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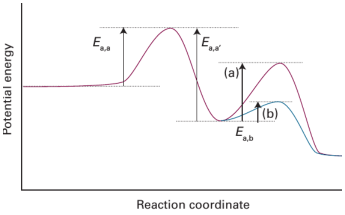

3 activation energies to take into account:

two referring to reversible steps of pre-equilibrium and one for final step

relative magnitudes of activation energies determine

overall activation energy (a) > 0 or (b) < 0

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same as before for $k'_a \gg k_b$

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secondary : bond involving isotope not broken form product

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$$
\begin{aligned}
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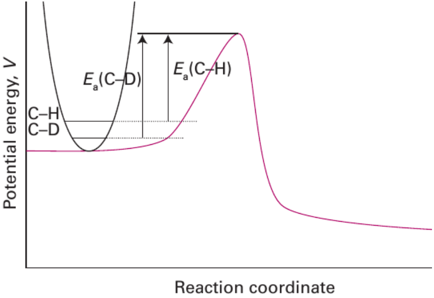

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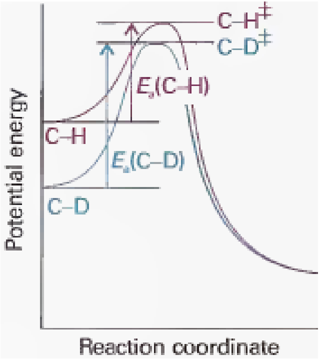

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conclusion supported by a number of experimental observations

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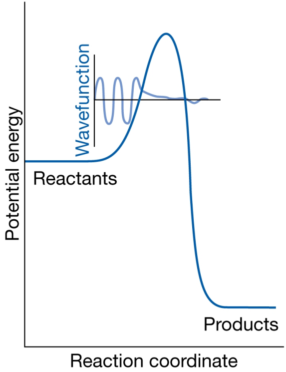
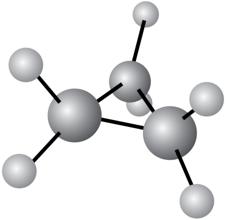
probability of tunnelling through a barrier decreases as mass of particle increases, so D tunnels less efficiently than H and its reactions are slower

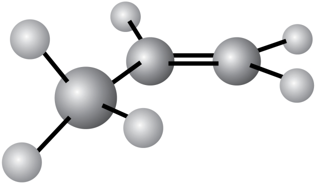


unimolecular process: example



1 Cyclopropane

$\longrightarrow$

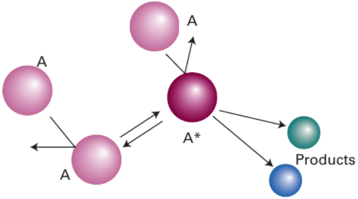


2 Propene

Lindemann-Hinshelwood mechanism

Assumpn. : reactant molecule A becomes energetically excited by collision with another molecule in a bimolecular step

$$\text{activation : } A+A \xrightarrow{k_a} A^*$$
$$\text{deactivation : } A+A^* \longrightarrow 2A$$
$$\text{reaction : } A^* \longrightarrow P$$



$$\mathrm{A} \underset{k_a'}{\overset{k_a}{\leftrightarrows}} \mathrm{A}^* \xrightarrow{k_b} \mathrm{P}$$

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k_a'[A][A^*] - k_b[A^*] = 0 \text{ (s.s.)}$$

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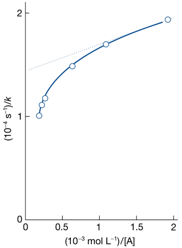
generally, equating the empirical and theoretical expressions,

rate$= k[A] = k_b[A^*] = \frac{k_b k_a [A]^2}{k_b + k_a'[A]}$

or, $\frac{1}{k} = \frac{k_a'}{k_a k_b} + \frac{1}{k_a[A]}$



unimolecular isomerization of trans-CHD=CHD shows departure from straight line predicted by L-H mechanism

