

**Supplementary Online Material**

**Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): Implications for NO<sub>x</sub> release from the Arctic and coastal Antarctic snowpack**

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**This PDF file includes:**

**Supporting online text**

**Table 1**

**References**

### **Radiation and gas phase scheme**

Photolysis rates are calculated off-line from reported absorption cross-sections and quantum yields using a 2-stream radiative transfer code,<sup>1</sup> where the irradiance reaching the surface is computed after photon attenuation through fifty 1 km layers in the atmosphere.

Some species in the model are constrained to their typical values measured during the Chemistry of the Antarctic Boundary Layer and Interface with Snow (CHABLIS) measurement field campaign that took place at Halley Bay in coastal Antarctica<sup>2,3</sup> with diurnal mixing ratio profiles peaking at [CO] = 35 ppb; [DMS] = 80 ppt; [SO<sub>2</sub>] = 15 ppt; [CH<sub>4</sub>] = 1750 ppb; [CH<sub>3</sub>CHO] = 150 ppt; [HCHO] = 150 ppt; [isoprene] = 60 ppt; [propane] = 25 ppt; [propene] = 15 ppt. During the model simulations all other species are allowed to vary. The model is solved using a variable step-size fourth-order Runge-Kutta integrator.

The dry deposition of a species *i* is computed as  $V_i C_i(t)/H$ , where  $C$  is the concentration of a gaseous species at a given time and  $V_i$  is the deposition velocity of species over a fixed boundary layer over time with a depth  $H$  of 100 m.

**Table 1. Gas Phase Reactions and Rate Constants**

#	Bimolecular Reactions	Rate Constants	References
1.	$O(^1D) + N_2 \rightarrow O + N_2$	$1.8 \times 10^{-11} e^{(110/T)}$	5
2.	$O(^1D) + O_2 \rightarrow O + O_2$	$3.2 \times 10^{-11} e^{(70/T)}$	5
3.	$O(^1D) + H_2O \rightarrow OH + OH$	$2.2 \times 10^{-10}$	5
4.	$O(^1D) + CH_4 \rightarrow CH_3 + OH$ (0.75), $CH_3O + H$ (0.2), $HCHO + H_2$ (0.05)	$1.5 \times 10^{-10}$	5
5.	$O(^1D) + H_2 \rightarrow OH + H$	$1.1 \times 10^{-10}$	5
6.	$OH + CO \rightarrow H + CO_2$	$1.5 \times 10^{-13} \times (1 + 0.6 \times P_{atm})$	5
7.	$HO_2 + NO \rightarrow NO_2 + OH$	$3.5 \times 10^{-12} e^{(250/T)}$	5
8.	$O_3 + HO_2 \rightarrow OH + 2O_2$	$1.1 \times 10^{-14} e^{(-500/T)}$	5
9.	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} e^{(600/T)}$	5
10.	$OH + H_2 \rightarrow H_2O + H$	$5.5 \times 10^{-12} e^{(-2000/T)}$	5
11.	$O_3 + OH \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} e^{(-940/T)}$	5
12.	$OH + HNO_3 \rightarrow H_2O + NO_3$	$k_0 = 7.2 \times 10^{-15} e^{(785/T)}$ $k_2 = 4.1 \times 10^{-16} e^{(1440/T)}$ $k_3 = 1.9 \times 10^{-33} e^{(725/T)}$ $k = k_0 + (k_3 \times [M]) / (1 + k_3 \times [M] / k_2)$	5
13.	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$2.9 \times 10^{-12} e^{(-160/T)}$	5
14.	$OH + HO_2NO_2 \rightarrow NO_2 + HO_2 + OH$	$1.3 \times 10^{-12} e^{(380/T)}$	5
15.	$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} e^{(250/T)}$	5
16.	$OH + HONO \rightarrow H_2O + NO_2$	$1.8 \times 10^{-11} e^{(390/T)}$	5
17.	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$2 \times 10^{-14}$	5,b
18.	$OH + CH_4 \rightarrow CH_3 + H_2O$	$2.45 \times 10^{-12} e^{(-1775/T)}$	5
19.	$O(^3P) + CH_3 \rightarrow CH_3O$	$1.1 \times 10^{-10}$	5
20.	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	$3.8 \times 10^{-13} e^{(800/T)}$	5
21.	$CH_3OOH + OH \rightarrow CH_3(O)O + H_2O$	$0.7 \times 3.8 \times 10^{-12} e^{(200/T)}$	5
22.	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$3.9 \times 10^{-14} e^{(-900/T)}$	5
23.	$OH + HCHO \rightarrow H_2O + HCO$	$8.8 \times 10^{-12} e^{(25/T)}$	5
24.	$HCO + O_2 \rightarrow CO + HO_2$	$3.5 \times 10^{-12} e^{(140/T)}$	5
25.	$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$ 29%	$0.29 \times 2.5 \times 10^{-13} e^{(190/T)}$	5
26.	$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$	$3 \times 10^{-12} e^{(280/T)}$	5
27.	$NO + O_3 \rightarrow NO_2 + O_2$	$2 \times 10^{-12} e^{(-1400/T)}$	5
28.	$NO + NO_3 \rightarrow 2NO_2$	$1.5 \times 10^{-11} e^{(170/T)}$	5
29.	$NO_3 + HCHO \rightarrow$ Products	$5.8 \times 10^{-16}$	5,b
30.	$HO_2 + SO_2 \rightarrow$ Products	$1 \times 10^{-18}$	5,b
31.	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$2.5 \times 10^{-22}$	5,b
32.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{(-2450/T)}$	5
33.	$OH + O(^3P) \rightarrow H + O_2$	$2.2 \times 10^{-11} e^{(120/T)}$	5
34.	$O(^3P) + HO_2 \rightarrow OH + O_2$	$3 \times 10^{-11} e^{(200/T)}$	5
35.	$H_2O_2 + O(^3P) \rightarrow OH + HO_2$	$1.4 \times 10^{-12} e^{(-2000/T)}$	5
36.	$OH + OH \rightarrow H_2O + O(^3P)$	$4.2 \times 10^{-12} e^{(-240/T)}$	5
37.	$O_3 +$ Alkenes $\rightarrow$ Products	$1.2 \times 10^{-14} e^{(-2630/T)}$	5,b

