Reactions

Inorganic photochemistry

#	Reaction	Rate constant
1	$O_2 + h\nu \longrightarrow 2\,O(^3P)$	$j = 6.0 \times 10^{-34}$
2	$O_3 + h\nu \longrightarrow O_2 + O(^3P)$	$j = 10^{-6}$
3	$O_3 + h\nu \longrightarrow O(^1D) + O_2$	$j = 1.2 \times 10^{-7}$
4	$O_2 + O(^3P) \longrightarrow O_3$	$k_0 = 6.0 \times 10^{-34}(T/300)^{-2.4}$, $k_\infty = 3.0 \times 10^{-12}$
5	$H_2O + O(^1D) \longrightarrow 2\,OH$	2.2×10^{-10}
6	$HO_2 + O_3 \longrightarrow 2\,O_2 + OH$	$1.1 \times 10^{-14} \exp(-490/T)$
7	$O(^3P) + OH \longrightarrow O_2 + H$	$2.2 \times 10^{-11} \exp(-120/T)$
8	$O(^3P) + HO_2 \longrightarrow OH + O_2$	$3 \times^{-11} \exp(-200/T)$
9	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	$3.0 \times 10^{-13} \times \exp(460/T) + 1.7 \times 10^{-33} \times M \exp(1000/T)$
10	$NO_3 \longrightarrow NO_2 + O(^3P)$	$j = 0.099$
11	$NO_3 \longrightarrow NO + O_2$	$j = 0.04$
12	$O_3 + OH \longrightarrow HO_2 + O_2$	$1.7 \times 10^{-12} \exp(-940/T)$
13	$NO + O_3 \longrightarrow NO_2 + O_2$	$1.7 \times 10^{-12} \exp(-1400/T)$
14	$NO_2 \longrightarrow NO + O(^3P)$	$j = 4 \times 10^{-3}$
15	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	3.2×10^{-17}
16	$NO_2 + NO_3 \longrightarrow N_2O_5$	$k_0 = 2 \times 10^{-30}(T/300)^{-4.4}$, $k_\infty = 1.4 \times 10^{-12}(T/300)^{-0.7}$
17	$N_2O_5 \longrightarrow NO_2 + NO_3$	$j = 2.5 \times 10^{-5}$
18	$NO + NO_3 \longrightarrow 2\,NO_2$	2.6×10^{-11}
19	$NO_2 + OH \longrightarrow HNO_3$	$k_0 = 1.8 \times 10^{-30}(T/300)^{-3}$, $k_\infty = 2.8 \times 10^{-11}$
20	$NO_2 + O(^3P) \longrightarrow NO_3$	$k_0 = 2.5 \times 10^{-31}(T/300)^{-1.8}$, $k_\infty = 2.2 \times 10^{-11}(T/300)^{-0.7}$
21	$NO_2 + O(^3P) \longrightarrow NO + O_2$	1×10^{-11}
22	$HO_2 + NO \longrightarrow NO_2 + OH$	$3.5 \times 10^{-12} \exp(250/T)$

