Chapter 4

Exercise 1:

Proposed mechanism:

\[
\begin{align*}
\text{N}_2\text{O}_5 & \xrightarrow{k_1} \text{NO}_2 + \text{NO}_3 \\
\text{NO}_2 + \text{NO}_2 & \xrightarrow{k_2} \text{NO}_2 + \text{O}_2 + \text{NO} \\
\text{NO} + \text{NO}_3 & \xrightarrow{k_3} 2\text{NO}_2
\end{align*}
\]  

(1)  

(2)  

(3)

Write the rate expression for reaction (2):

\[
\tau = \frac{d[\text{O}_2]}{dt} = k_2[\text{NO}_2][\text{NO}_2]
\]  

(4)

Write the equilibrium expression for reaction (1):

\[
\frac{k_1}{k_{-1}} = K = \frac{[\text{NO}_2][\text{NO}_2]}{[\text{N}_2\text{O}_5]}
\]  

(5)

Rewrite equation (4), substituting information from equation (5):

\[
\frac{d[\text{O}_2]}{dt} = k_2K[\text{N}_2\text{O}_5] = k'[\text{N}_2\text{O}_5]
\]  

(6)

Therefore, the proposed mechanism is consistent with the experimental rate expression.
Another Approach for 4.1

$$2N_2O_5 \rightarrow O_2 + 4NO_2$$

**Mechanism:**

$$N_2O_5 \rightleftharpoons k_k NO_2 + NO_3$$  \hspace{1cm} (1)

$$NO_3 + NO_2 \rightarrow 2NO_2O_2 + NO_2$$  \hspace{1cm} (2)

$$NO + NO_3 \rightarrow ZNO_2$$  \hspace{1cm} (3)

**Rate-determining expression for overall reaction:**

$$r = -\frac{1}{2} \frac{d[NO_3]}{dt} = \frac{d[NO_2]}{dt} \text{ at } O_2 \text{ step Z}$$

$$[NO_2] = k_k [NO_3][NO_2]$$

$$\frac{d[NO_3]}{dt} = k_k [NO_3] - k_2 [NO_2][NO_2] - k_3 [NO_3][NO_2] - k_4 [NO_3][NO_2] = 0$$

*by SSA*

Thus, \[ \frac{d[NO_3]}{dt} = \frac{k_k [NO_3]}{k_3 [NO_2][NO_2]} = \text{ but involves } [NO_2] \text{ an intermediate} \]

$$\frac{d[NO_3]}{dt} = k_2 [NO_2][NO_2] = k_4 [NO_3][NO_2]$$

*by SSA*

$$\text{Mass: } [NO_3] = \frac{k_3 [NO_2][NO_2]}{k_4 [NO_3][NO_2]} = \frac{k_4 [NO_3]}{k_4}$$

$$\text{R.H.S: } [NO_3] = \frac{k_3 [NO_2][NO_2]}{k_2 [NO_2][NO_2] + k_3 [NO_2][NO_2] + k_4 [NO_3][NO_2]} = \frac{k_4 [NO_3]}{k_2 + 2k_3}$$

Illustration 4.2 (p.122) by HILL

Problem 4.1 (p.126) by Davis and Davis

(consistent)
Exercise 3:

part a)

An explosion will occur if the rate of termination is less than the rate of branching.

\[
\text{Rate of termination} = k_4 C_B \\
\text{Rate of branching} = k_3 C_A C_R
\]

Therefore, an explosion occurs if \( C_B > \frac{k_4}{k_3} \).

part b)

Write the rates of accumulation for both \( A \) and \( R \).

\[
\frac{dC_A}{dt} = k_2 C_J C_R + k_3 C_A C_R
\]  

\[
\frac{dC_R}{dt} = k_1 C_J - k_3 C_A C_R + 2k_3 C_R C_B - k_4 C_R
\]

Using the steady-state approximation to set \( \frac{dC_B}{dt} = 0 \) and find an expression for \( C_B \).

\[
C_B = \frac{-k_3 C_A}{k_3 C_A - k_4}
\]

Substitute equation (5) into equation (3) to find the overall reaction rate.

\[
\text{rate} = -\frac{dC_A}{dt} = \frac{(k_2 + k_1)k_2 C_J C_R}{k_2 - k_3 C_A}
\]
Exercise 8:

Proposed mechanism:

\[
\begin{align*}
Br + H_2 &\rightarrow HBr + H \\
H + Br_2 &\rightarrow HBr + Br \\
Br_2 &\rightarrow 2Br
\end{align*}
\]

Since equation (3) is equilibrated,

\[
K_3 = \frac{[Br]^2}{[Br_2]} \quad \text{or} \quad [Br] = K_3^{1/2}[Br_2]^{1/2}
\]

Using equations (1)-(3), write the expression for the change in concentration of dihydrogen with time.

\[
\frac{d[H_2]}{dt} = -k_1[Br][H_2] + k_2[HBr][H] \tag{5}
\]

Using equations (1)-(3), write the expression for the change in concentration of hydrogen, \( H \), with time.

\[
\frac{d[H]}{dt} = k_1[Br][H_2] - k_{r_1}[HBr][H] - k_{r_2}[H][Br_2] \tag{6}
\]

Since at steady state, \( \frac{d[H]}{dt} = 0 \), the concentration of \( H \) can be determined. After simplifying,

\[
[H] = \frac{k_1[Br][H_2]}{k_{r_1}[HBr] + k_{r_2}[Br_2]} \tag{7}
\]

After substituting equations (4) and (7) into the expression for the reaction rate, equation (5), the result is

\[
r = \frac{d[H_2]}{dt} = \frac{k_1K_3^{1/2}[Br_2]^{1/2}[H_2]}{1 + \frac{k_{r_1}[HBr]}{k_2[Br_2]}} \tag{8}
\]

Therefore, \( \alpha_1 = k_1K_3^{1/2} \) and \( \alpha_2 = \frac{k_{r_1}}{k_2} \).