) shown by Hofzumahaus et al. (2009) and averaged diurnal profiles of the model calculations constrained by time resolved data (expression (E2)) is shown in Fig. S1. Both kinds of model calculations for the PRIDE-PRD2006 data set are not significantly different since photochemical conditions were highly reproducible from day to day during the PRIDE-PRD2006 campaign for those days when HOx observations were available.

$$\overline{\text{OH}} = \text{model}(\overline{j}, \overline{\text{NOx}}, \overline{\text{VOC}}, \overline{\text{etc}}) \quad (\text{E1})$$

$$\overline{\text{OH}} = \overline{\text{model}(j, \text{NOx}, \text{VOC}, \text{etc})} \quad (\text{E2})$$

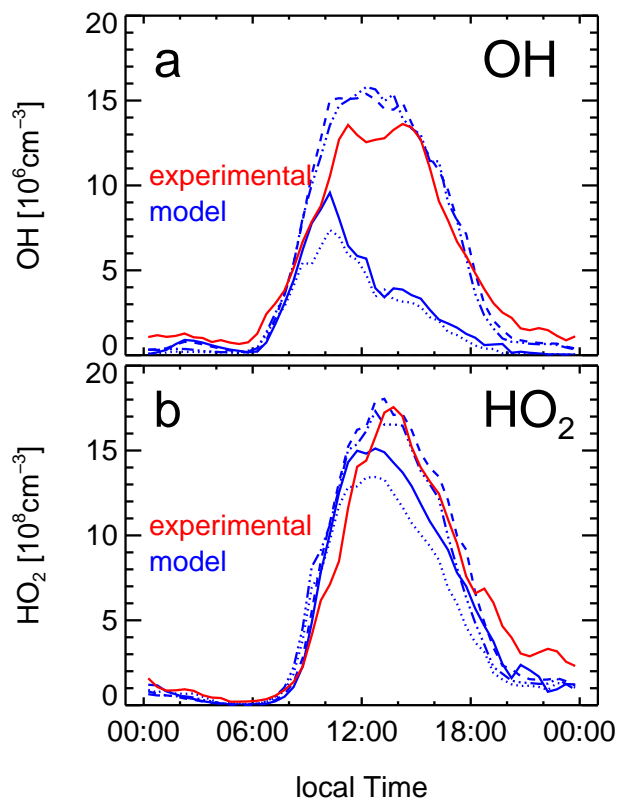


Figure S1: Comparison of measured and modelled mean diurnal profiles of (a) OH and (b) HO₂. Red lines represent experimental data. Blue solid lines represent the results from the M0 case, blue dashed lines those from the M1 case both constrained with averaged diurnal profiles. Blue dotted lines represent the results from the M0 case, blue dashed-dotted lines those from the M1 case both averaged using the full time resolved data. The figure uses that subset of field campaign data, for which all required measurements are simultaneously available for full diurnal cycles.

RO₂ analysis for M0 and M0 + OHobs model runs

The NO_x dependence of the RO₂ speciation in the M0 model run and in an additional M0 model run constrained by observed OH concentrations is shown in Fig. S2a and S2b, respectively. The eight most abundant RO₂ radicals in both model runs are listed explicitly. The list of the most abundant RO₂ radicals does not change significantly when the OH concentrations in the model is changed by a factor of 3-5. The detailed speciation of RO₂ in both model runs for the high and low NO_x regime (the split appears at 4 ppb as discussed in the main text) is given in Table S7.

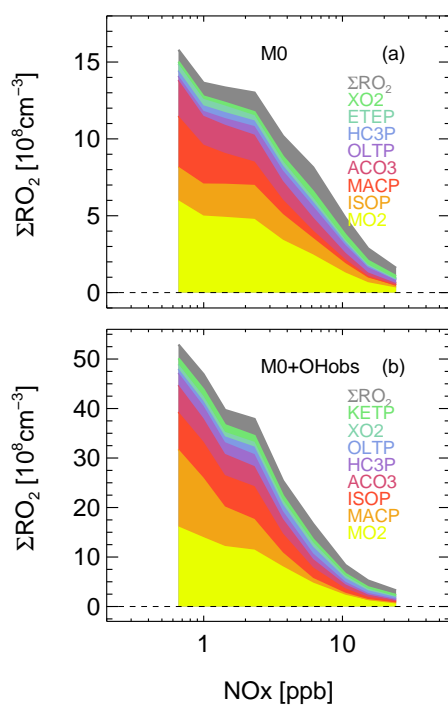


Figure S2: NO_x dependence of the RO₂ speciation during daytime calculated in the M0 model and the additional M0 model run constrained by observed OH concentrations.

Table S7: RO₂ speciation in the M0 model scenario and in the additional M0 model scenario constrained by observed OH concentrations.

RO ₂	M0		RO ₂	M0 + OHobs	
	NO _x <4ppb	NO _x > 4ppb		NO _x <4ppb	NO _x > 4ppb
MO2	0.36	0.28	MO2	0.31	0.31
ISOP	0.16	0.12	MACP	0.20	0.05
MACP	0.16	0.06	ISOP	0.15	0.10
ACO3	0.13	0.09	ACO3	0.11	0.11
OLTP	0.04	0.10	HC3P	0.06	0.06
ETEP	0.03	0.03	KETP	0.03	0.03
HC3P	0.03	0.04	ETEP	0.03	0.03
ETHP	0.02	0.01	OLTP	0.03	0.08
KETP	0.02	0.02	XO2	0.02	0.06
XO2	0.01	0.06	TOLP	0.01	0.04
TOLP	0.01	0.05	ETHP	0.01	0.01
XYLP	0.01	0.04	XYLP	0.01	0.04
OLIP	0.01	0.02	OLIP	0.01	0.02
HC8P	0.01	0.04	HC8P	0.01	0.03
HC5P	0.01	0.02	HC5P	0.00	0.02
TCO3	0.00	0.01	TCO3	0.00	0.01
OLND	0.00	0.00	CSLP	0.00	0.00
CSLP	0.00	0.00	OLND	0.00	0.00
OLNN	0.00	0.00	OLNN	0.00	0.00
LIMP	0.00	0.00	LIMP	0.00	0.00
APIP	0.00	0.00	APIP	0.00	0.00

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