P10-3

$$I + S \longleftrightarrow I \cdot S$$

$$r_{ADI} = k_{AI}\left[C_I C_V - \frac{C_{I\cdot S}}{K_I}\right]$$

$$W + S \longleftrightarrow W \cdot S$$

$$r_{ADW} = k_{AW}\left[C_W C_V - \frac{C_{W\cdot S}}{K_W}\right]$$

$$W\cdot S + I\cdot S \longleftrightarrow TBA\cdot S + S$$

$$r_S = k_S\left[C_{W\cdot S} C_{I\cdot S} - \frac{C_V C_{TBA\cdot S}}{K_S}\right]$$

$$TBA\cdot S \longleftrightarrow TBA + S$$

$$r_D = k_D\left[C_{TBA\cdot S} - \frac{C_{TBA} C_V}{K_D}\right]$$

a) Surface reaction limited

$$\frac{r_{ADI}}{k_{AI}} = 0 \Rightarrow C_{I\cdot S} = K_I C_I C_V$$

$$\frac{r_{ADW}}{k_{AW}} = 0 \Rightarrow C_{W\cdot S} = K_W C_W C_V$$

$$\frac{r_D}{k_D} = 0 \Rightarrow C_{TBA\cdot S} = \frac{C_{TBA} C_V}{K_D}$$

$$K_D = \frac{1}{K_{TBA}}$$

~~$C_{TBA \cdot S} = \epsilon$~~

$$C_{TBA \cdot S} = K_{TBA} C_{TBA} C_V$$

$$\therefore r_S = k_S K_W K_I C_V^2 \left[C_I C_W - C_{TBA} \left(\frac{K_{TBA}}{K_S K_I K_W} \right) \right]$$

$$r_S = k_S K_W K_I C_V^2 \left[C_I C_W - \frac{C_{TBA}}{K_P} \right]$$

$$K_P = \frac{k_S K_I K_W}{K_{TBA}}$$

Site balance

$$C_T = C_V + C_{I \cdot S} + C_{W \cdot S} + C_{TBA \cdot S}$$

$$= C_V (1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})$$

$$-r'_I = -r'_W = r_S = \frac{k_S K_W K_I C_T^2 \left[C_I C_W - \frac{C_{TBA}}{K_P} \right]}{(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})^2}$$

b) Adsorption of isobutene limited

$$r_{ADI} = k_{AI}\left[C_I - \frac{C_{TBA}}{C_w K_p}\right] C_v$$

$$r_{ADI} = k_{AI}\left[C_I C_v - \frac{C_{I\cdot S}}{K_I}\right]$$

$$\frac{r_{ADW}}{k_{AW}} = 0 \quad ; \quad \frac{r_D}{k_D} = 0 \quad ; \quad \frac{r_S}{k_S} = 0$$

$$C_{W\cdot S} = C_W C_V K_W$$

$$C_{TBA\cdot S} = K_{TBA} C_{TBA} C_V$$

$$C_{I\cdot S} = \frac{C_V C_{TBA\cdot S}}{C_{W\cdot S} K_S} = \frac{K_{TBA} C_{TBA} C_V}{C_W K_W K_S}$$

$$r_{ADI} = \frac{k_{AI}\left[C_I - \frac{C_{TBA}}{C_W K_P}\right] C_T}{(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})}$$

$$K_P = \frac{K_W K_S K_I}{K_{TBA}}$$

c) Eley Rideal Kinetics

$I\cdot S + W \leftrightarrow TBA\cdot S$

$$r_S = k_S\left[C_W C_{I\cdot S} - \frac{C_{TBA\cdot S}}{K_S}\right]$$

$$C_{I\cdot S} = K_I C_I C_V$$

$$C_{TBA \cdot S} = K_{TBA} C_{TBA} C_V$$

$$-r_I' = \frac{k_s \left[C_W C_I - \frac{C_{TBA}}{K_H} \right] K_I C_T}{1 + K_I C_I + K_{TBA} C_{TBA} + K_W C_W}$$

d)

$$I + S_1 \longleftrightarrow I \cdot S_1$$

$$W + S_2 \longleftrightarrow W \cdot S_2$$

$$I \cdot S_1 + W \cdot S_2 \longleftrightarrow TBA + S_1 + S_2$$

$$r_s = k_s \left[C_{I \cdot S_1} C_{W \cdot S_2} - \frac{C_{TBA} C_{V_1} C_{V_2}}{K_s} \right]$$

$$C_{T_1} = C_{V_1} + C_{I \cdot S_1}$$

$$C_{T_2} = C_{V_2} + C_{W \cdot S_2}$$

$$C_{I \cdot S_1} = K_I C_I C_{V_1} \qquad C_{T_1} = C_{V_1} (1 + K_I C_I)$$

$$C_{W \cdot S_2} = K_W C_W C_{V_2} \qquad C_{T_2} = C_{V_2} (1 + K_W C_W)$$

$$r_I = \frac{k \left[C_I C_W - \frac{C_{TBA}}{K_s} \right]}{(1 + K_I C_I)(1 + K_W C_W)}$$

$$k = k_s K_W K_I C_{T_1} C_{T_2}$$