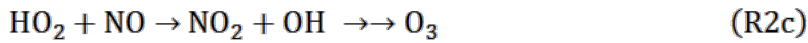
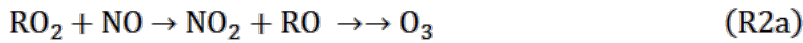


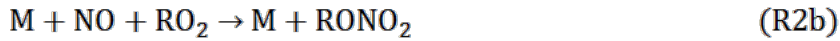
Description of simplified total oxidant production calculation method

The reactions describing HO_x chain propagation and termination are used to derive the equations about ozone production, assuming that these radicals and peroxy nitrates are in steady state, which means that P(HO_x) = L(HO_x). The branch reaction producing alkyl nitrates is considered, α is denoted as this production probability (5, 6).

Reactions that propagate the HO_x cycle include:



Reactions referred to HO_x chain termination include:



Considering R2b, R3-R6, terminal loss rate of HO_x can be formulated as:

$$\begin{aligned} \text{L}(\text{HO}_x) = & k_3[\text{OH}][\text{NO}_2] + \alpha k_{2b}[\text{RO}_2][\text{NO}] + 2k_4[\text{RO}_2][\text{R}'\text{O}_2] + 2k_5[\text{RO}_2][\text{HO}_2] \\ & + 2k_6[\text{HO}_2][\text{HO}_2] \end{aligned} \quad (1)$$

Assuming $[\text{HO}_2] = [\text{RO}_2]$ (this can be acceptable for two radicals over Beijing are at the same magnitude in closure modeling(7)) and peroxy radicals are in steady state P[HO_x] = L[HO_x], we can yield that:

$$\text{P}(\text{HO}_x) = k_3[\text{NO}_2][\text{OH}] + \alpha k_{2b}[\text{HO}_2][\text{NO}] + 2(k_4 + k_5 + k_6)[\text{HO}_2]^2 \quad (2)$$

Apart from the alkyl nitrates production reaction between NO and RO₂ (R2b), the main reaction (R2a) consume most RO₂ radicals, thus:

$$[\text{HO}_2] = [\text{RO}_2] = k_1[\text{VOC}][\text{OH}] / (1 - \alpha)k_{2a} [\text{NO}] \quad (3)$$

Substituting equation (3) into equation (2) yields:

$$\begin{aligned} P(\text{HO}_x) = & k_3[\text{OH}][\text{NO}_2] + \alpha k_{2b} \frac{k_1[\text{VOC}][\text{OH}]}{(1 - \alpha)} [\text{NO}] \\ & + 2(k_4 + k_5 + k_6) [k_1[\text{VOC}][\text{OH}] / (1 - \alpha)k_{2a} [\text{NO}]]^2 \quad (4) \end{aligned}$$

$$P(\text{O}_x) = k_{2a}[\text{RO}_2][\text{NO}] + k_{2c}[\text{HO}_2][\text{NO}] = 2k_1[\text{VOC}][\text{OH}] \quad (5)$$

HO_x production rate P(HO_x) mainly consist of HONO, OVOCs and ozone photolysis. According to measurement or modeling results of HO_x budget, given a certain value of P(HO_x) and other proper parameters, the instantaneous [OH] and corresponding P(O_x) can be solved through a quadratic equation to indicate the variations of total oxidant:

(6) [OH]

$$\begin{aligned} & - \left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{(1 - \alpha)} \right) + \sqrt{\left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{1 - \alpha} \right)^2 + \frac{8P(\text{HO}_x)(k_4 + k_5 + k_6)(k_1[\text{VOC}])^2}{((1 - \alpha)k_{2a}[\text{NO}])^2}} \\ = & \frac{4(k_4 + k_5 + k_6)(k_1[\text{VOC}] / (1 - \alpha)k_{2a}[\text{NO}])^2}{2P(\text{HO}_x)} \\ = & \frac{2P(\text{HO}_x)}{\left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{(1 - \alpha)} \right) + \sqrt{\left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{1 - \alpha} \right)^2 + \frac{8P(\text{HO}_x)(k_4 + k_5 + k_6)(k_1[\text{VOC}])^2}{((1 - \alpha)k_{2a}[\text{NO}])^2}}} \end{aligned}$$

(7) P(O_x) = 2k₁[VOC] * [OH]

$$\begin{aligned} & = \frac{2k_1[\text{VOC}] * 2P(\text{HO}_x)}{\left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{(1 - \alpha)} \right) + \sqrt{\left(k_3[\text{NO}_2] + \frac{\alpha k_1[\text{VOC}]}{1 - \alpha} \right)^2 + \frac{8P(\text{HO}_x)(k_4 + k_5 + k_6)(k_1[\text{VOC}])^2}{((1 - \alpha)k_{2a}[\text{NO}])^2}}} \end{aligned}$$

$$= \frac{4P(\text{HO}_x)}{\left(\frac{k_3[\text{NO}_2]}{k_1[\text{VOC}] + 1 - \alpha}\right) + \sqrt{\left(\frac{k_3[\text{NO}_2]}{k_1[\text{VOC}] + 1 - \alpha}\right)^2 + \frac{8P(\text{HO}_x)(k_4 + k_5 + k_6)}{((1 - \alpha)k_{2a}[\text{NO}])^2}}}$$

In above equations, $k_1[\text{VOC}]$ is the total VOC reactivity; $k_{2a}=k_{2b}=k_{2c}$ is the effective reaction constant between NO and RO_2 in the normal atmosphere(8); k_3 is the reaction constant between OH and NO_2 , k_4 , k_5 and k_6 are the reaction constants between RO_2 themselves, RO_2 and HO_2 , HO_2 and itself, respectively(6).