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$$N^* = \frac{(n-n^*+s-1)!}{(n-n^*)!(s-1)!}$$

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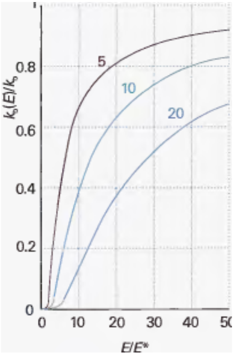
$k_b(E) = \left(1 - \frac{E^*}{E}\right)^{s-1} k_b$ for $E \geq E^*$



Energy dependence of rate constant for three values of s

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consider the high-pressure limit of the L-H mechanism

$$k = \frac{k_a k_b}{k'_a} = \frac{\left(A_a e^{-\frac{E_a}{RT}}\right)\left(A_b e^{-\frac{E_b}{RT}}\right)}{\left(A_{a'} e^{-\frac{E_{a'}}{RT}}\right)}$$

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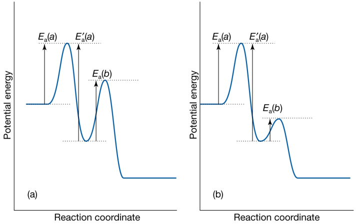
reaction with a pre-equilibrium: 3 activation energies to take into account



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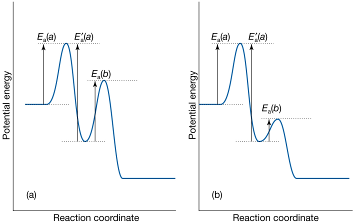

There are reactions in which negative activation energy is observed

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Ex., $CH_3CHO(g) \longrightarrow CH_4\ (g) + CO(g)$; $\quad v = k[CH_3CHO]^{\frac{3}{2}}$

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Initiation	$CH_3CHO \rightarrow .CH_3 + \cdot CHO$	$v = k_i[CH_3CHO]$
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mechanism does not explain other by-products like propanone and propanal

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

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Initiation:

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	$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	$v = k_p'[H\cdot][Br_2]$
Retardation:	$H\cdot + HBr \rightarrow H_2 + Br\cdot$	$v = k_r[H\cdot][HBr]$
Termination:	$Br\cdot + Br\cdot + M \rightarrow Br_2 + M^*$	$v = k_t[Br\cdot]^2[M]$

M is either Br_2 or H_2.

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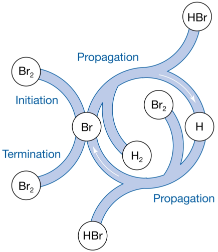
net rate:

$$\frac{d[HBr]}{dt} = k_p[Br][H_2] + k_{p'}[H][Br_2] - k_r[H][HBr]$$



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using $k_{p'}[\mathrm{H}][\mathrm{Br}_2] = k_p[\mathrm{Br}][\mathrm{H}_2] - k_r[\mathrm{H}][\mathrm{HBr}]$

$\therefore$ net rate: $\frac{d[\mathrm{HBr}]}{dt} = 2k_{p'}[\mathrm{H}][\mathrm{Br}_2]$

$$= \frac{2k_p\sqrt{\frac{k_i}{k_t}}[\mathrm{H}_2][\mathrm{Br}_2]^{\frac{3}{2}}}{[\mathrm{Br}_2]+\frac{k_r}{k_{p'}}[\mathrm{HBr}]} = \frac{k[\mathrm{H}_2][\mathrm{Br}_2]^{\frac{3}{2}}}{[\mathrm{Br}_2]+k'[\mathrm{HBr}]}$$

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Reaction slows down as HBr forms, $\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}$ increases $\Leftarrow$

Br_2 competes with HBr for H atoms, with propagation

H + Br_2 $\rightarrow$ HBr + Br yielding HBr

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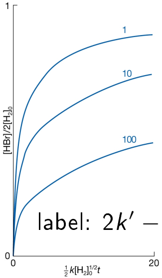
numerical integrn :



