REB, The Book
Example 4.8.2 Calculations

Rate expressions for r_1:

$$r_{j_{non}} = r_{j_{rds}} = k_{j_{rds},f} \prod_{i_r} [i_r]^{-\nu_{i_r,j_{rds}}} - k_{j_{rds},r} \prod_{i_p} [i_p]^{\nu_{i_p,j_{rds}}}$$

$$r_1 = r_2 = k_{2,f}[C_3H_5I] - k_{2,r}[C_3H_5\cdot][I\cdot] \tag{8a}$$

$$r_1 = k_{3,f}[C_3H_5I][I\cdot] - k_{3,r}[C_3H_5\cdot][I_2] \tag{8b}$$

$$r_1 = k_{4,f}[C_3H_5\cdot]^2 - k_{4,r}[C_6H_{10}] \tag{8c}$$

Quasi-equilibrium expressions for each mechanistic step:

$$K_{j_{nrd}} = \prod_i [i]^{\nu_{i,j_{nrd}}}$$

$$K_2 = \frac{[C_3H_5\cdot][I\cdot]}{[C_3H_5I]} \tag{9}$$

$$K_3 = \frac{[C_3H_5\cdot][I_2]}{[C_3H_5I][I\cdot]} \tag{10}$$

$$K_4 = \frac{[C_6H_{10}]}{[C_3H_5\cdot]^2} \tag{11}$$

<u>For case (a),</u> solve equations (10) and (11) for the concentrations of $C_3H_5\cdot$ and $I\cdot$ and substitute in equation (8a). Equation (11) can be solved for the concentration of $C_3H_5\cdot$, equation (12).

$$[C_3H_5\cdot] = \frac{\sqrt{[C_6H_{10}]}}{\sqrt{K_4}} \tag{12}$$

Substitute equation (12) in equation (10) and solve for the concentration of I·, equation (13).

$$[I\cdot] = \frac{\sqrt{[C_6H_{10}]}I_2]}{K_3\sqrt{K_4}[C_3H_5I]} \tag{13}$$

Substitute equations (12) and (13) into equation (8a) to get the rate expression, equation (14).

$$r_1 = k_{2,f}[C_3H_5I] - k_{2,r}\frac{\sqrt{[C_6H_{10}]}}{\sqrt{K_4}}\frac{\sqrt{[C_6H_{10}]}I_2]}{K_3\sqrt{K_4}[C_3H_5I]}$$

$$r_1 = k_{2,f}[C_3H_5I] - \frac{k_{2,r}}{K_3K_4}\frac{C_6H_{10}][I_2]}{[C_3H_5I]} \tag{14}$$

<u>For case (b),</u> solve equations (9) and (11) for the concentrations of $C_3H_5\cdot$ and I· and substitute in equation (8b). As above the concentration of $C_3H_5\cdot$ is given by equation (12). Substituting equation (12) in equation (9) and solving for the concentration of I· gives equation (15).

$$[I\cdot] = \frac{K_2\sqrt{K_4}[C_3H_5I]}{\sqrt{[C_6H_{10}]}} \tag{15}$$

Substitute equations (12) and (15) into equation (8b) to get the rate expression, equation (16).

$$r_1 = k_{3,f}K_2\sqrt{K_4}\frac{[C_3H_5I]^2}{\sqrt{[C_6H_{10}]}} - \frac{k_{3,r}}{\sqrt{K_4}}\sqrt{[C_6H_{10}]}[I_2] \tag{16}$$

<u>For case (c),</u> solve equations (9) and (10) for the concentrations of $C_3H_5\cdot$ and I·, equations (20) and (21). Substitute those results in equation (8c) to get the rate expression shown in equation (22).

$$[C_3H_5\cdot] = \sqrt{K_2K_3}\frac{[C_3H_5I]}{\sqrt{[I_2]}} \tag{20}$$

$$[I\cdot] = \frac{\sqrt{K_2}}{\sqrt{K_3}}\sqrt{[I_2]} \tag{21}$$

$$r_1 = \frac{k_{4,f}K_2K_3[C_3H_5I]^2}{[I_2]} - k_{4,r}[C_6H_{10}] \tag{22}$$