α-pinene (AP) chemistry

#	Reaction	Rate constant
23	$AP + O_3 \longrightarrow 0.75\,RO_2 + 0.25\,SVOC + 0.8\,OH$	8×10^{-17}
24	$AP + OH \longrightarrow 0.75\,RO_2 + 0.25\,SVOC$	5.4×10^{-11}
25	$AP + NO_3 \longrightarrow 0.75\,RO_2 + 0.25\,SVOC$	6.2×10^{-12}
26	$RO_2 \longrightarrow Ox_1RO_2$	$10^8 \exp(-7500/T)$
27	$NO + RO_2 \longrightarrow 0.75\,NO_2 + 0.75\,RO + 0.25\,RONO_2$	10^{-11}
28	$HO_2 + RO_2 \longrightarrow ROOH$	10^{-11}
29	$2\,RO_2 \longrightarrow 2\,RO + ROOR$	10^{-13}
30	$RO_2 \longrightarrow RO$	$10^{15} \exp(-13000/T)$
31	$Ox_1RO_2 \longrightarrow Ox_2RO_2$	$7 \times 10^7 \exp(-7500/T)$
32	$NO + Ox_1RO_2 \longrightarrow 0.75\,NO_2 + 0.75\,Ox_1RO + 0.25\,Ox_1RONO_2$	10^{-11}
33	$HO_2 + Ox_1RO_2 \longrightarrow Ox_1ROOH$	10^{-11}
34	$Ox_1RO_2 + RO_2 \longrightarrow Ox_1RO + Ox_1ROOR + RO$	$\sqrt{10^{-12} \times 10^{-13}}$
35	$2\,Ox_1RO_2 \longrightarrow Ox_1Ox_1ROOR + 2\,Ox_1RO$	10^{-12}
36	$Ox_1RO_2 \longrightarrow Ox_1RO$	$10^{15} \exp(-13000/T)$
37	$Ox_2RO_2 \longrightarrow Ox_3RO_2$	$6 \times 10^7 \exp(-7500/T)$
38	$NO + Ox_2RO_2 \longrightarrow 0.75\,NO_2 + 0.75\,Ox_2RO + 0.25\,Ox_2RONO_2$	10^{-11}
39	$HO_2 + Ox_2RO_2 \longrightarrow Ox_2ROOH$	10^{-11}
40	$Ox_2RO_2 + RO_2 \longrightarrow Ox_2RO + Ox_2ROOR + RO$	$\sqrt{10^{-11} \times 10^{-13}}$
41	$Ox_1RO_2 + Ox_2RO_2 \longrightarrow Ox_1RO + Ox_2Ox_1ROOR + Ox_2RO$	$\sqrt{10^{-12} \times 10^{-11}}$
42	$2\,Ox_2RO_2 \longrightarrow Ox_2Ox_2ROOR + 2\,Ox_2RO$	10^{-11}
43	$Ox_2RO_2 \longrightarrow Ox_2RO$	$10^{15} \exp(-13000/T)$
44	$NO + Ox_3RO_2 \longrightarrow 0.75\,NO_2 + 0.75\,Ox_3RO + 0.25\,Ox_3RONO_2$	10^{-11}
45	$HO_2 + Ox_3RO_2 \longrightarrow Ox_3ROOH$	10^{-11}
46	$Ox_3RO_2 + RO_2 \longrightarrow Ox_3RO + Ox_3ROOR + RO$	$\sqrt{10^{-10} \times 10^{-13}}$
47	$Ox_1RO_2 + Ox_3RO_2 \longrightarrow Ox_1RO + Ox_3Ox_1ROOR + Ox_3RO$	$\sqrt{10^{-12} \times 10^{-10}}$
48	$Ox_2RO_2 + Ox_3RO_2 \longrightarrow Ox_2RO + Ox_3Ox_2ROOR + Ox_3RO$	$\sqrt{10^{-11} \times 10^{-10}}$
49	$2\,Ox_3RO_2 \longrightarrow Ox_3Ox_3ROOR + 2\,Ox_3RO$	10^{-10}
50	$Ox_3RO_2 \longrightarrow Ox_3RO$	$10^{15} \exp(-13000/T)$

Reactions specified with k_0 and k_∞ are pressure-dependent reactions with the rate constant at a specific pressure given by

$$k = \frac{k_0 * M}{1 + \frac{M}{k_\infty}} * 0.6^{(1+(log(\frac{k_0 * M}{k_\infty}))^2)^{-1}} \qquad (1)$$

Volatility class temperature dependence

To show the temperature dependence of the volatility classes, we shift them using the Clausius-Claperyon equation and the enthalpy of vaporization estimation equation from Donahue et al 2011 and Epstein and Donahue 2009.

