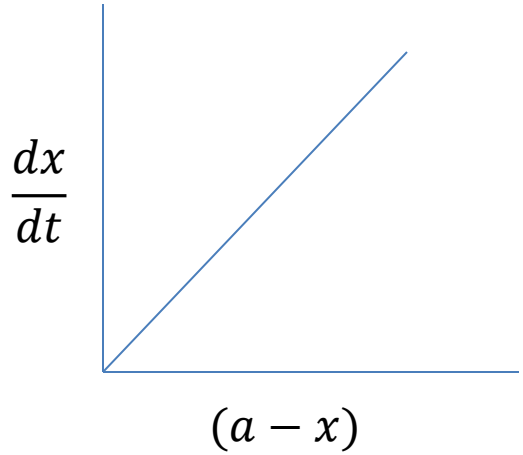
2 (ii) Kinetic Requirements

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

$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$

Rate = k $[NO_2]^2$

$NO_2 + NO_2 \xrightarrow{\text{slow}} NO_3 + NO$ *(rate determining step)*

NO_3

CO+[O]

$NO_2 + [O]$

CO_2

Rate = k $[NO_2]^2$

$NO_2 + NO_2 \xrightarrow{\text{slow}} NO_3 + NO$ *(rate determining step)*

$NO_3 + CO \xrightarrow{\text{fast}} NO_2 + CO_2$

Rate = k $[NO_2]^2$

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

Example 2: Formation of thioethers

rate = k_2[MeSNa][MeI]

If [MeSNa] is constant, the equation becomes

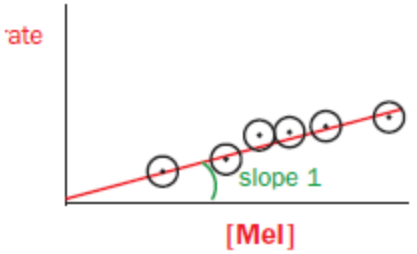
rate = k_a[MeI] where $k_a = k_2$[MeSNa]

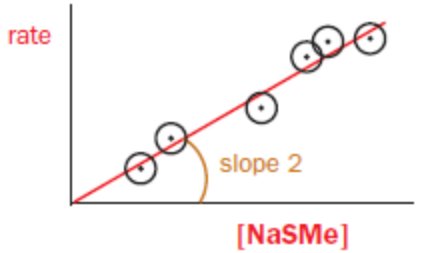
If [MeI] is constant, the equation becomes

rate = k_b[MeSNa] where $k_b = k_2$[MeI]

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

slope 1 = $k_a = k_2$[MeSNa], but slope 2 = $k_b = k_2$[MeI]

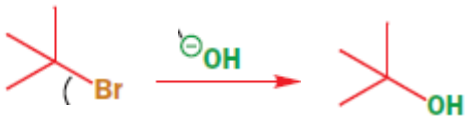




The rate of S_N2 reaction depends upon

(I) The nucelophile **(ii) The carbon skeleton (Structure of substrate)** **(iii) The leaving group**

Example 3: Hydrolysis of *t*-butyl bromide

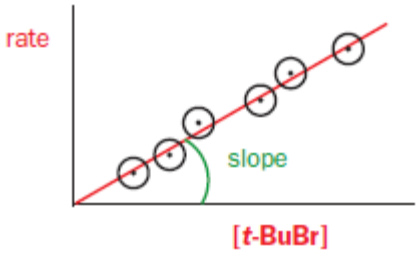


rate = k_1[*t*-BuBr]

The rate of S_N1 reaction depends upon

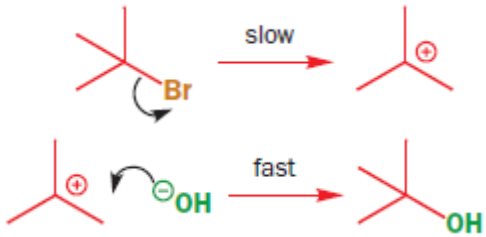
(i) The carbon skeleton (Structure of substrate)

