

## < Chemical Kinetics III >

### \* Reaction Mechanism

The sequence of elementary chemical reactions that occur as a fuel is oxidized is termed the reaction mechanism.

H<sub>2</sub> combustion → tens of rxns  
Hydrocarbon → hundreds of rxns.

### \* Chain Reactions.

① Initiation ( The chain is initiated by the production of highly reactive intermediates from stable molecular reactants.

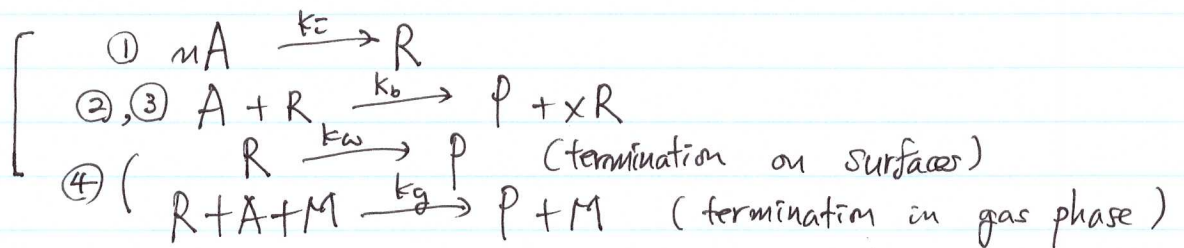
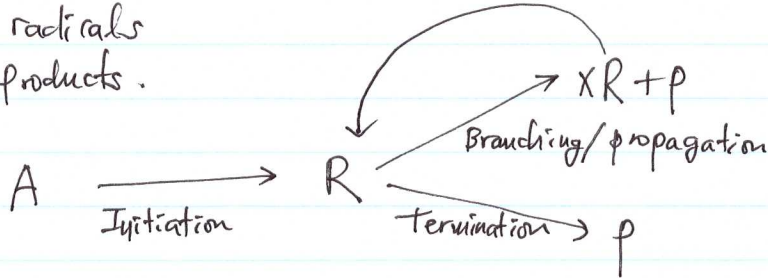
The intermediates are free radical species, e.g. H, O, OH.  
The radicals react with stable molecules.

② Branching - to produce more radicals

③ Propagation - to generate new radicals of same number.

④ Termination - to eliminate radicals.

A: reactants  
R: radicals  
P: products.



$$\frac{d[R]}{dt} = k_i [A]^m + (\alpha - 1) k_b [R][A] - k_g [R][A][M] - k_w [R]$$

$$r_0 \equiv k_i [A]^m$$

$$k_1 \equiv k_b [A]$$

$$k_2 \equiv k_g [A][M] + k_w$$

$$\therefore \frac{d[R]}{dt} = r_0 + (\alpha - 1) k_1 [R] - k_2 [R]$$

$$\frac{d[R]}{dt} = r_0 - \underbrace{(k_1 + k_2)}_{\equiv k_{\text{total}}} [R] \left( 1 - \frac{\alpha k_1}{k_1 + k_2} \right)$$

$$\boxed{\therefore \frac{d[R]}{dt} = r_0 - k_{\text{total}} [R] (1 - \alpha \alpha)}$$

$$\alpha \equiv \frac{k_1}{k_{\text{total}}}$$

$$\frac{d[P]}{dt} = k_{\text{total}} [R]$$

• Case 1 :  $\alpha \alpha = 0$

$\alpha > 0 \quad \therefore \alpha = 0 \Rightarrow$  no R (radical) production.

$$\frac{d[R]}{dt} = r_0 - k_{\text{total}} [R]$$

$\uparrow$  fast removal of radicals  
 $\uparrow$  initiation rxn is very slow.

$$\therefore \frac{d[R]}{dt} \approx 0 = r_0 - k_{\text{total}} [R]$$

$$\Rightarrow \frac{d[P]}{dt} = r_0 \Leftarrow \text{very slow rxn.}$$

Non-explosive

• Case 2 :  $0 < \alpha \alpha < 1$

Assumption.  $k_{\text{total}}$  &  $r_0 = \text{constant}$ .

$\Leftrightarrow$  no depletion of reactants &  $T = \text{constant}$ .

$$R = R(t)$$

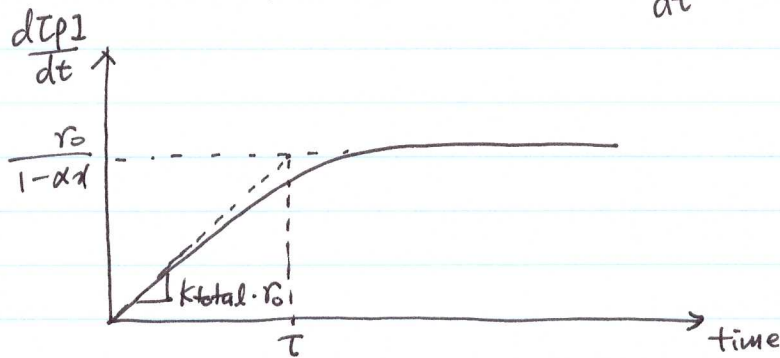
then,  $\frac{d[R]}{dt} = r_0 - k_{\text{total}} [R] (1 - \alpha \alpha)$  is a first-order O.D.E.