38.	$\text{NO}_3 + \text{CO} \rightarrow \text{Products}$	$4 \times 10^{-19}$	5,b
39.	$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{OOH} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{OH} + \text{H}_2\text{O}$	$0.3 \times 3.8 \times 10^{-12} e^{(200/T)}$	5
40.	$\text{O}({}^3\text{P}) + \text{HCHO} \rightarrow \text{OH} + \text{HCO}$	$3.4 \times 10^{-11} e^{(-1600/T)}$	5
41.	$\text{HCHO} + \text{HO}_2 \rightarrow \text{HO}_2\text{CH}_2\text{O}$	$6.7 \times 10^{-15} e^{(600/T)}$	5
42.	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$1.4 \times 10^{-10} e^{(-470/T)}$	5
43.	$\text{HO}_2 + \text{H} \rightarrow 2\text{OH}$	$0.9 \times 8.1 \times 10^{-11}$	5
44.	$\text{O}({}^3\text{P}) + \text{HO}_2\text{NO}_2 \rightarrow \text{Products}$	$7.8 \times 10^{-11} e^{(-3400/T)}$	5
45.	$\text{O}({}^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2$	$1.2 \times 10^{-10}$	5
46.	$\text{O}({}^1\text{D}) + \text{O}_3 \rightarrow \text{O}_2 + 2\text{O}$	$1.2 \times 10^{-10}$	5
47.	$\text{CH}_3\text{O}_2 + \text{SO}_2 \rightarrow \text{Products}$	$5 \times 10^{-17}$	4,b
48.	$\text{NO}_3 + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2$	$3.5 \times 10^{-12}$	5
49.	$\text{CH}_3 + \text{O}_3 \rightarrow \text{Products}$	$5.4 \times 10^{-12} e^{(-220/T)}$	5
50.	$\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$	$3 \times 10^{-12} e^{(-7000/T)}$	5,b
51.	$\text{NO}_3 + \text{OH} \rightarrow \text{NO}_2 + \text{HO}_2$	$2.2 \times 10^{-11}$	5
52.	$\text{O}_3 + \text{O}({}^3\text{P}) \rightarrow 2\text{O}_2$	$8 \times 10^{-12} e^{(-2060/T)}$	5
53.	$\text{O}_3 + \text{HONO} \rightarrow \text{O}_2 + \text{HNO}_3$	$5 \times 10^{-19}$	5,b
54.	$\text{CH}_3\text{O}_2 + \text{O}_3 \rightarrow \text{Products}$	$3 \times 10^{-17}$	5,b
55.	$\text{NO}_3 + \text{Alkenes} \rightarrow \text{HOCH}_2\text{CH}_2 + \text{NO}_2$	$3 \times 10^{-14}$	4
56.	$\text{SO}_2 + \text{NO}_2 \rightarrow \text{Products}$	$2 \times 10^{-26}$	4,b
57.	$\text{NO}_3 + \text{Alkanes} \rightarrow \text{C}_2\text{H}_5 + \text{HNO}_3$	$3.6 \times 10^{-17}$	4
58.	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	$0.71 \times 2.5 \times 10^{-13} e^{(190/T)}$	5
59.	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	$4.5 \times 10^{-14} e^{(-1260/T)}$	5
60.	$\text{OH} + \text{Alkanes} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	$1.1 \times 10^{-11} e^{(-1100/T)}$	4
61.	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{C}_2\text{H}_5\text{O}$	$2.6 \times 10^{-12} e^{(365/T)}$	5
