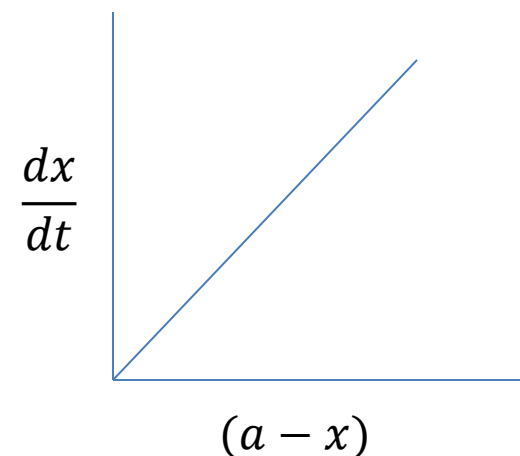


2 (ii) Kinetic Requirements

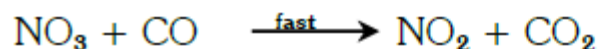
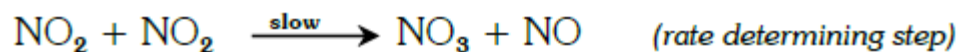
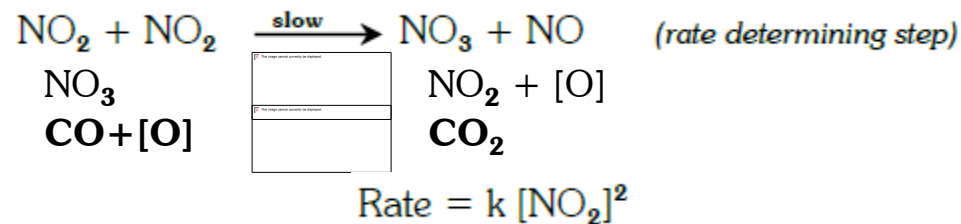
Order	Differential Form	Integrated Form
Zero Order	$\frac{dx}{dt} = k$	$x = k t$
First Order	$\frac{dx}{dt} = k(a - x)$	$k = \frac{2.303}{t} \log \frac{a}{(a - x)}$
Second Order	$\frac{dx}{dt} = k(a - x)^2$	$k = \frac{1}{t} \frac{x}{a(a - x)}$



Example 1



$$\text{Rate} = k [\text{NO}_2]^2$$



$$\text{Rate} = k [\text{NO}_2]^2$$

Kinetic evidence is a NECESSARY CONDITION for reaction mechanism but NOT A SUFFICIENT CONDITION

Example 2: Formation of thioethers



$$\text{rate} = k_2[\text{MeSNa}][\text{MeI}]$$

If $[\text{MeSNa}]$ is constant, the equation becomes

$$\text{rate} = k_a[\text{MeI}] \text{ where } k_a = k_2[\text{MeSNa}]$$

If $[\text{MeI}]$ is constant, the equation becomes

$$\text{rate} = k_b[\text{MeSNa}] \text{ where } k_b = k_2[\text{MeI}]$$

If you examine the graphs you will see that the slopes are different because

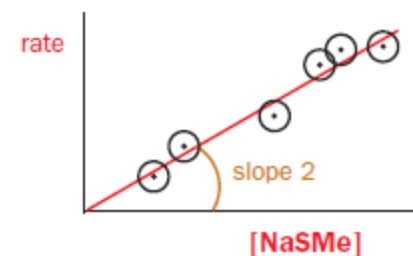
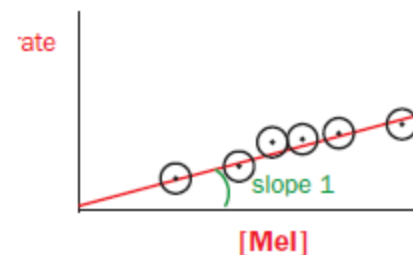
$$\text{slope 1} = k_a = k_2[\text{MeSNa}], \text{ but slope 2} = k_b = k_2[\text{MeI}]$$

The rate of S_N2 reaction depends upon

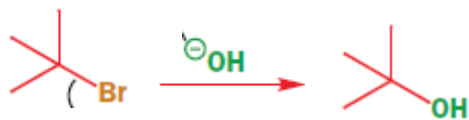
(i) The nucleophile

(ii) The carbon skeleton (Structure of substrate)