$$C^{\circ}(T) = C^{\circ}(300K)\exp\left[\frac{\Delta H^{\text{vap}}_{300K}}{R}\left(\frac{1}{300K} - \frac{1}{T}\right)\right] \tag{2}$$

$$\Delta H^{\text{vap}}_{300K} = -5.7\log_{10} C^{\circ}(300K) + 129 \text{ kJ mole}^{-1} \tag{3}$$

Auto-oxidation rate constant depedence

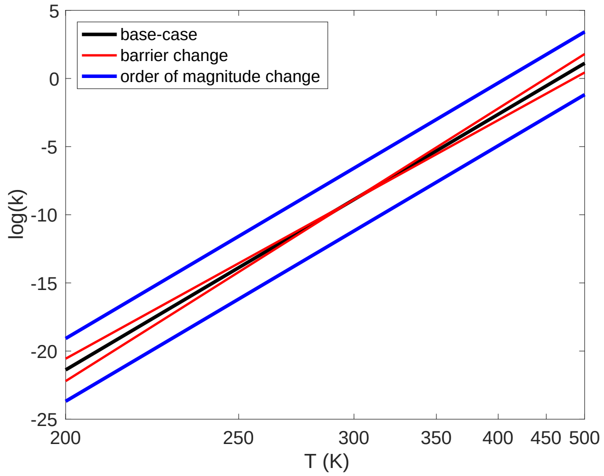

Figure 1. The rate constant of auto-oxidation plotted for the base-case scenario (black), assuming an order of magnitude change over the temperature range (blue), and using a Clausius-Claperyon relation to fix the rate constant at 298 K and varying it using a second barrier height ± 500 K from the base-case (red).

Kernels

The kernels are matrixes showing the change in volatility (decades of $\log_{10}$ C°) along the x direction and oxygenation (O:C) along the y for each type of RO_2 termination. The change is an offset to a reference value of $\log_{10}$ C° and O:C representing the peroxy radical that reacted to form the products. For dimers this reference value is the arithmetic mean of these values for the two reacting peroxy radicals.

For example if an Ox_1RO_2, with reference $\log_{10}$ C° $= 1$ and O:C = 0.6, and an Ox_2RO_2, with reference $\log_{10}$ C° $= -1$ and O:C = 0.8, react to form a dimer, the new reference value will be $\log_{10}$ C° $= 0$ and O:C = 0.7. If we look at the dimer kernel in the first cell, we see that 2% of the product from this reaction would end up at a $\log_{10}$ C° $= 0 - 8 = -8$ and O:C $= 0.7 + 0.1 = 0.8$ and so on for the rest of the table.

All the products called "RO" and "Ox_nRO" in the reaction mechanism above will either go through the fragmentation or the functionalization kernel below. The fragmentation kernel is implemented by assuming a certain fraction of the RO and Ox_nRO in the reaction scheme fragments rather than functionalizes leading to a spread in products across lower and higher volatilities. The probability of fragmentation increases as the carbon backbone of a molecule is destabilized by increasing oxidation and is given in our implementation by (O:C)$^{\frac{1}{6}}$.

Dimer Kernel

-8	-7	-6	-5	O:C
.02	.16	.08	0	$+0.1$
.01	.13	.30	.1	$+0.0$
0	0	.05	.15	-0.1

RO_2 + HO_2 and RO_2 + NO Kernel

-4	-3	-2	-1	O:C
.02	.16	.08	0	+0.1
.01	.13	.30	.1	+0.0
0	0	.05	.15	-0.1

Fragmentation Kernel

-2	-1	0	+1	+2	+3	+4	O:C
0	0	0	0	.02	.04	.08	+0.4
.02	.01	.02	.03	.04	.05	.02	+0.3
.04	.04	.04	.03	.02	.01	.01	+0.2
.02	.08	.06	.04	.03	0	0	+0.1
.00	.04	.12	.06	.03	0	0	+0.0

RO Functionalization Kernel

-3	-2	-1	0	1	O:C
.05	.08	.07	.04	0	+0.0
.02	.07	.18	.20	.12	-0.1
0	.02	.04	.08	.03	-0.2