62.	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CH}_3\text{CO} (\rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2)$	$1.4 \times 10^{-12} e^{(-1900/T)}$	5
63.	$\text{CH}_3\text{CHO} + \text{O}({}^3\text{P}) \rightarrow \text{OH} + \text{CH}_3\text{CO} (\rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2)$	$1.8 \times 10^{-11} e^{(-1100/T)}$	5
64.	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO} (\rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2)$	$5.6 \times 10^{-12} e^{(270/T)}$	5
65.	$\text{O}({}^3\text{P}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$4.11 \times 10^{-18}$	4
66.	$\text{NO} + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3 + \text{CO}_2$	$5.3 \times 10^{-12} e^{(360/T)}$	5
67.	$\text{OH} + \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{C}_2\text{H}_4\text{OOH} + \text{H}_2\text{O}$	$3.64 \times 10^{-12}$	4
68.	$\text{OH} + \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{H}_2\text{O}$	$5.95 \times 10^{-12}$	4
69.	$\text{NO}_2 + \text{O}({}^3\text{P}) \rightarrow \text{NO} + \text{O}_2$	$6.5 \times 10^{-12} e^{(120/T)}$	5
70.	$\text{NO}_3 + \text{O}({}^3\text{P}) \rightarrow \text{NO}_2 + \text{O}_2$	$1 \times 10^{-11}$	5
71.	$\text{HNO}_3 + \text{O}({}^3\text{P}) \rightarrow \text{NO}_3 + \text{OH}$	$3 \times 10^{-17}$	5,b
71.	$\text{C}_2\text{H}_5\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$6.3 \times 10^{-14} e^{(-550/T)}$	5
73.	$\text{HO}_2\text{CH}_2\text{O} \rightarrow \text{HO}_2 + \text{CH}_2\text{O}$	$2.4 \times 10^{12} e^{(-7000/T)}$	4
74.	$\text{HO}_2\text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{HCOOH} + \text{O}_2 + \text{H}_2\text{O}$	$5.6 \times 10^{-15} e^{(2300/T)}$	4
<b>Halogen chemistry</b>			
75.	$\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$	$2 \times 10^{-11} e^{(-890/T)}$	5
76.	$\text{I} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_2$	$1.5 \times 10^{-11} e^{(-1190/T)}$	5
77.	$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$	$7.3 \times 10^{-12} e^{(330/T)}$	5
78.	$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	$5.8 \times 10^{-11}$	5
79.	$\text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I} / \text{I}_2\text{O}_2$	$8.6 \times 10^{-11}$	5
80.	$\text{IO} + \text{OIO} (+\text{M}) \rightarrow \text{I}_2\text{O}_3$	$1.5 \times 10^{-11}$	5
81.	$\text{IONO}_2 \rightarrow \text{IO} + \text{NO}_2$	$2.07 \times 10^{15} e^{(-11859/T)}$	5

