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5.60 Thermodynamics & Kinetics
Spring 2008

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Complex Reactions and Mechanisms (continued)

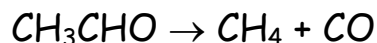
IV) Chain Reactions

Where a product from a step in the mechanism is a reactant for a previous step (i.e. the reaction feeds itself).

a) Stationary or stable chain reactions.

The concentration of reactive intermediates is constant in time or slowly decreasing.

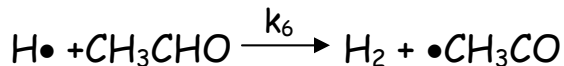
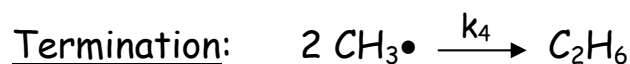
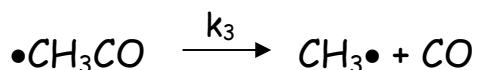
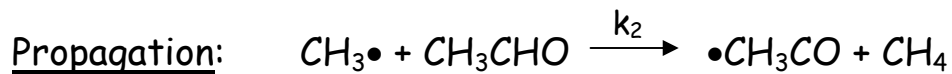
Example:



Experimental observations: Small amounts of C_2H_6 and H_2 are also produced, and the Rate of Reaction $\propto [\text{CH}_3\text{CHO}]^{3/2}$.

(These are signatures of a chain reaction mechanism)

Proposed mechanism for this reaction:



Kinetic Equations:

$$\frac{d[CH_4]}{dt} = k_2 [CH_3\bullet][CH_3CHO]$$

$$\frac{d[CH_3\bullet]}{dt} = k_1 [CH_3CHO] - k_2 [CH_3\bullet][CH_3CHO] + k_3 [\bullet CH_3CO] - 2k_4 [CH_3\bullet]^2$$

$$\frac{d[\bullet CH_3CO]}{dt} = k_2 [CH_3\bullet][CH_3CHO] - k_3 [\bullet CH_3CO]$$

Assume S. S. approximation

([Intermediates = small])

$$\frac{d[\text{CH}_3\bullet]}{dt} = \frac{d[\bullet\text{CH}_3\text{CO}]}{dt} = 0$$

Steady State Approximation



$$\Rightarrow [\text{CH}_3\bullet]_{SS} = \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

So...

$$\boxed{\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}}$$

Chain Length: The # of propagation steps per initiation step

$$= \frac{\text{rate of product formation}}{\text{rate of initial radical formation}}$$

$$= \frac{k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}}{k_1 [\text{CH}_3\text{CHO}]}$$

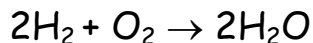
$$= \frac{k_2}{\sqrt{2k_1k_4}} [\text{CH}_3\text{CHO}]^{1/2} \quad (\text{experimentally} = 300)$$

b) Non-stationary or unstable chain reactions:

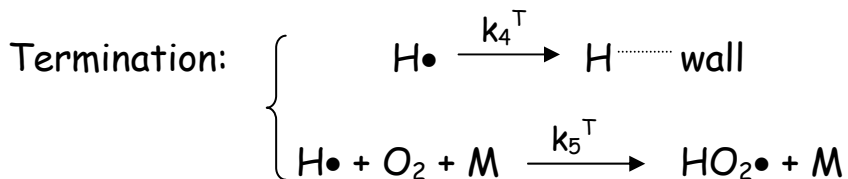
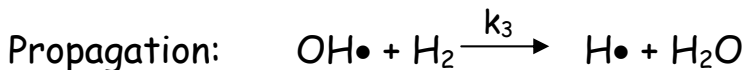
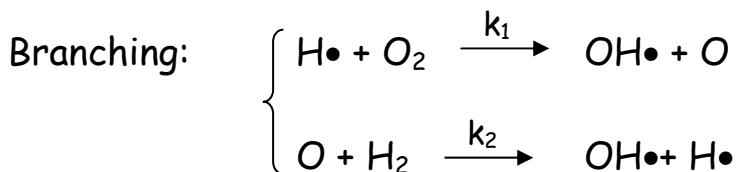
The propagation includes a branching step, which increases the concentration of reactive intermediates.