(iii) The leaving group



Example 3: Hydrolysis of *t*-butyl bromide

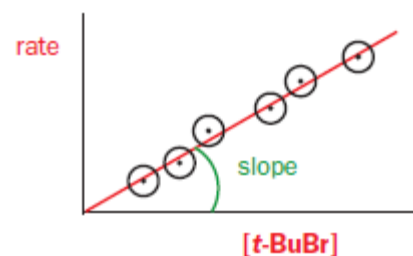


$$\text{rate} = k_1[\text{t-BuBr}]$$

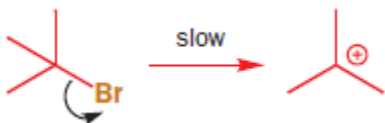
The rate of S_N1 reaction depends upon

(i) The carbon skeleton (Structure of substrate)

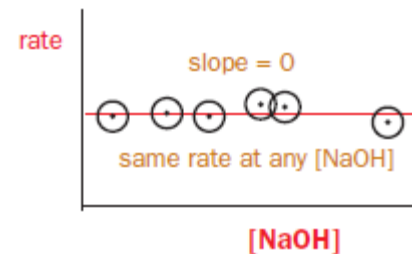
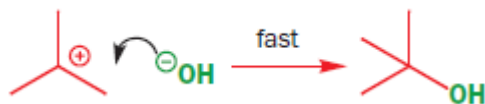
(ii) The leaving group



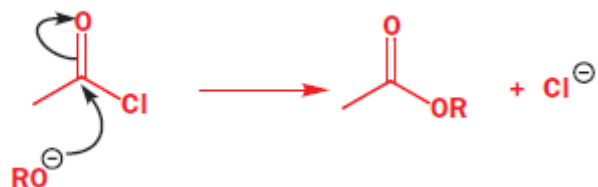
Step-I



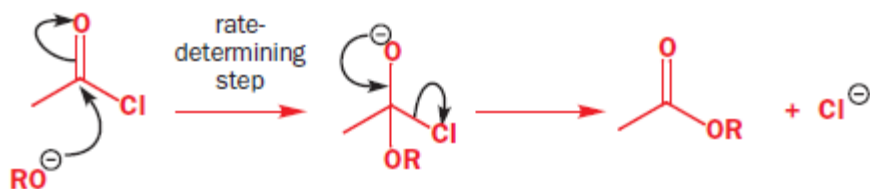
Step-II



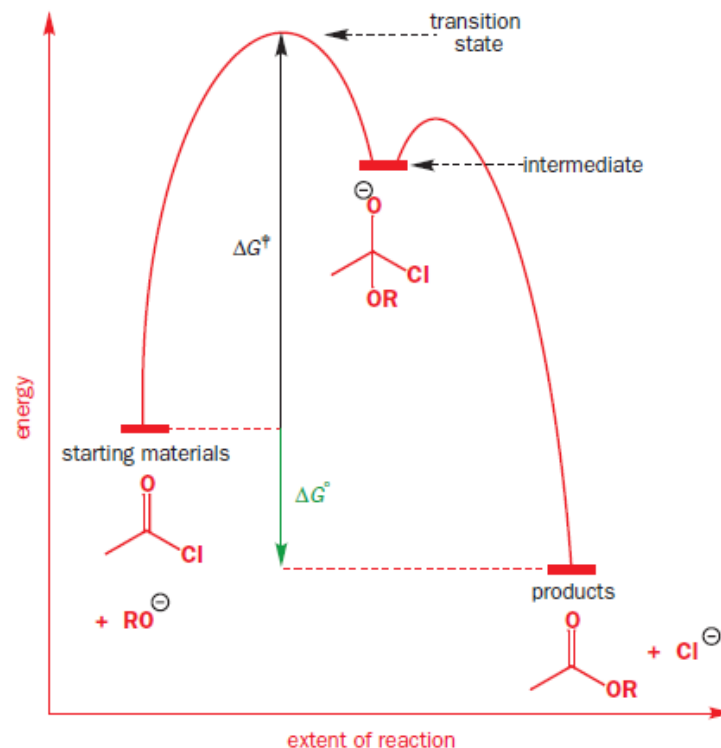
Example 4: Conversion of acid chlorides into esters