82.	$\text{OH} + \text{HI} \rightarrow \text{I} + \text{H}_2\text{O}$	$3 \times 10^{-11}$	5
83.	$\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O}$	$2 \times 10^{-13}$	5
84.	$\text{IO} + \text{DMS} \rightarrow \text{Products}$	$1.2 \times 10^{-14}$	5
85.	$\text{INO}_2 \rightarrow \text{I} + \text{NO}_2$	$(2.4 / 0.005) \times 2.07 \times 10^{15} e^{(-11859/T)}$	5
86.	$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.7 \times 10^{-11} e^{(-800/T)}$	5
87.	$\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$	$1.1 \times 10^{-11}$	5
88.	$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	$1.5 \times 10^{-11} e^{(-600/T)}$	5
89.	$\text{Br} + \text{HCHO} \rightarrow \text{HBr} + \text{HCO}$	$7.7 \times 10^{-13} e^{(-580/T)}$	5
90.	$\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{HBr} + \text{CH}_3\text{CO}$	$1.8 \times 10^{-12} e^{(-460/T)}$	5
91.	$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	$3.4 \times 10^{-12} e^{(540/T)}$	5
92.	$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	$8.8 \times 10^{-12} e^{(260/T)}$	5
93.	$\text{BrO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SOCH}_3 + \text{Br}$	$1.5 \times 10^{-14} e^{(850/T)}$	5
94.	$\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2$	$2.4 \times 10^{-12} e^{(40/T)}$	5
95.	$\text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2$	$2.8 \times 10^{-14} e^{(860/T)}$	5
96.	$\text{BrONO}_2 \rightarrow \text{BrO} + \text{NO}_2$	$2.8 \times 10^{13} e^{-(12360/T)}$	7
97.	$\text{BrO} + \text{IO} \rightarrow \text{Br} + \text{I} + \text{O}_2 / \text{Br} + \text{OIO}$	$1.5 \times 10^{-12} e^{(510/T)}$	5
98.	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$1.1 \times 10^{-11} e^{(-1400/T)}$	5
99.	$\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.6 \times 10^{-12} e^{(-350/T)}$	5
100.	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.9 \times 10^{-11} e^{(-260/T)}$	5
101.	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$5.0 \times 10^{-12} e^{(700/T)}$	5
102.	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$6.4 \times 10^{-12} e^{(290/T)}$	5
103.	$\text{ClO} + \text{IO} \rightarrow 0.2 (\text{I} + \text{Cl} + \text{O}_2)$	$1.3 \times 10^{-12} e^{(280/T)}$	5
104.	$\text{Cl} + \text{Alkanes} \rightarrow \text{HCl} + \text{CH}_3\text{OO}$	$5.7 \times 10^{-11} e^{(-90/T)}$	5,4
105.	$\text{Cl} + \text{Alkenes} \rightarrow \text{HCl} + \text{CH}_3\text{OO}$	$1.0 \times 10^{-10}$	5,4
106.	$\text{Cl} + \text{HCHO} \rightarrow \text{HCl} + \text{HO}_2 + \text{CO}$	$7.3 \times 10^{-11} e^{(-30/T)}$	5
107.	$\text{ClO} + \text{CH}_3\text{OO} \rightarrow \text{Cl} + \text{HCHO} + \text{HO}_2$	$2.2 \times 10^{-12} e^{(-115/T)}$	5
108.	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$	$3.5 \times 10^{-13}$	5
109.	$\text{Cl}_2\text{O}_2 \rightarrow \text{ClO} + \text{ClO}$	50	5
110.	$\text{ClONO}_2 \rightarrow \text{ClO} + \text{NO}_2$	0.0022	5
111.	$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	$9.6 \times 10^{-12} e^{(140/T)}$	5
112.	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$4.1 \times 10^{-13} e^{(-980/T)}$	5
113.	$\text{Br}_2 + \text{Cl} \rightarrow \text{BrCl} + \text{Br}$	$1.2 \times 10^{-10} e^{(-260/T)}$	5,4
114.	$\text{BrCl} + \text{Br} \rightarrow \text{Br}_2 + \text{Cl}$	$3.3 \times 10^{-15}$	5,4
115.	$\text{Cl}_2 + \text{Br} \rightarrow \text{BrCl} + \text{Cl}$	$1.1 \times 10^{-15}$	5,4
116.	$\text{BrCl} + \text{Cl} \rightarrow \text{Cl}_2 + \text{Br}$	$1.5 \times 10^{-11}$	5,4
117.	$\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{OCIO}$	$6.0 \times 10^{-12} e^{(550/T)}$	5,4
118.	$\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$	$5.6 \times 10^{-12} e^{(260/T)}$	5,4
119.	$\text{ClO} + \text{BrO} \rightarrow \text{BrCl} + \text{O}_2$	$1.1 \times 10^{-12} e^{(290/T)}$	5,4