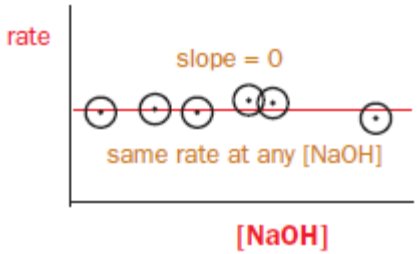
(ii) The leaving group



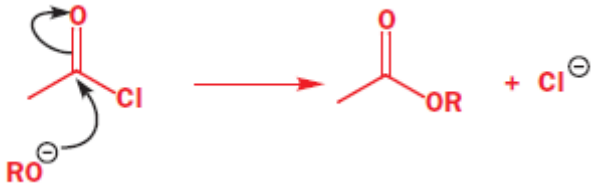
Step-I

Step-II

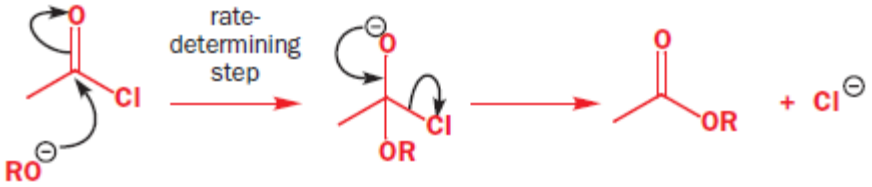




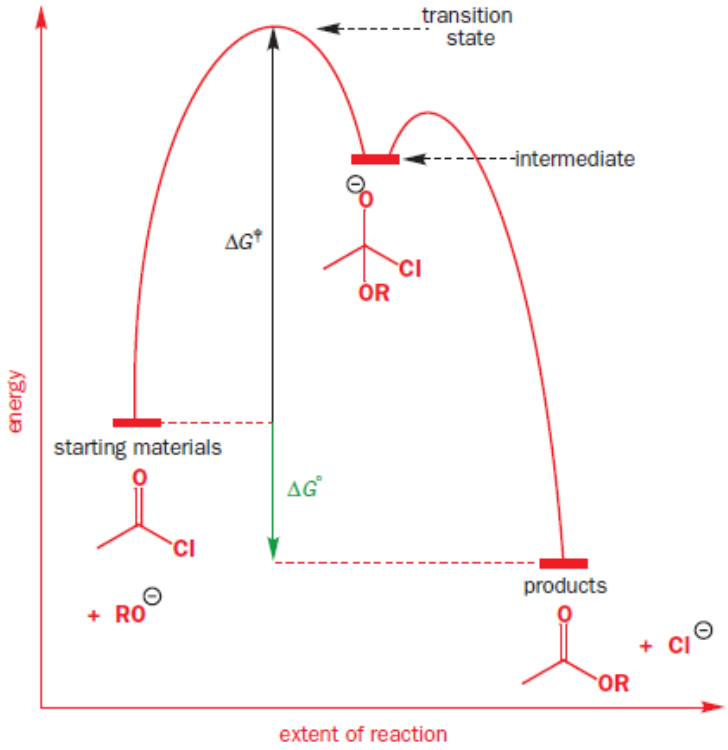
Example 4: Conversion of acid chlorides into esters



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



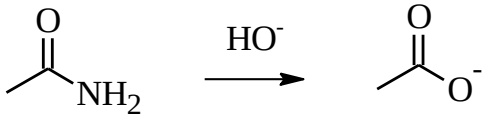
Mechanism is addition-elimination with a tetrahedral intermediate



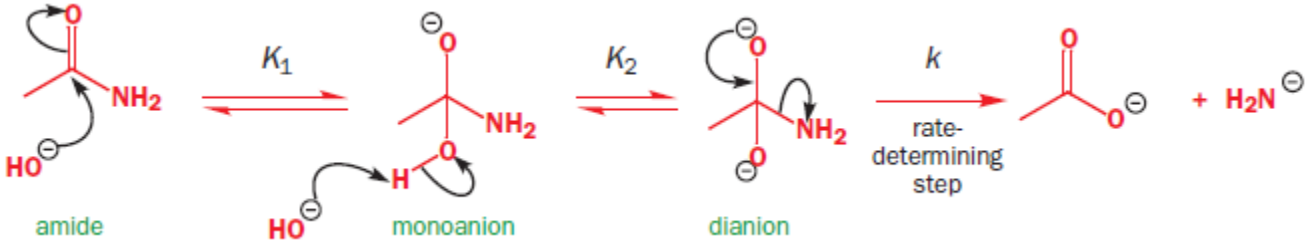
Intermediates and transition states

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



$$\text{rate} = k_3[\text{MeCONH}_2][\text{HO}^-]^2$$



The rate of the reaction is the rate of the rate-determining step

rate = k[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 [dianion] = K_2[monanion][HO^-]

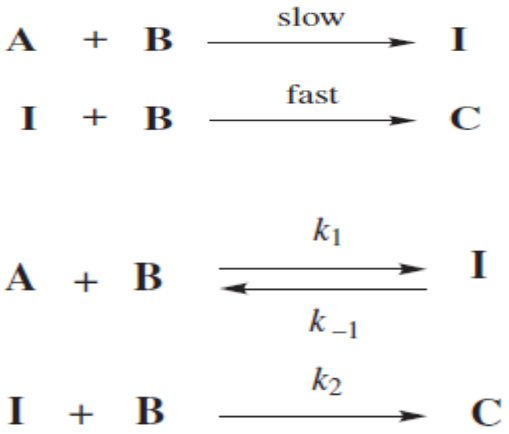
In the same way we don't want the unknown [monoanion] in our rate expression and we can get rid of it using the first equilibrium