$$\text{rate} = k[\text{MeCOCl}][\text{RO}^-]$$



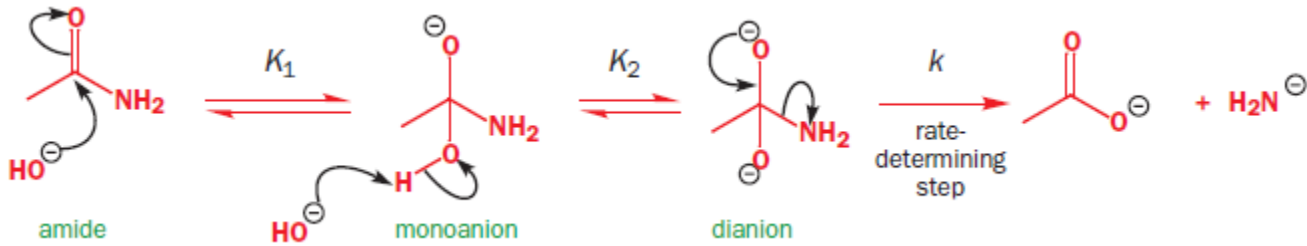
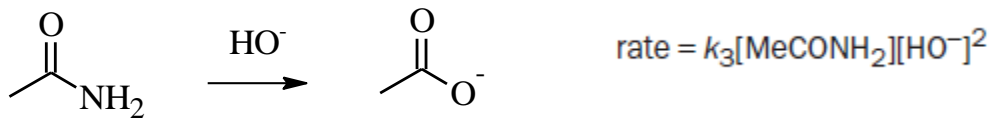
Mechanism is addition-elimination with a tetrahedral intermediate



Intermediates and transition states

A transition state represents an energy maximum—any small displacement leads to a more stable product. An intermediate, on the other hand, is a molecule or ion that represents a *localized* energy minimum—an energy barrier must be overcome before the intermediate forms something more stable. As you have seen in Chapter

Example 5: Hydrolysis of Amides



The rate of the reaction is the rate of the rate-determining step
 $\text{rate} = k[\text{dianion}]$

We don't know the concentration of the dianion but we do know that it's in equilibrium with the monoanion so we can write

$$K_2 = \frac{[\text{dianion}]}{[\text{monoanion}][\text{HO}^-]}$$

and so $[\text{dianion}] = K_2[\text{monoanion}][\text{HO}^-]$

In the same way we don't want the unknown [monoanion] in our rate expression and we can get rid of it using the first equilibrium

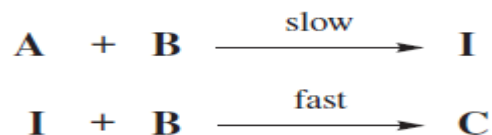
$$K_1 = \frac{[\text{monoanion}]}{[\text{amide}][\text{HO}^-]}$$

and so $[\text{monoanion}] = K_1[\text{amide}][\text{HO}^-]$

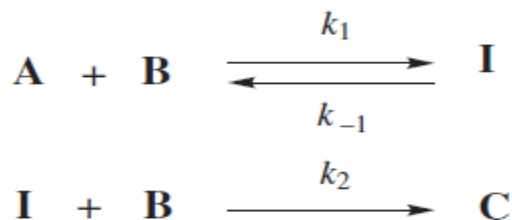
Hence $[\text{dianion}] = K_1K_2[\text{amide}][\text{HO}^-][\text{HO}^-]$

Substituting these values in the simple rate equation we discover that $\text{rate} = k[\text{dianion}]$ becomes
 $\text{rate} = kK_1K_2[\text{amide}][\text{HO}^-]^2$

Steady State Approximation



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



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

$$\text{Rate of appearance of I} = k_1[\text{A}][\text{B}]$$

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

$$\text{Rate of appearance of I} = \text{Rate of disappearance of I} \quad \text{i.e. } \frac{d[\text{I}]}{dt} = 0$$