#### Recombination Reactions

1.	$\text{O}(^1\text{D}) + \text{N}_2 (+\text{M}) \rightarrow \text{N}_2\text{O} (+\text{M})$	$[\text{M}] \times 3.5 \times 10^{-37} \times (\text{T} / 300)^{-0.6}$	5
2.	$\text{HO}_2 + \text{HO}_2 (+\text{M}) \rightarrow \text{H}_2\text{O}_2 (+\text{M})$	$[\text{M}] \times 1.7 \times 10^{-33} e^{(1000/T)}$	5
3.	$\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$	$k_0 = 5.7 \times 10^{-32} \times (\text{T} / 300)^{-1.6}$ $k_\infty = 7.5 \times 10^{-11}$	5
4.	$\text{O}_2 + \text{O}(^3\text{P}) \rightarrow \text{O}_3$	$[\text{M}] \times 6 \times 10^{-34} \times (\text{T} / 300)^{-2.3}$	5
5.	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$k_0 = 2.5 \times 10^{-30} \times (\text{T} / 300)^{-4.4}$	5

6.	$\text{NO} + \text{OH} (+ \text{M}) \rightarrow \text{HONO} (+ \text{M})$	$k_{\infty} = 1.6 \times 10^{-11} \times (\text{T} / 300)^{-1.7}$ $k_0 = 7 \times 10^{-31} \times (\text{T} / 300)^{-2.6}$	5
7.	$\text{HO}_2 + \text{NO}_2 (+ \text{M}) \rightarrow \text{HO}_2\text{NO}_2 (+ \text{M})$	$k_{\infty} = 1.5 \times 10^{-11} \times (\text{T} / 300)^{-0.5}$ $k_0 = 1.8 \times 10^{-31} \times (\text{T} / 300)^{-3.2}$ $k_{\infty} = 4.7 \times 10^{-12} \times (\text{T} / 300)^{-1.4}$	5
8.	$\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	$k_{\text{R}} = k_{\text{F}} / k_{\text{EQ}}$ $k_{\text{R}} = k_{\text{F}} / (2.1 \times 10^{-27} e^{(10900/\text{T})})$	5
9.	$\text{O}_2 + \text{CH}_3 (+ \text{M}) \rightarrow \text{CH}_3\text{O}_2 (+ \text{M})$	$k_0 = 4.5 \times 10^{-31} \times (\text{T} / 300)^{-3}$ $k_{\infty} = 1.8 \times 10^{-12} \times (\text{T} / 300)^{-1.7}$	5
10.	$\text{NO}_2 + \text{NO}_3 (+ \text{M}) \rightarrow \text{N}_2\text{O}_5 (+ \text{M})$	$k_0 = 2.2 \times 10^{-30} \times (\text{T} / 300)^{-3.9}$ $k_{\infty} = 1.5 \times 10^{-12} \times (\text{T} / 300)^{-0.7}$	5
11.	$\text{N}_2\text{O}_5 (+ \text{N}_2) \rightarrow \text{NO}_2 + \text{NO}_3 (+ \text{N}_2)$	$k_{\text{R}} = k_{\text{F}} / k_{\text{EQ}}$ $k_{\text{R}} = k_{\text{F}} / (2.7 \times 10^{-27} e^{(11000/\text{T})})$	5
12.	$\text{OH} + \text{OH} (+ \text{M}) \rightarrow \text{H}_2\text{O}_2 (+ \text{M})$	$k_0 = 6.2 \times 10^{-31} \times (\text{T} / 300)^{-1}$ $k_{\infty} = 2.6 \times 10^{-11}$	5
13.	$\text{NO} + \text{O}(\text{}^3\text{P}) (+ \text{M}) \rightarrow \text{NO}_2 (+ \text{M})$	$k_0 = 9 \times 10^{-32} \times (\text{T} / 300)^{-1.5}$ $k_{\infty} = 3 \times 10^{-11}$	5
14.	$\text{NO}_2 + \text{O}(\text{}^3\text{P}) (+ \text{M}) \rightarrow \text{NO}_3 (+ \text{M})$	$k_0 = 9 \times 10^{-32} \times (\text{T} / 300)^{-2}$ $k_{\infty} = 2.2 \times 10^{-11}$	5