⇒ **EXPLOSION!!**

Example: the combustion of hydrogen to form water



Mechanism:



Kinetic Equations

$$\frac{d[H]}{dt} = R_I - k_1[H][O_2] + k_2[O][H_2] + k_3[OH][H_2] - k_4^T[H] - k_5^T[H][O_2][M]$$

$$\frac{d[O]}{dt} = k_1[H][O_2] - k_2[O][H_2]$$

$$\frac{d[OH]}{dt} = k_1[H][O_2] + k_2[O][H_2] - k_3[OH][H_2]$$

Assume S. S. Approximation ([Intermediates]=small, $d[Int.]/dt \sim 0$)

**** If S.S. App. Fails \Rightarrow EXPLOSION (because not true) ****

Solve for $[Int.]_{SS}$

$$[O]_{SS} = \frac{k_1 [H][O_2]}{k_2 [H_2]}$$

$$[OH]_{SS} = \frac{k_1[H][O_2] + k_2[O]_{SS}[H_2]}{k_3[H_2]} = \frac{2k_1[H][O_2]}{k_3[H_2]}$$

$$\left. \frac{d[H]}{dt} \right|_{SS} = R_I + \left\{ 2k_1[O_2] - (k_4^T[H]_{SS} + k_5^T[H]_{SS}[O_2][M]) \right\} [H]_{SS} = 0$$

$$\text{So... } [H]_{SS} = \frac{R_I}{k_4^T + k_5^T[O_2][M] - 2k_1[O_2]}$$

Limiting Cases

i) Low Pressure $(k_1[O_2], k_5^T[O_2][M]) \ll k_4^T$

Wall collisions dominate over branching \Rightarrow S.S. app. is valid
No explosion

ii) Medium Pressure $2k_1[O_2] \sim k_4^T + k_5^T[O_2][M]$

Branching is important, $[H]_{SS}$ is large! \Rightarrow S.S. is NOT valid!
EXPLOSION!!

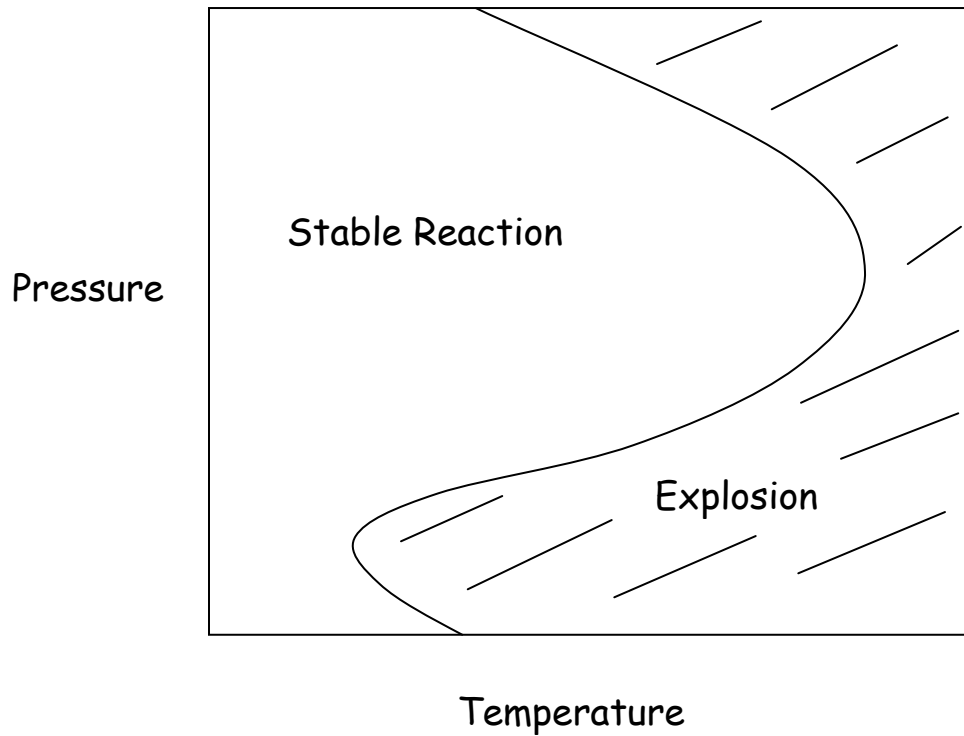
iii) Higher Pressure $k_5^T[O_2][M] > 2k_1[O_2]$

Termination dominates over branching \Rightarrow S.S. is valid
No explosion

iv) Very High Pressure

$HO_2\bullet + H_2 \rightarrow H_2O + OH\bullet$ becomes important

This feeds $OH\bullet \Rightarrow$ **EXPLOSION!!**



P-T phase diagram for stability of Hydrogen Combustion.

Branching chain reactions also occur in nuclear reactions, for example. In fission reactions of ^{235}U , 3 neutrons are produced for each neutron that starts the reaction. In a nuclear reactor, control rods that absorb neutrons terminate the chain and moderate the reaction (unless the operator is reckless and forgets to insert the rods, in which case there is a meltdown of the reactor core...).