P 9-6

low temperature – no antioxident

$$\frac{dC_{I\cdot}}{dt} = r_{I\cdot} = 2k_o C_{I_2} - k_i C_I \cdot C_{RH} \quad \text{—①}$$

$$\frac{dC_{RH}}{dt} = -k_i C_I \cdot C_{RH} - k_{p_2} C_{RO_2} \cdot C_{RH} \quad \text{—②}$$

$$\frac{dC_{RO_2\cdot}}{dt} = k_{p_1} C_R \cdot C_{O_2} - k_{p_2} C_{RO_2} \cdot C_{RH} - k_t C_{RO_2\cdot}^2 \quad \text{—③}$$

$$\frac{dC_{R\cdot}}{dt} = k_i C_{RH} C_{I\cdot} - k_{p_t} C_R \cdot C_{O_2} + k_{p_2} C_{RO_2} \cdot C_{RH} \quad \text{—④}$$

PSSA $\Rightarrow$ $\frac{dC_{radicals}}{dt} = 0$

From ①

$$C_{I\cdot} = \frac{2k_o C_{I_2}}{k_i C_{RH}} \quad \text{—⑤}$$

From ④

$$0 = k_i C_{RH} \left[\frac{2k_o C_{I_2}}{k_i C_{RH}}\right] - k_{p_t} C_R \cdot C_{O_2} + k_{p_2} C_{RO_2} \cdot C_{RH}$$

$$C_{R\cdot} = \frac{2k_o C_{I_2} + k_{p_2} C_{RO_2} \cdot C_{RH}}{k_{p_t} C_{O_2}} \quad \text{—⑥}$$

$\Rightarrow$ still need to eliminate $C_{RO_2\cdot}$.

From (3)

$$0 = k_{p_1} C_{R\cdot} C_{O_2} - k_{p_2} C_{RO_2\cdot} C_{RH} - k_t C_{RO_2\cdot}^2$$

$$2k_o C_{I_2} + k_{p_2} C_{RO_2\cdot} C_{RH} - k_{p_2} C_{RO_2\cdot} C_{RH} - k_t C_{RO_2\cdot}^2 = 0$$

$$\Rightarrow \quad C_{RO_2\cdot} = \sqrt{\frac{2k_o C_{I_2}}{k_t}} \qquad \text{— (7)}$$

substitute in eq. (2)

$$\frac{dC_{RH}}{dt} = -k_i \left[\frac{2k_o C_{I_2}}{k_i C_{RH}}\right] C_{RH} - k_{p_2} \left[\sqrt{\frac{2k_o}{k_t} C_{I_2}}\right] C_{RH}$$

$$\boxed{-\frac{dC_{RH}}{dt} = 2k_o C_{I_2} + \left[\frac{2k_{p_2}^2 k_o}{k_t}\right]^{1/2} C_{I_2}^{1/2} C_{RH}} \qquad \text{— (8)}$$

b) Low temperature with antioxident

$\frac{dC_{R\cdot}}{dt}$ ⇒ same as eq. ④

$$\frac{dC_{A\cdot}}{dt} = k_{A1} C_{AH} C_{RO_2\cdot} - k_{A2} C_{A\cdot} C_{RO_2\cdot} \quad -⑨$$

$$\frac{dC_{RH}}{dt} = -k_i C_{I\cdot} C_{RH} - k_{P2} C_{RO_2\cdot} C_{RH} \quad \text{-... same as eq. ②}$$

PSSH >

$$\frac{dC_{I\cdot}}{dt} = 0$$

⇒ $C_{I\cdot}$ ⇒ eq ⑤

$$\frac{dC_{A\cdot}}{dt} = 0$$

$$\Rightarrow C_{A\cdot} = \frac{k_{A1} C_{AH}}{k_{A2}}$$

$C_{R\cdot}$ ⇒ eq. ⑥

$$\frac{dC_{RO_2\cdot}}{dt} = 2k_0 C_{I_2} - k_t C_{RO_2\cdot}^2 - 2k_{A1} C_{AH} C_{RO_2\cdot}$$