15.	$\text{SO}_2 + \text{OH} (+ \text{M}) \rightarrow \text{HOSO}_2 (+ \text{M})$	$k_0 = 3 \times 10^{-31} \times (\text{T} / 300)^{-3.3}$ $k_{\infty} = 1.5 \times 10^{-12}$	5
16.	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 (+ \text{M}) \rightarrow \text{PAN} (+ \text{M})$	$k_0 = 9.7 \times 10^{-29} \times (\text{T} / 300)^{-5.6}$ $k_{\infty} = 9.3 \times 10^{-12} \times (\text{T} / 300)^{-1.5}$	5
17.	$\text{PAN} (+ \text{M}) \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 (+ \text{M})$	$k_{\text{R}} = k_{\text{F}} / k_{\text{EQ}}$ $k_{\text{R}} = k_{\text{F}} / (9 \times 10^{-29} e^{(14000/\text{T})})$	5
18.	$\text{OH} + \text{Alkenes} (+ \text{M}) \rightarrow \text{HOCH}_2\text{CH}_2 (+ \text{M})$	$k_0 = 1.5 \times 10^{-28} \times (\text{T} / 300)^{-0.8}$ $k_{\infty} = 8.8 \times 10^{-12}$	5,4
19.	$\text{C}_2\text{H}_5 + \text{O}_2 (+ \text{M}) \rightarrow \text{C}_2\text{H}_5\text{O}_2 (+ \text{M})$	$k_0 = 1.5 \times 10^{-28} \times (\text{T} / 300)^{-3.8}$ $k_{\infty} = 8 \times 10^{-12}$	5
20.	$\text{NO}_2 + \text{CH}_3\text{O}_2 (+ \text{M}) \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 (+ \text{M})$	$k_0 = 1.5 \times 10^{-30} \times (\text{T} / 300)^{-4}$ $k_{\infty} = 6.5 \times 10^{-12} \times (\text{T} / 300)^{-2}$	5
21.	$\text{CH}_3\text{O}_2\text{NO}_2 \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$	$k_{\text{R}} = k_{\text{F}} / k_{\text{EQ}}$ $k_{\text{R}} = k_{\text{F}} / (1.3 \times 10^{-28} e^{(11200/\text{T})})$	5
22.	$\text{I} + \text{NO}_2 (+ \text{M}) \rightarrow \text{INO}_2 (+ \text{M})$	$k_0 = 3 \times 10^{-31} \times (\text{T} / 300)^{-1}$ $k_{\infty} = 6.6 \times 10^{-11}$ $F_{\text{c}} = e^{(-\text{T} / 650)} + e^{(-2600 / \text{T})}$	5
23.	$\text{IO} + \text{NO}_2 (+ \text{M}) \rightarrow \text{IONO}_2 (+ \text{M})$	$k_0 = 7.7 \times 10^{-31} \times (\text{T} / 300)^{-5}$ $k_{\infty} = 1.6 \times 10^{-11}$ $F_{\text{c}} = 0.4$	5
24.	$\text{Br} + \text{NO}_2 + \text{M} \rightarrow \text{BrNO}_2$	$k_0 = 4.2 \times 10^{-31} \times (\text{T} / 300)^{-2.4}$ $k_{\infty} = 2.7 \times 10^{-11} \times (\text{T} / 300)^{-0}$	5
25.	$\text{BrO} + \text{NO}_2 + \text{M} \rightarrow \text{BrONO}_2$	$k_0 = 5.2 \times 10^{-31} \times (\text{T} / 300)^{-3.2}$ $k_{\infty} = 6.9 \times 10^{-12} \times (\text{T} / 300)^{-2.9}$	5
25.	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2$	$k_0 = 1.6.2 \times 10^{-31} \times (\text{T} / 300)^{-3.4}$ $k_{\infty} = 1.5 \times 10^{-11}$	5

