Description of simplified total oxidant production calculation method

The reactions describing HO\textsubscript{x} chain propagation and termination are used to derive the equations about ozone production, assuming that these radicals and peroxynitrates are in steady state, which means that \( P(\text{HO}_x) = L(\text{HO}_x) \). The branch reaction producing alkyl nitrates is considered, \( \alpha \) is denoted as this production probability (5, 6).

Reactions that propagate the HO\textsubscript{x} cycle include:

\begin{align*}
\text{VOC} + \text{OH} & \rightarrow \text{RO}_2 + \text{H}_2\text{O} & (R1) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{NO}_2 + R0 \rightarrow \text{O}_3 & (R2a) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \rightarrow \text{O}_3 & (R2c)
\end{align*}

Reactions referred to HO\textsubscript{x} chain termination include:

\begin{align*}
\text{M} + \text{OH} + \text{NO}_2 & \rightarrow \text{M} + \text{HNO}_3 & (R3) \\
\text{M} + \text{NO} + \text{RO}_2 & \rightarrow \text{M} + \text{RO}_2\text{NO}_2 & (R2b) \\
\text{RO}_2 + \text{R'}\text{O}_2 & \rightarrow \text{R'}\text{OOR} + \text{O}_2 & (R4) \\
\text{RO}_2 + \text{HO}_2 & \rightarrow \text{ROOH} + \text{O}_2 & (R5) \\
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & (R6)
\end{align*}

Considering R2b, R3-R6, terminal loss rate of HO\textsubscript{x} can be formulated as:

\[
L(\text{HO}_x) = k_5[\text{OH}][\text{NO}_2] + \alpha k_{2b}[\text{RO}_2][\text{NO}] + 2k_4[\text{RO}_2][\text{R'}\text{O}_2] + 2k_5[\text{RO}_2][\text{HO}_2] + 2k_6[\text{HO}_2][\text{HO}_2]
\]  

(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 \( P[\text{HO}_x] = L[\text{HO}_x] \), we can yield that:

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

(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:

$$P(\text{HO}_2) = k_3[\text{OH}][\text{NO}_2] + \alpha k_{2b} \frac{k_1[\text{VOC}][\text{OH}]}{(1 - \alpha)} [\text{NO}]$$

$$+ 2(k_4 + k_5 + k_6)[k_1[\text{VOC}][\text{OH}]/(1 - \alpha)k_{2a} [\text{NO}]]^2 \quad (4)$$

$$P(\text{O}_3) = k_{2a}[\text{RO}_2][\text{NO}] + k_{2c}[\text{HO}_2][\text{NO}] = 2k_2 [\text{VOC}][\text{OH}] \quad (5)$$

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

$$[\text{OH}]$$

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

$$= \frac{2P(\text{HO}_2)}{k_5[\text{NO}_2] + \alpha k_4[\text{VOC}] + \frac{2P(\text{HO}_2)}{(1 - \alpha)k_{2a} [\text{NO}])^2}$$

$$P(\text{O}_3) = 2k_3[\text{VOC}] \cdot [\text{OH}]$$

$$= \frac{2k_1[\text{VOC}] + 2P(\text{HO}_2)}{k_5[\text{NO}_2] + \alpha k_4[\text{VOC}] + \frac{2P(\text{HO}_2)}{(1 - \alpha)k_{2a} [\text{NO}])^2}$$
In above equations, $k_1[VOC]$ 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; $k_3$ 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.