**2.1 Surface O3 chemical budget (278)**

The surface O3 chemical budget involves the consideration of production and loss, which are represented by P(O3) and L(O3), respectively, while excluding the deposition and atmospheric dynamic-driven fluxes. The production rate of O3 is equivalent to the instantaneous photolysis of NO2 when subjected to radiation of wavelength <330 nm. The production of NO2, on the other hand, originates from the oxidation of NO by HO2, CH3O2, and RO2 peroxide radicals. This results in the O3 production formula, as described in Equation 1. The destruction of O3 occurs through photolysis under radiation of wavelength <330 nm, reactions with HOX (i.e. OH and HO2) radicals, and unsaturated VOCs, such as alkenes, as indicated in Equation 2. The temperature-dependent kinetic rate coefficients are determined based on the atmospheric chemistry module's configuration coupled into the Earth system model, for example, UKCA1 embedded in UKESM1-0-LL2. These values are calculated using the simulated surface air temperature and are detailed in Supplementary Table 1, with reference values evaluated by IUPAC.

NO2 + *hv* → NO + O(3P) (R1)

O(3P) + O2 + M → O3 + M (R2)

NO + HO2 → NO2 + OH (R3)

NO + CH3O2 → NO2 + CH3O (R4)

NO + RO2 → NO2 + RO (R5)

O3 → O2 + O(1D) (R6)

O(1D) + H2O → 2OH (R7)

O3 + OH → O2 + HO2 (R8)

O3 + HO2 → 2O2 + OH (R9)

P(O3) = *k*1[NO][HO2] + *k*2[NO][CH3O2] + ∑*ki*[NO][RO2] (Equation 1)

L(O3) = *k*3[O(1D)][H2O] + *k*4[O3][OH] + *k*5[O3][HO2] + ∑*kj*[O3][VOCs] (Equation 2)

, preferred value as 8.5×10–12 cm3 molecule-1 s-1 at 298 K.

, preferred value as 7.7×10–12 cm3 molecule-1 s-1 at 298 K.

, preferred value as 2.14×10–10 cm3 molecule-1 s-1 independent of temperature over the range 200–350 K.

, preferred value as 7.3×10–14 cm3 molecule-1 s-1 at 298 K.

, preferred value as 2.0×10–15 cm3 molecule-1 s-1 at 298 K.

In the polluted areas, the sinks of HOX radicals are the formation of a mixture of HNO3 and H2O2, depending on the relative abundance of NOX and VOCs. The chemical budgets of HOX radicals were calculated by Equation 3 and 4, where α represents the proportion of the O(1D) formed by O3 photolysis and reacting with H2O. The concentration of N2 [N2] in molecule cm–3 is calculated by ideal gas law, as 1 cm3 air comprises 0.78 cm3 N2, equivalent to 0.78×10-6×*P*/*RT*×*N*A molecules of N2. At standard atmospheric pressure (101.325 kPa), *k*6 can be written as *k*6 = 1.9×10–8×(*T*/300)–4.5×*T*–1.

OH + NO2 + M → HNO3 + M (R10)

HO2 + HO2 + M → H2O2 + O2 + M (R11)

∂[OH]/∂t = 2·J[O(1D)][O3]·*α*·*k*3[H2O] + *k*5[O3][HO2] – *k*4[O3][OH] – *k*6[OH][NO2]

∂[HO2]/∂t = *k*4[O3][OH] – *k*5[O3][HO2] – 2*k*7[HO2]2 – *k*1[HO2][NO]

*k*6 = 3.3×10–30×(T/300)–4.5 [N2], preferred value as 6.5×10–11 cm3 molecule–1 s–1 over the temperature range 220–400 K.

*k*7 = 2.2×10–13×exp(600/T), preferred value as 1.6×10–12 cm3 molecule-1 s-1 at 298 K.

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