	Photochemical Reactions	References
J1.	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	5,4,c
J2.	$H_2O_2 + h\nu \rightarrow 2OH$	5,4,c
J3.	$HNO_3 + h\nu \rightarrow OH + NO_2$	5,4,c
J4.	$HO_2NO_2 + h\nu \rightarrow OH + NO_3$	5,4,c
J5.	$HONO + h\nu \rightarrow OH + NO$	5,4,c
J6.	$CH_3OOH + h\nu \rightarrow CH_3O + OH$	5,4,c
J7.	$CH_2O + h\nu \rightarrow HCO + H$	5,4,c
J8.	$CH_2O + h\nu \rightarrow CO + H_2$	5,4,c
J9.	$NO_2 + h\nu \rightarrow NO + O$	5,4,c
J10.	$NO_3 + h\nu \rightarrow NO_2 + O$	5,4,c
J11.	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	5,4,c
J12.	$C_2H_5O_2H + h\nu \rightarrow OH + C_2H_5O$	5,4,c
J13.	$CH_3CHO + h\nu \rightarrow CH_3 + HCO$	5,4,c
J15.	$PAN (CH_3C(O)O_2NO_2) + h\nu \rightarrow CH_3C(O)O_2 + NO_2$	5,4,c
J16.	$NO_3 + h\nu \rightarrow NO + O_2$	5,4,c
J17.	$CH_3I + h\nu \rightarrow CH_3 + I$	5,4,c
J18.	$CH_2I_2 + h\nu \rightarrow CH_2I + I \rightarrow CH_2 + 2I$	5,4,c
J19.	$CH_2IBr + h\nu \rightarrow CH_2Br + I$	5,4,c
J20.	$I_2 + h\nu \rightarrow 2I$	5,4,c
J21.	$INO_2 + h\nu \rightarrow I + NO_2 / IO + NO$	5,4,c
J22.	$IO + h\nu \rightarrow I + O$	5,4,c
J23.	$OIO + h\nu \rightarrow I + O_2$	5,4,c
J24.	$IONO_2 + h\nu \rightarrow I + NO_3$	5,4,c
J25.	$HOI + h\nu \rightarrow I + OH$	5,4,c
J26.	$BrO + h\nu \rightarrow Br + O$	5,4,c
J27.	$Br_2 + h\nu \rightarrow 2Br$	5,4,c
J28.	$IBr + h\nu \rightarrow Br + I$	5,4,c
J29.	$BrCl + h\nu \rightarrow Br + Cl$	5,4,c
J30.	$BrNO_2 + h\nu \rightarrow Br + NO_2$	5,4,c
J31.	$BrONO_2 + h\nu \rightarrow 0.7 (BrO + NO_2) / 0.3 (Br + NO_3)$	5,4,c
J32.	$HOBr + h\nu \rightarrow Br + OH$	5,4,c
J33.	$Cl_2 + h\nu \rightarrow 2Cl$	5,4,c
J34.	$ICl + h\nu \rightarrow I + Cl$	5,4,c
J35.	$ClO + h\nu \rightarrow Cl + O$	5,4,c
J36.	$HOCl + h\nu \rightarrow Cl + OH$	5,4,c
J37.	$ClNO_2 + h\nu \rightarrow Cl + NO_2$	5,4,c
J38.	$ClONO_2 + h\nu \rightarrow 0.9 (Cl + NO_3) / 0.1 (ClO + NO_2)$	5,4,c

Species	Deposition velocities, cm s <sup>-1</sup>	References
HOI	1.0	8
HOBr	1.0	d
HOCl	1.0	d
HBr	2.0	d
HCl	2.0	d
HI	1.0	8
BrONO <sub>2</sub>	1.0	d
IONO <sub>2</sub>	1.0	8
ClONO <sub>2</sub>	1.0	d
INO <sub>2</sub>	1.0	d

<sup>a</sup>Units: unimolecular reactions, s<sup>-1</sup>; photolysis rate constants, s<sup>-1</sup>; bimolecular reactions, cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; termolecular reactions, cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, calculated using the formalism of *Sander et al.* (2006), where  $k = ((k_0 [M] / (1 + k_0 [M] / k_\infty)) \times F_c^n)$ ,  $F_c = 0.6$  (unless otherwise noted) and  $n = (1 + (\log_{10}(k_0 [M] / k_\infty))^2)^{-1}$ .

<sup>b</sup>set as upper limit.

<sup>c</sup>absorption cross-sections taken from *Atkinson et al.*, 2000.

<sup>d</sup>deposition velocities estimated.



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