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$\therefore$ net rate: $\frac{d[\mathrm{HBr}]}{dt} = 2k_{p'}[\mathrm{H}][\mathrm{Br_2}]$

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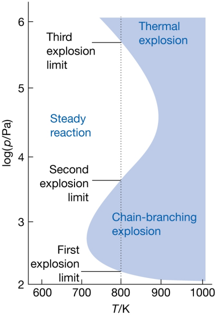
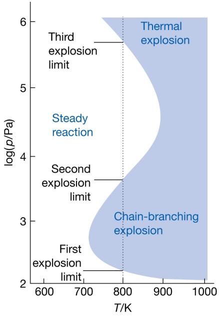
Ex. $2H_2(g)+O_2(g)\rightarrow 2H_2O(g)$



		v
Initiation :	$H_2 \rightarrow H\cdot + H\cdot$	constant (v_{init})
Propagation :	$H_2 + \cdot OH \rightarrow H\cdot + H_2O$	$k_p[H_2][\cdot OH]$
Branching :	$\cdot O_2\cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
	$\cdot O\cdot + H_2 \rightarrow \cdot OH + \cdot H$	$k_b'[\cdot O\cdot][H_2]$
Termination :	$H\cdot + \text{wall} \rightarrow \frac{1}{2}H_2$	$k_t[\cdot H]$
	$H\cdot + O_2 + M \rightarrow HO_2\cdot + M^*$	$k_t'[\cdot H][O_2][M]$



		v
Initiation :	$H_2 \rightarrow H\cdot + H\cdot$	constant (v_{init})
Propagation :	$H_2 + \cdot OH \rightarrow H\cdot + H_2O$	$k_p[H_2][\cdot OH]$
Branching :	$\cdot O_2\cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
	$\cdot O\cdot + H_2 \rightarrow \cdot OH + \cdot H$	$k_b'[\cdot O\cdot][H_2]$
Termination :	$H\cdot + \text{wall} \rightarrow \frac{1}{2}H_2$	$k_t[\cdot H]$
	$H\cdot + O_2 + M \rightarrow HO_2\cdot + M^*$	$k_t'[\cdot H][O_2][M]$
.		.

branching step :

elementary reaction producings more than one chain carrier

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$H_2 \rightarrow H\cdot + H\cdot$	constant (v_{init})
$H_2 + \cdot OH \rightarrow H\cdot + H_2O$	$k_p[H_2][\cdot OH]$
$\cdot O_2\cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
$\cdot O\cdot + H_2 \rightarrow \cdot OH + \cdot H$	$k_b'[\cdot O\cdot][H_2]$
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$H_2 \to H\cdot + H\cdot$	constant (v_{init})
$H_2 + \cdot OH \to H\cdot + H_2O$	$k_p[H_2][\cdot OH]$
$\cdot O_2\cdot + \cdot H \to \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
$\cdot O\cdot + H_2 \to \cdot OH + \cdot H$	$k_b'[\cdot O\cdot][H_2]$
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rate of formation of H· radical, $v_{\text{rad}} \equiv \frac{d[H]}{dt}$

$$v_{rad} = v_{init} + k_p[OH][H_2] - k_b[O_2][H] + k_b'[O][H_2] - k_t[H] - k_t'[H][O_2][M]$$

SS:

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Reaction	v
$H_2 \rightarrow H\cdot + H\cdot$	constant (v_{init})
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$\cdot O_2\cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
$\cdot O\cdot + H_2 \rightarrow \cdot OH + \cdot H$	$k_b'[\cdot O\cdot][H_2]$
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$$= v_{init} + (2k_b[O_2] - k_t - k_t'[O_2][M])[H] = v_{init} + (k_{branch} - k_{term})[H]$$