$$\Rightarrow [R] = \left( \frac{r_0}{k_{\text{total}} (1 - \alpha \alpha)} \right) (1 - \exp(-k_{\text{total}} (1 - \alpha \alpha) t))$$

$$\text{characteristic time } \tau \equiv \frac{1}{k_{\text{total}} (1 - \alpha \alpha)}$$

$$\therefore [R] = r_0 \tau (1 - e^{-\frac{t}{\tau}})$$

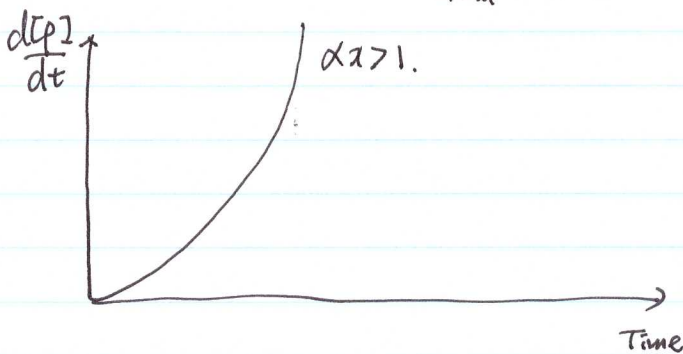
for  $t \ll \tau$ ,  $[R] = r_0 t$   
 $t \gg \tau$ ,  $[R] = r_0 \tau \Rightarrow \frac{d[P]}{dt} = \frac{r_0}{1-\alpha} = \text{constant} > r_0$



• Case 3:  $\alpha > 1$ .  
 $\alpha > 1$ ,  $\tau > 1$

ODE soln:  $[R] = - \left\{ \frac{r_0}{k_{total}(1-\alpha)} \right\} (\exp(k_{total}(\alpha-1)t) - 1)$

$$\tau' \equiv \frac{1}{k_{total}(\alpha-1)}$$



$t \ll \tau'$ ,  $[R] = r_0 t$

$$\frac{d[P]}{dt} = k_{total} r_0 t$$

$t \gg \tau'$ ,  $[R] = r_0 \tau' \exp(t/\tau')$

$$\frac{d[P]}{dt} = - \left[ \frac{r_0}{1-\alpha} \right] \exp(t/\tau') \Rightarrow \text{exponentially increasing.}$$

\*  $\alpha = 1$  is the boundary between fast ( $\alpha > 1$ ) and slow ( $\alpha < 1$ ) rxns

at this limit  $k_1(\alpha-1) = k_2$

recall  $\alpha = \frac{k_1}{k_1+k_2}$ ,  $\alpha\alpha=1 \Rightarrow \frac{\alpha k_1}{k_1+k_2}$ .

$\therefore (\alpha-1)k_b[A] = k_g[A][M] + k_w \leftarrow$  independent of initiation rxn.

$\Rightarrow R \text{ production} = R \text{ removal} \Rightarrow \frac{d[R]}{dt} = 0.$

$\therefore [R]_{\text{gss}} = \frac{k_i[A_i]^m}{(1-\alpha)k_b[A] + k_g[A][M] + k_w}$

Explosive behavior can be expressed by  $[R]_{\text{gss}} \rightarrow \infty$

$\Rightarrow$  denominator = 0.

$\therefore \alpha = 1 + \frac{[A][M] + \frac{k_w}{k_g}}{k_b[A]/k_g} \equiv f$

o if  $\alpha < f \Rightarrow$  slow rxn with steady  $[R]$

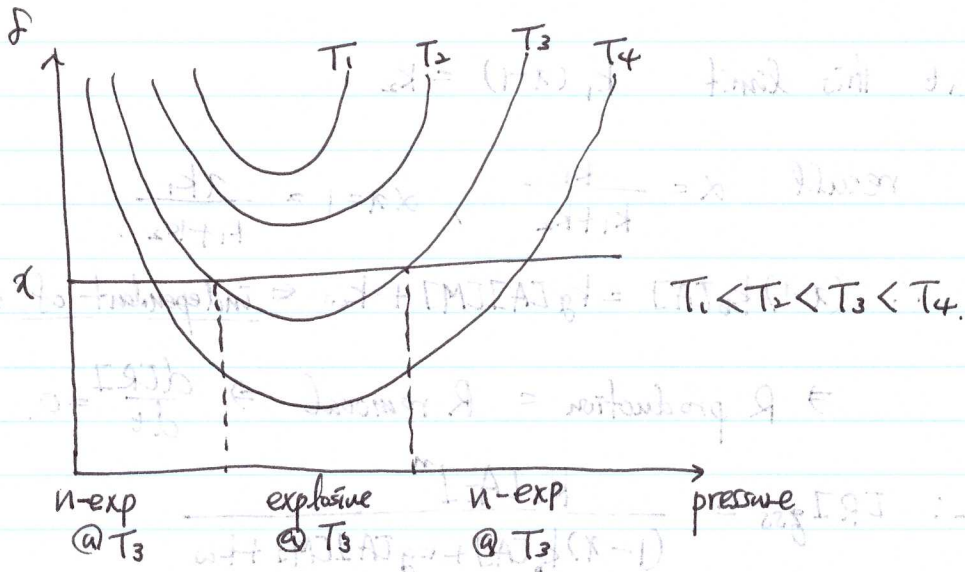
\*  $[M]$  &  $[A]$  are proportional to pressure

$\Rightarrow P \rightarrow \infty \Rightarrow f \rightarrow \infty \therefore \alpha$  is always less than  $f$ .  
 $\Rightarrow$  non-explosive

\* When  $P \rightarrow \infty \Rightarrow f \rightarrow \infty \therefore \alpha$  is always less than  $f$ .  
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o  $k_b/k_g$  increases rapidly with increasing temperature, while  $k_w/k_g$  is a weak function of temperature.  
 $\therefore T \uparrow \Rightarrow f$  decreases.

\* Cross-over temperature: branching and termination rates are equal.



Explosive behavior can be explained by ...

$$\gamma = \frac{C_p}{C_v} + 1 = 5 \dots$$

...  $\gamma < 5$  ...

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