REB, The Book
Example 4.8.2 Solution

Suppose that iodopropane disproportionates to produce iodine according to the apparent non-elementary reaction (1). By separately assuming each of the three mechanistic steps in the proposed mechanism, equations (2) through (4), to be rate-determining, generate three possible mechanistic rate expressions for reaction (1).

$$2\ C_3H_5I \rightleftarrows C_6H_{10} + I_2 \tag{1}$$

$$C_3H_5I \rightleftarrows C_3H_5\cdot + I\cdot \tag{2}$$

$$C_3H_5I + I\cdot \rightleftarrows C_3H_5\cdot + I_2 \tag{3}$$

$$2\ C_3H_5\cdot \rightleftarrows C_6H_{10} \tag{4}$$

Assignment Summary

Apparent Reaction:

$$2\ C_3H_5I \rightleftarrows C_6H_{10} + I_2 \tag{1}$$

Mechanistic Steps:

$$C_3H_5I \rightleftarrows C_3H_5\cdot + I\cdot \tag{2}$$

$$C_3H_5I + I\cdot \rightleftarrows C_3H_5\cdot + I_2 \tag{3}$$

$$2\ C_3H_5\cdot \rightleftarrows C_6H_{10} \tag{4}$$

Quantifiable Reagents: C_3H_5I, C_6H_{10}, and I_2

Reactive Intermediates: $C_3H_5\cdot$ and $I\cdot$

Deliverables: simplified expression for r_1 if the rate-determining step is (a) step (2), (b) step (3), and (c) step (4).

Equations for Generating the Mechanistic Rate Expression

Rates of the Mechanistic Steps

$$r_2 = k_{2,f}[C_3H_5I] - k_{2,r}[C_3H_5\cdot][I\cdot] \tag{5}$$

$$r_3 = k_{3,f}[C_3H_5I][I\cdot] - k_{3,r}[C_3H_5\cdot][I_2] \tag{6}$$

$$r_4 = k_{4,f}[C_3H_5\cdot]^2 - k_{4,r}[C_6H_{10}] \tag{7}$$

<u>Apparent Rate of the Non-Elementary Reaction</u>

$$r_1 = r_2 \tag{8a}$$

$$r_1 = r_3 \tag{8b}$$

$$r_1 = r_4 \tag{8c}$$

<u>Quasi-Equilibrium Expressions</u>

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

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

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

Calculations

The algebraic details for the calculations in this section are presented in the file, Example 4.8.2 Calculations.pdf. The calculations proceed as follows:

1. Substitute the expressions for the rates of the mechanistic steps, equations (5) through (7), into equations (8a), (8b), and (8c).
2. For case (a) where step (2) is rate-determining
    a. Solve the quasi-equilibrium expressions for the other steps, equations (10) and (11), for the concentrations of the reactive intermediates.

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

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

b. Substitute equations (12) and (13) into the version of equation (8a) from step 1 and rearrange to get the mechanistic rate expression, equation (14).

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

3. For case (b) where step (3) is rate-determining
   a. Solve the quasi-equilibrium expressions for the other steps, equations (9) and (11), for the concentrations of the reactive intermediates.

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

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

   b. Substitute equations (12) and (15) into the version of equation (8b) from step 1 and rearrange to get the mechanistic rate expression, equation (16).

$$r_1 = k_{2,f}[C_3H_5I] - \frac{k_{2,r}}{K_3K_4}\frac{C_6H_{10}][I_2]}{[C_3H_5I]} \tag{16}$$

4. For case (c) where step (4) is rate-determining
   a. Solve the quasi-equilibrium expressions for the other steps, equations (9) and (10), for the concentrations of the reactive intermediates.

$$[C_3H_5\cdot] = \sqrt{K_2K_3}\frac{[C_3H_5I]}{\sqrt{[I_2]}} \tag{17}$$

$$[I\cdot] = \frac{\sqrt{K_2}}{\sqrt{K_3}}\sqrt{[I_2]} \tag{18}$$

b. Substitute equations (17) and (18) into the version of equation (8c) from step 1 and rearrange to get the mechanistic rate expression, equation (19).

$$r_1 = \frac{k_{4,f}K_2K_3[C_3H_5I]^2}{[I_2]} - k_{4,r}[C_6H_{10}] \tag{19}$$

Simplification and Discussion

In all three cases there are two terms in the rate expression, and each term contains true rate coefficients and equilibrium constants. There is no way for one term to only have concentrations, so two apparent rate coefficients, k_f and k_r, can be defined for each case. Table 1 shows the definitions of k_f and k_r and the rate expressions for all three cases.

Rate-Determining Step	Apparent Forward Rate Coefficient (k_f)	Apparent Reverse Rate Coefficient (k_r)	Rate Expression for Reaction (1)
2	$k_f = k_{2,f}$	$k_r = \frac{k_{2,r}}{K_3K_4}$	$r_1 = k_f[C_3H_5I] - k_r\frac{C_6H_{10}][I_2]}{[C_3H_5I]}$
3	$k_f = k_{3,f}K_2\sqrt{K_4}$	$k_r = \frac{k_{3,r}}{\sqrt{K_4}}$	$r_1 = k_f\frac{[C_3H_5I]^2}{\sqrt{[C_6H_{10}]}} - k_r\sqrt{[C_6H_{10}]}[I_2]$
4	$k_f = k_{4,f}K_2K_3$	$k_r = k_{4,r}$	$r_1 = k_f\frac{[C_3H_5I]^2}{[I_2]} - k_r[C_6H_{10}]$

The apparent forward and reverse rate coefficients are each a product of true rate coefficients and equilibrium constants raised to constant powers. As long as the equilibrium constants display Arrhenius temperature dependence, the apparent rate coefficients will as well.

Deliverables

If the proposed mechanism is correct and if one of the three steps is rate-determining, equation (20) is the expression for the apparent rate of reaction (1) if step (2) is rate-determining. If step (3) is rate-determining, equation (21) is the rate expression, and if step (4) is rate-determining, equation (22) is the rate expression. Experimental studies will need to be performed to determine whether any of those rate expressions captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = k_f[C_3H_5I] - k_r\frac{C_6H_{10}][I_2]}{[C_3H_5I]} \tag{20}$$

$$r_1 = k_f\frac{[C_3H_5I]^2}{\sqrt{[C_6H_{10}]}} - k_r\sqrt{[C_6H_{10}]}[I_2] \tag{21}$$

$$r_1 = k_f\frac{[C_3H_5I]^2}{[I_2]} - k_r[C_6H_{10}] \tag{22}$$

Results and Discussion

The mechanistic rate expressions are given in equations (14), (19), and (25) for the cases where step (2), (3), and (4), respectively, are rate-determining.

$$r_1 = k_f[C_3H_5I] - k_r\frac{C_6H_{10}][I_2]}{[C_3H_5I]} \tag{14}$$

$$r_1 = k_f\frac{[C_3H_5I]^2}{\sqrt{[C_6H_{10}]}} - k_r\sqrt{[C_6H_{10}]}[I_2] \tag{19}$$

$$r_1 = k_f\frac{[C_3H_5I]^2}{[I_2]} - k_r[C_6H_{10}] \tag{25}$$

As long as the equilibrium constants for steps (2) through (4) display Arrhenius-like temperature dependence, the effective rate coefficients, k_f and k_r, will also display Arrhenius temperature dependence. Experimental studies will need to be performed to determine whether any of those rate expressions capture the composition and temperature dependence of the rate with sufficient accuracy.