Topic 7C - Reaction Mechanisms

Mechanisms of Chemical Reactions

Elementary Reaction Steps

Sum must equal stoichiometric reaction

Reaction intermediates

Rate-determining step (RDS)

Reaction Molecularity

Uni -
Bi -
Ter -

Reaction order and rate law gives molecularity of RDS

Reaction Mechanism and Equilibrium Constant

At equilibrium, all elementary steps of a reaction's mechanism must be at equilibrium, and for each step:

$$K_i = \frac{k_i}{k_{-i}}$$

That is, the equilibrium constant is the ratio of the rate constants of the forward and reverse reactions. This is the principle of detailed balance or Microscopic Reversibility.

so that

$$K = K_1 \cdot K_2 \cdot K_3 \cdot \ldots = \frac{k_1 k_2 k_3 \ \ldots}{k_{-1} k_{-2} k_{-3} \ \ldots}$$

For the following reaction, for example,

$$2\ NO + 2\ H_2 \rightleftarrows N_2 + 2\ H_2O$$

the mechanism is:

$$NO + NO \underset{k_{-1}}{\longleftarrow} \xrightarrow{k_1} N_2O_2$$

$$N_2O_2 + H_2 \underset{k_{-2}}{\longleftarrow} \xrightarrow{k_2} N_2O + H_2O$$

$$N_2O + H_2 \underset{k_{-3}}{\longleftarrow} \xrightarrow{k_3} N_2 + H_2O$$

At equilibrium, the **rate** (<u>not</u> rate constant) of <u>each</u> **elementary step** in the forward direction equals the rate in the reverse direction. Thus,

$$k_1\,[NO]^2 = k_{-1}\,[N_2O_2]$$

$$k_2\,[N_2O_2]\,[H_2] = k_{-2}\,[N_2O]\,[H_2O]$$

$$k_3\,[N_2O]\,[H_2] = k_{-3}\,[N_2]\,[H_2O]$$

The equilibrium constant, K_i, for each step is thus the ratio of the rate constants for the forward and reverse reactions:

$$K_1 = \frac{[N_2O_2]}{[NO]^2} = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{[N_2O][H_2O]}{[N_2O_2][H_2]} = \frac{k_2}{k_{-2}}$$

$$K_3 = \frac{[N_2][H_2O]}{[N_2O][H_2]} = \frac{k_3}{k_{-3}}$$

The overall equilibrium constant is the product of the equilibrium constants for all steps:

$$K = K_1K_2K_3 = \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}}$$

$$= \frac{[N_2O_2]\,[N_2O]\,[H_2O]\,[N_2]\,[H_2O]}{[NO]^2[N_2O_2]\,[H_2]\,[N_2O]\,[H_2]}$$

$$= \frac{[N_2]\,[H_2O]^2}{[NO]^2[H_2]^2}$$

TABLE 15.7 **Examples of Elementary Steps and Corresponding Rate Laws**

Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ products	*Uni*molecular	Rate $= k[A]$
$A + A \longrightarrow$ products ($2A \longrightarrow$ products)	*Bi*molecular	Rate $= k[A]^2$
$A + B \longrightarrow$ products	*Bi*molecular	Rate $= k[A][B]$
$A + A + B \longrightarrow$ products ($2A + B \longrightarrow$ products)	*Ter*molecular	Rate $= k[A]^2[B]$
$A + B + C \longrightarrow$ products	*Ter*molecular	Rate $= k[A][B][C]$

Reaction Orders vs. Mechanisms

If the first step is the RDS:

$$2\,NO_2 + F_2 \rightarrow 2\,NO_2F$$

$$\text{Rate} = k\,[NO_2]\,[F_2]$$

Mechanism:

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{(slow)}$$

$$NO_2 + F \xrightarrow{k_2} NO_2F \qquad \text{(fast)}$$

$$NO_2 + CO \rightarrow NO + CO_2$$

$$\text{Rate} = k\,[NO_2]^2$$

Mechanism:

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \qquad \text{(slow)}$$

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \qquad \text{(fast)}$$

If the first step is a rapid equilibrium that is followed by a slow step:

$$H_2 + I_2 \rightarrow 2\ HI$$

$$\text{Rate} = k\ [H_2]\ [I_2]$$

Mechanism:

$I_2 \overset{K}{\longleftrightarrow} 2\ I$ (rapid equilibrium)

$H_2 + 2\ I \xrightarrow{k'} 2\ HI$ (slow)

For which the rate is given by:

$$\text{Rate} = k'\ [H_2]\ [I]^2$$

But since

$$K = \frac{[I]^2}{[I_2]} \quad \text{then} \quad [I]^2 = K[I_2]$$

then

$$\text{Rate} = k'K\ [H_2]\ [I_2] = k\ [H_2]\ [I_2]$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$\text{Rate} = k\,[NO]^2[O_2]$$

