

Complex Reactions and Mechanisms (continued)

Some comments about analyzing kinetic data

A) Reactions with one reactant:



- a) Plot or analyze [A] vs. t
 ln[A] vs. t
 1/[A] vs. t

...

and find which gives a straight line.

- b) Half-life method: measure $t_{1/2}$ vs. $[A]_0$

$$1^{\text{st}} \text{ order} \rightarrow t_{1/2} \propto [A]_0^0$$

$$2^{\text{nd}} \text{ order} \rightarrow t_{1/2} \propto [A]_0^{-1}$$

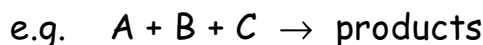
etc....

- c) Multiple lifetimes ($t_{3/4}$ and $t_{1/2}$) (at $t_{3/4}$, $[A]=[A]_0/4$)

$$1^{\text{st}} \text{ order} \rightarrow t_{3/4} = (2 \ln 2)/k \Rightarrow \frac{t_{3/4}}{t_{1/2}} = 2$$

$$2^{\text{nd}} \text{ order} \rightarrow t_{3/4} = 3/([A]_0 k) \Rightarrow \frac{t_{3/4}}{t_{1/2}} = 3$$

B) Reactions with more than one reactant:



- a) Initial Rate Method

$$\text{For } [A]_o \quad \left. \frac{\Delta[A]}{\Delta t} \right|_{t=0} = R_o \approx k[A]_o^\alpha [B]_o^\beta [C]_o^\gamma$$

$$\text{For } [A]'_o \quad \left. \frac{\Delta[A]'}{\Delta t} \right|_{t=0} = R'_o \approx k[A]'_o^\alpha [B]_o^\beta [C]_o^\gamma$$

$$\text{Experimentally determine } \frac{R_o}{R'_o} = \left(\frac{[A]_o}{[A]'_o} \right)^\alpha$$

$$\text{If } 2[A]'_o = [A]_o \text{ then, if } \frac{R_o}{R'_o} = 1 \Rightarrow \alpha = 0$$

$$\text{if } \frac{R_o}{R'_o} = \sqrt{2} \Rightarrow \alpha = 1/2$$

$$\text{if } \frac{R_o}{R'_o} = 2 \Rightarrow \alpha = 1$$

$$\text{if } \frac{R_o}{R'_o} = 4 \Rightarrow \alpha = 2$$

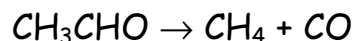
VI) Chain Reactions

In chain reactions, 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:

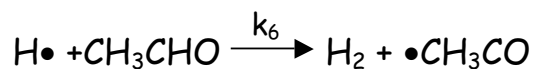
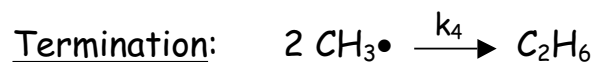
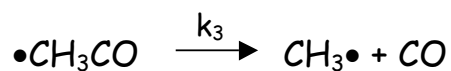
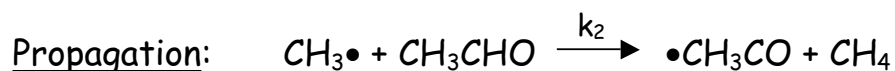


Experimental observations: Small amounts of C_2H_6 and H_2 are also produced, and the Rate of Reaction $\propto [\text{CH}_3\text{CHO}]^{3/2}$.

(These are signatures of a chain reaction mechanism)

Proposed mechanism for this reaction (Rice - Herzfeld mechanism) :

[The \bullet means a free radical, i.e., a molecular fragment with an unpaired electron]



Kinetic Equations:

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

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

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

We can also write kinetic equations for $[HCO\bullet]$, $[H\bullet]$

Assume Steady State approximation for all free radical species

($[R\bullet]$ is small, $d[R\bullet]/dt \approx 0$)

$$\frac{d[CH_3\bullet]}{dt} = \frac{d[\bullet CH_3CO]}{dt} = 0$$

Steady State Approximation

$$\Rightarrow [\bullet CH_3CO]_{ss} = (k_2/k_3) [CH_3\bullet] [CH_3CHO]$$

$$\Rightarrow [CH_3\bullet]_{ss} = \left(\frac{k_1}{2k_4} \right)^{1/2} [CH_3CHO]^{1/2}$$

So...
$$\boxed{\frac{d[CH_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [CH_3CHO]^{3/2}}$$

Note: in agreement with observed rate law;

"phenomenological" rate coefficient is composite of three elementary reaction rate constants

Chain Length: The # of propagation steps per initiation step before a termination step kills the free radical

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

For acetaldehyde decomposition,

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

$$= \frac{k_2}{\sqrt{2k_1k_4}} [\text{CH}_3\text{CHO}]^{1/2}$$

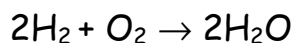
(experimentally ≈ 300 at typical pressures)

b) Non-stationary or unstable chain reactions:

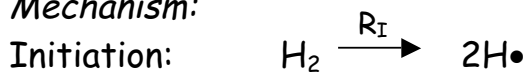
The propagation includes a branching step, which increases the concentration of reactive intermediates.