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

and so [monoanion] = K_1[amide][HO^-] Hence [dianion] = K_1K_2[amide][HO^-][HO^-]

Substituting these values in the simple rate equation we discover that rate = k[dianion] becomes

rate = kK_1K_2[amide][HO^-]^2



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

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

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

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

$$Rate\ of\ appearance\ of\ I = Rate\ of\ dissapearnance\ of\ I \qquad i.e.\ \frac{d[I]}{dt} = 0$$

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

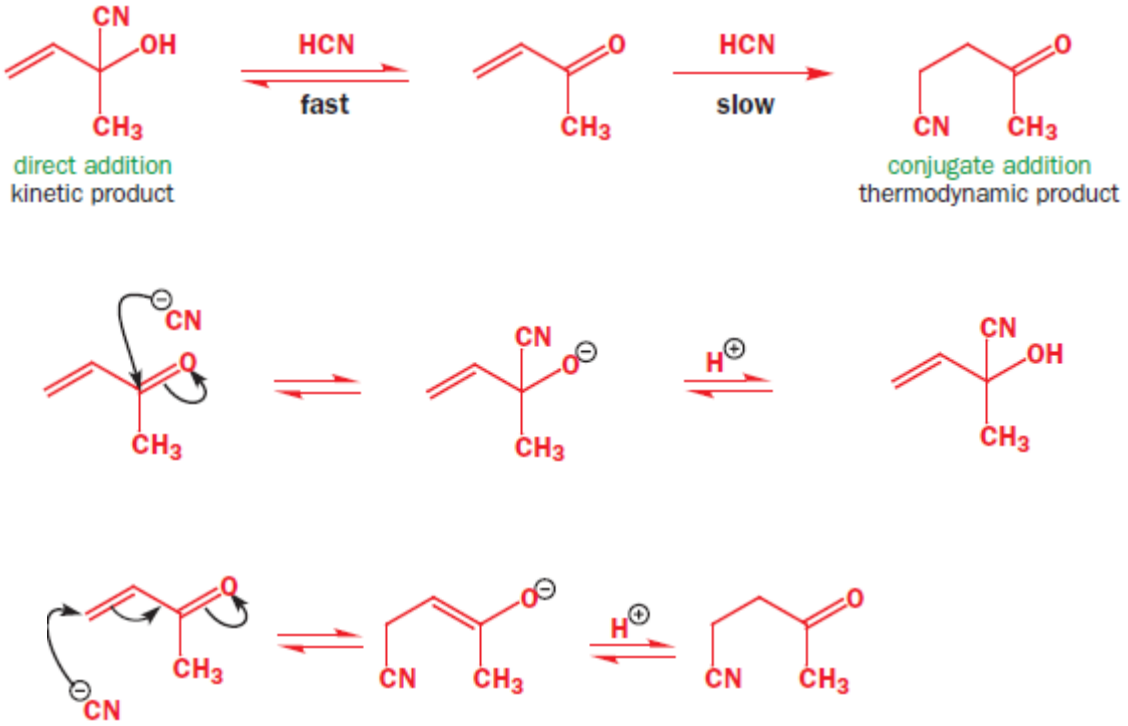
$$\text{or } [I] = \frac{k_1[A][B]}{k_{-1} + k_2[B]}$$

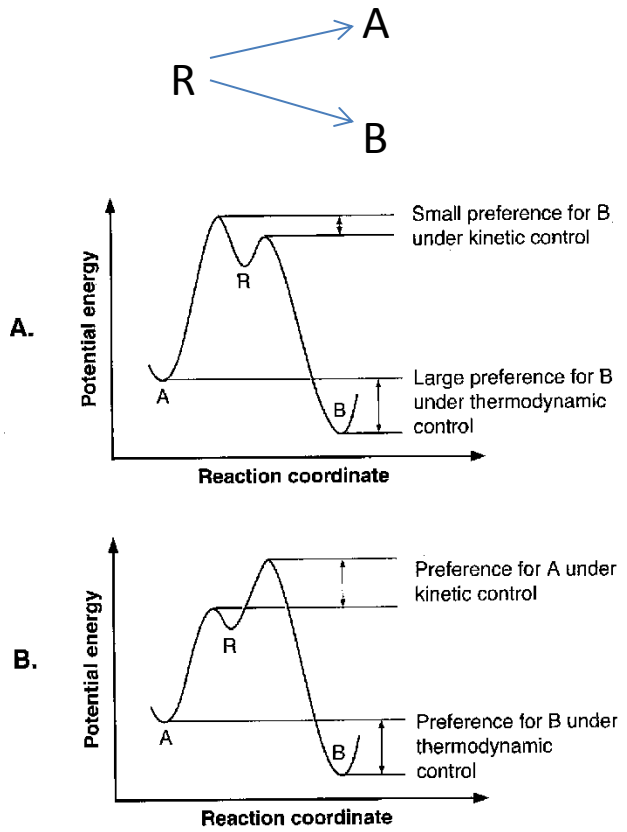
$$Rate = \frac{k_1[A][B][B]}{k_{-1} + k_2[B]} = \frac{k_1[A][B]2}{k_{-1} + k_2[B]}$$