Mechanism:

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(rapid equilibrium)}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2 \qquad \text{(slow)}$$

For which the rate is given by:

$$\text{Rate} = k_2[N_2O_2]\ [O_2]$$

But since

$$K_1 = \frac{[N_2O_2]}{[NO]^2} = \frac{k_1}{k_{-1}} \quad \text{then} \quad [N_2O_2] = K_1[NO]^2$$

then

$$\text{Rate} = k_2K_1[NO]^2[O_2] = k\,[NO]^2[O_2]$$

For a multi-step mechanism with rapid equilibration:

$$Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$$

$$\text{Rate} = k\,[Cl_2]^{1/2}[CHCl_3]$$

Mechanism:

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl \quad \text{(rapid equilibration)}$$

$$Cl + CHCl_3 \xrightarrow{k_2} HCl + CCl_3 \quad \text{(slow)}$$

$$CCl_3 + Cl \xrightarrow{k_3} CCl_4 \quad \text{(fast)}$$

For which the rate is given by:

$$\text{Rate} = k_2[Cl]\,[CHCl_3]$$

But since

$$k_1[Cl_2] = k_{-1}[Cl]^2 \quad \text{and} \quad [Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}$$

then

$$\text{Rate} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}[CHCl_3]$$

$$= k[Cl_2]^{1/2}[CHCl_3]$$

Steady-State Approximation

For reactions that have no single slow step, can make the assumption that the concentration of an intermediate remains essentially constant during reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

The rate of <u>formation</u> of B is given by:

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A]$$

The rate of <u>disappearance</u> of B is given by:

$$\text{Rate} = k_{-1}[B] + k_2[B]$$

Thus, the <u>net</u> rate of change of [B] is:

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

Assume that the "Steady-State" concentration of B remains essentially constant during reaction, *i.e.*, the <u>net</u> rate of change of [B] is zero:

$$\frac{d[B]}{dt} = 0$$

Then

$$\frac{d[B]}{dt} = 0 = k_1[A] - k_{-1}[B] - k_2[B]$$

Solving for [B] gives:

$$[B] = \frac{k_1[A]}{k_{-1} + k_2}$$

The overall rate of reaction is thus:

$$\text{Rate} = \frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2[A]}{k_{-1} + k_2}$$

If $k_2 >> k_{-1}$ (*i.e.*, second step is fast), then

$$\text{Rate} \approx k_1[A]$$

If $k_2 << k_{-1}$ (*i.e.*, second step is slow), then

$$\text{Rate} \approx \frac{k_1}{k_{-1}} k_2[A] = K_1 k_2[A]$$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

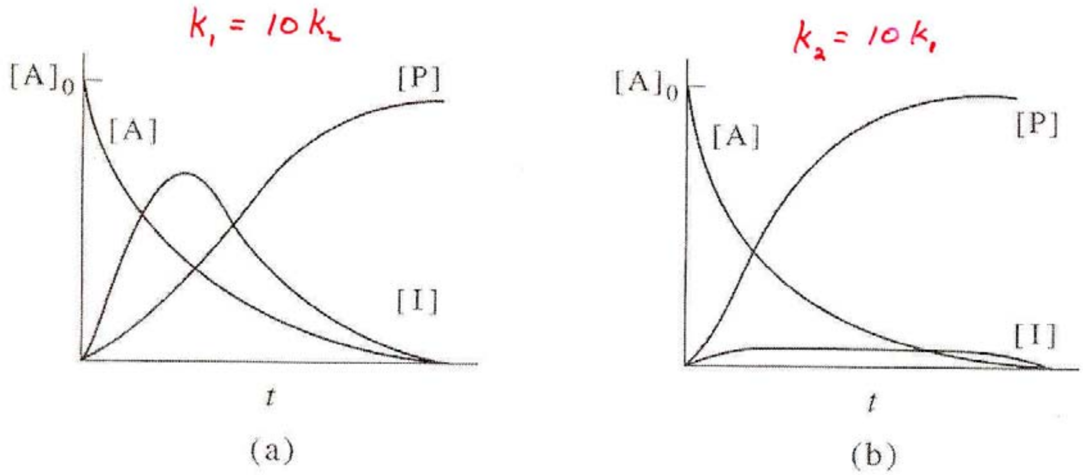

FIGURE 27.1

Concentration profiles for the consecutive reaction scheme $A \xrightarrow{k_1} I \xrightarrow{k_2} P$ with initial concentrations $[A] = [A]_0$, and $[I]_0 = [P]_0 = 0$. (a) $k_1 = 10k_2$: The concentration of I rises and then decays, changing significantly during the course of the reaction; (b) $k_2 = 10k_1$: The concentration of I rapidly builds up to a constant, but negligible, concentration that persists for a large extent of the reaction. In this case, the steady-state approximation can be applied to [I].