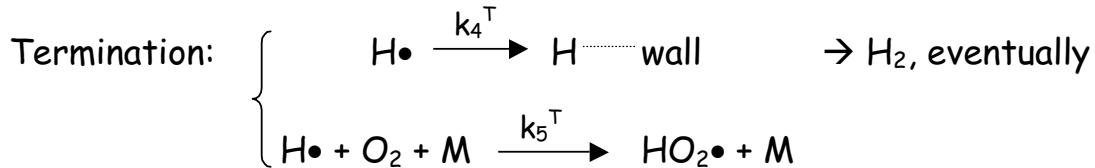
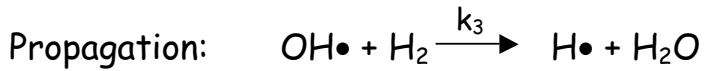
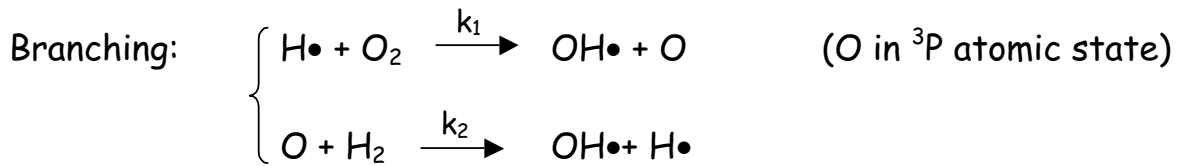
\Rightarrow one type of **EXPLOSION!!**

Example: the combustion of hydrogen to form water



Mechanism:





Kinetic Equations

$$\frac{d[\text{H}]}{dt} = R_i - k_1[\text{H}][\text{O}_2] + k_2[\text{O}][\text{H}_2] + k_3[\text{OH}][\text{H}_2] - k_4^T[\text{H}] - k_5^T[\text{H}][\text{O}_2][\text{M}]$$

$$\frac{d[\text{O}]}{dt} = k_1[\text{H}][\text{O}_2] - k_2[\text{O}][\text{H}_2]$$

$$\frac{d[\text{OH}]}{dt} = k_1[\text{H}][\text{O}_2] + k_2[\text{O}][\text{H}_2] - k_3[\text{OH}][\text{H}_2]$$

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

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

Solve for $[\text{Int.}]_{ss}$

$$[\text{O}]_{ss} = \frac{k_1 [\text{H}][\text{O}_2]}{k_2 [\text{H}_2]}$$

$$[\text{OH}]_{ss} = \frac{k_1[\text{H}][\text{O}_2] + k_2[\text{O}]_{ss}[\text{H}_2]}{k_3[\text{H}_2]} = \frac{2k_1[\text{H}][\text{O}_2]}{k_3[\text{H}_2]}$$

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

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

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

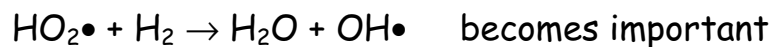
ii) Medium Pressure $2k_1[O_2] \sim k_4^T + k_5^T[O_2][M]$

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

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

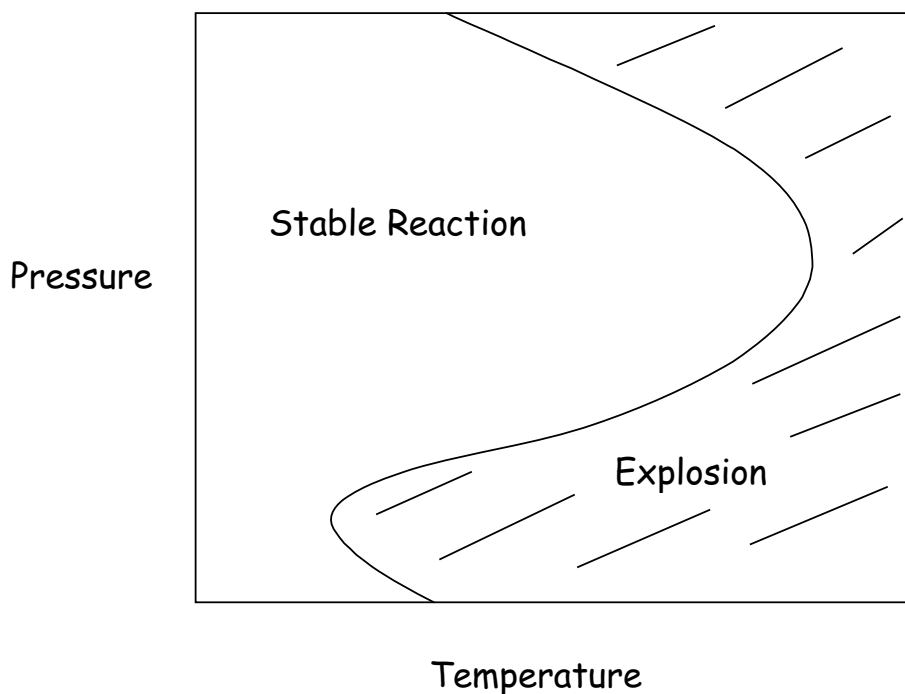
Termination dominates over branching \Rightarrow S.S. is valid
No explosion

iv) Very High Pressure



This increases $\text{OH}\bullet \Rightarrow$ **EXPLOSION!!**

So we have a stability diagram for 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 absorbed by a uranium nucleus. In a nuclear power reactor, control rods that absorb neutrons terminate the chain and moderate the reaction (usually).

Another example of a free radical chain reaction is the formation and destruction of ozone in the Earth's stratosphere. We will consider this mechanism in detail in a subsequent lecture.