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$[O_2]$	
low : $k_{term} > k_{branch}$	
high : $k_{branch} > k_{term}$	
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low : $k_{term} > k_{branch}$	$\frac{v_{init}}{k_{term} - k_{branch}}\left(1 - e^{-(k_{term} - k_{branch})t}\right)$
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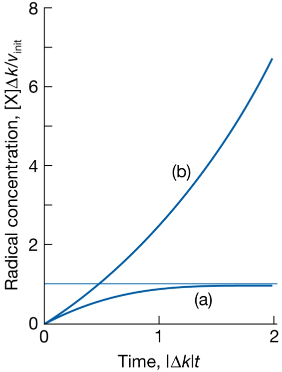

stepwise polymerisation:

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condensation reaction:

ex. Nylon-66

$$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \rightarrow H_2N(CH_2)_6NHCO(CH_2)_4COOH + H_2O$$
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other ex.: polyesters, polyurethanes, etc.

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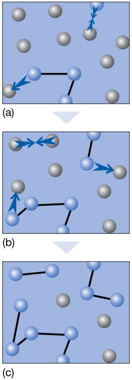
monomers removed early

average molar mass increases in time



.

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$\frac{d[A]}{dt} = -k[A]^2$

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fraction of A groups that have condensed at time t,

$p = \frac{[A]_0 - [A]}{[A]_0} = \frac{kt[A]_0}{1+kt[A]_0}$

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degree of polymerisation: average # monomer residues per polymer molecule

$\langle n \rangle = \frac{[A]_0}{[A]} = \frac{1}{1-p} = 1 + kt[A]_0$

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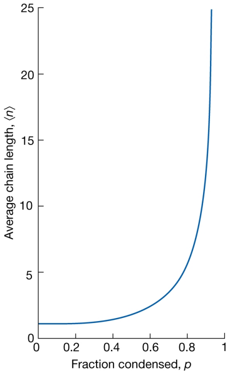
∴ longer a stepwise polymerisation proceeds, higher the average molar mass of product



Chain polymerisation: addition of monomers to a growing polymer
Ex. addition polyerisn of ethene, methyl methacrylate, styrene, etc.
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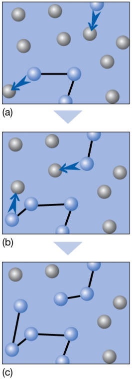

rate, $v = k\sqrt{[I]}[M]$; $I \equiv$ initiator

.

initiation:

initiation: I$\rightarrow$ R$\cdot$+R$\cdot$ $\qquad v_i = k_i[I]$

M+R$\cdot$ $\rightarrow$ $\cdot$M$_1$ (fast) initiation: I$\rightarrow$ R$\cdot$+R$\cdot$ $\qquad v_i = k_i[I]$

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$\vdots$

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termination: $\cdot$M$_n$+$\cdot$M$_m$ $\rightarrow$M$_{n+m}$ (mutual)

$\cdot$M$_n$+$\cdot$M$_m$ $\rightarrow$M$_n$+M$_m$ (disproportionation)

M+$\cdot$M$_n$ $\rightarrow \cdot$M+M$_n$ (chain transfer)

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SS: $\frac{d[\cdot M]}{dt} = 2fk_i[I] - 2k_t[\cdot M]^2 \implies [\cdot M] = \sqrt{\frac{fk_i}{k_t}}[I]^{\frac{1}{2}}$

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SS: $\frac{d[\cdot M]}{dt} = 2fk_i[I] - 2k_t[\cdot M]^2 \implies [\cdot M] = \sqrt{\frac{fk_i}{k_t}}[I]^{\frac{1}{2}}$

rate of propagation = − rate at which the monomer is consumed,
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For mutual termination, $\langle n\rangle = \nu + \nu = 2\nu = 2k[M][I]^{-\frac{1}{2}}$
$\therefore$slower initiation $\implies$ greater chain length≡higher average molar mass