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

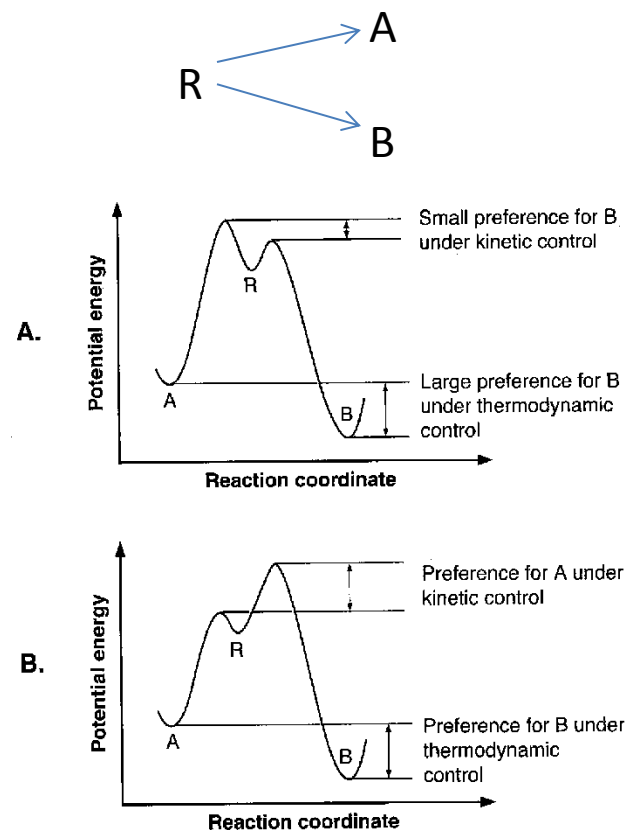
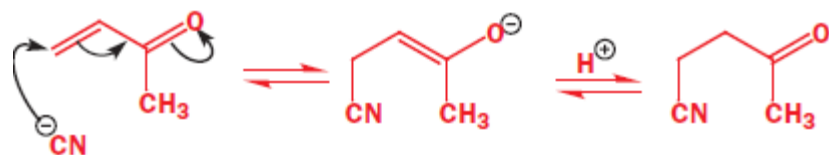
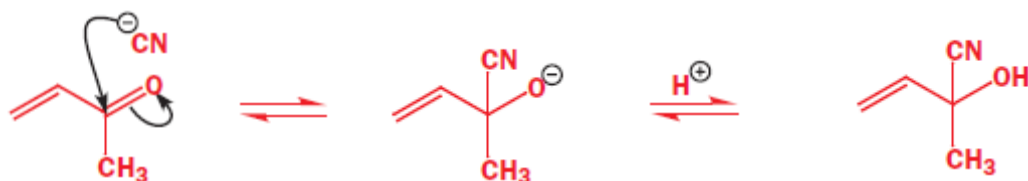
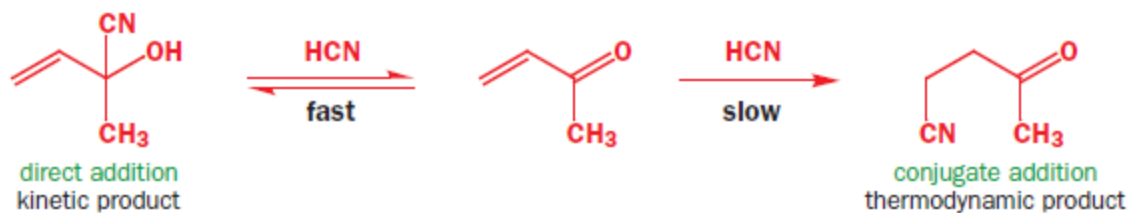
$$\text{or } [\text{I}] = \frac{k_1[\text{A}][\text{B}]}{k_{-1} + k_2[\text{B}]}$$

$$\text{Rate} = \frac{k_1[\text{A}][\text{B}][\text{B}]}{k_{-1} + k_2[\text{B}]} = \frac{k_1[\text{A}][\text{B}]^2}{k_{-1} + k_2[\text{B}]}$$

first step was faster than the second, $k_1[\text{A}][\text{B}] \gg k_2[\text{I}][\text{B}]$ $\text{Rate} = k_1[\text{A}][\text{B}]^2$ *Third Order*

if the first step is rate determining $k_2[\text{B}] \gg k_{-1}$ $\text{Rate} = \frac{k_1[\text{A}][\text{B}]^2}{k_2[\text{B}]} = k[\text{A}][\text{B}]$ *Second Order*

Kinetic vs Thermodynamic control



Kinetic and thermodynamic control

- The product that forms faster is called the **kinetic product**
 - The product that is the more stable is called the **thermodynamic product**
- Similarly,
- Conditions that give rise to the kinetic product are called **kinetic control**
 - Conditions that give rise to the thermodynamic product are called **thermodynamic control**