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

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

Kinetic vs Thermodynamic control



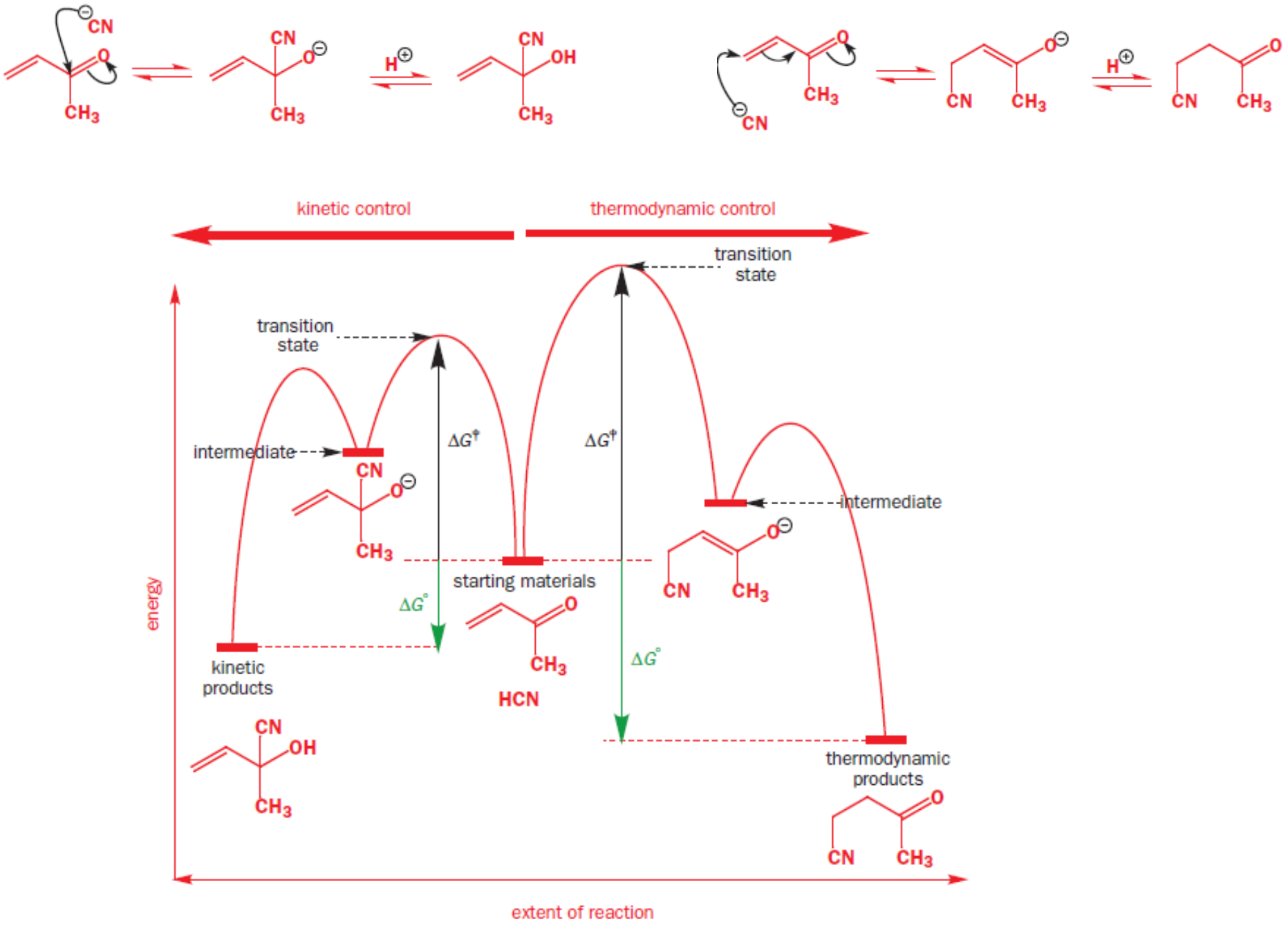


Kinetic and thermodynamic control

- 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**


kinetic control
thermodynamic control
transition state
transition state
intermediate
intermediate
starting materials
kinetic products
HCN
thermodynamic products
energy
extent of reaction
ΔG‡
ΔG‡
ΔG°
ΔG°
CN
OH
CH3
O
H