

Lecture 15

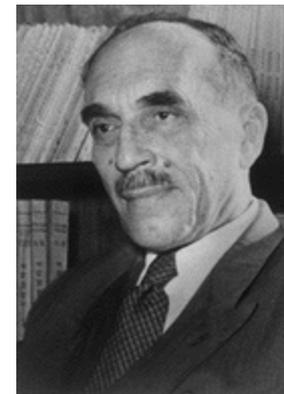
Unimolecular reactions and chain reactions

How do they occur?

Look at the following reaction.



Sir Cyril Hinshelwood
1897-1967, Nobel 1956



Nikolai Nikolaevic Semenov
1896-1986, Nobel 1956



These are unimolecular reactions.

The reactant molecules somehow have enough energy to react by themselves. How can energy transfer occur without collisions?

The first successful explanation of unimolecular reactions is by Frederick Lindemann in 1921 and elaborated later by Cyril Hinshelwood. This mechanism is called as Lindemann- Hinshelwood mechanism.

The generalised explanation is as follows.

The reactant molecule A gets activated by collisions with another molecule.



Collisions with other molecule can result in loss of this energy.



Some activated molecules may form products.



In case the unimolecular decay is slow, the net reaction is first order.

This can be demonstrated by applying steady state for the formation of A^* .

$$d[A^*]/dt = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0$$

Solution is,

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

The rate law for the formation of P is,

$$d[P]/dt = k_b[A^*] = k_a k_b [A]^2 / \{k_b + k'_a [A]\}$$

As can be seen, the rate law is not first order.

The important aspect is that rate of deactivation of A^* by collisions with A is much larger than the rate of unimolecular decay.

$$k'_a [A^*][A] \gg k_b [A^*] \text{ or } k'_a [A] \gg k_b$$

Thus we can neglect k_b in the denominator and write,

$$d[P]/dt \approx k[A] \quad \text{where} \quad k = k_a k_b / k'_a$$

This is a first order rate law.

The rate expression also shows that when the concentration (partial pressure) of A is small, then $k'_a [A] \ll k_b$, we get

$$d[P]/dt \approx k_a [A]^2$$

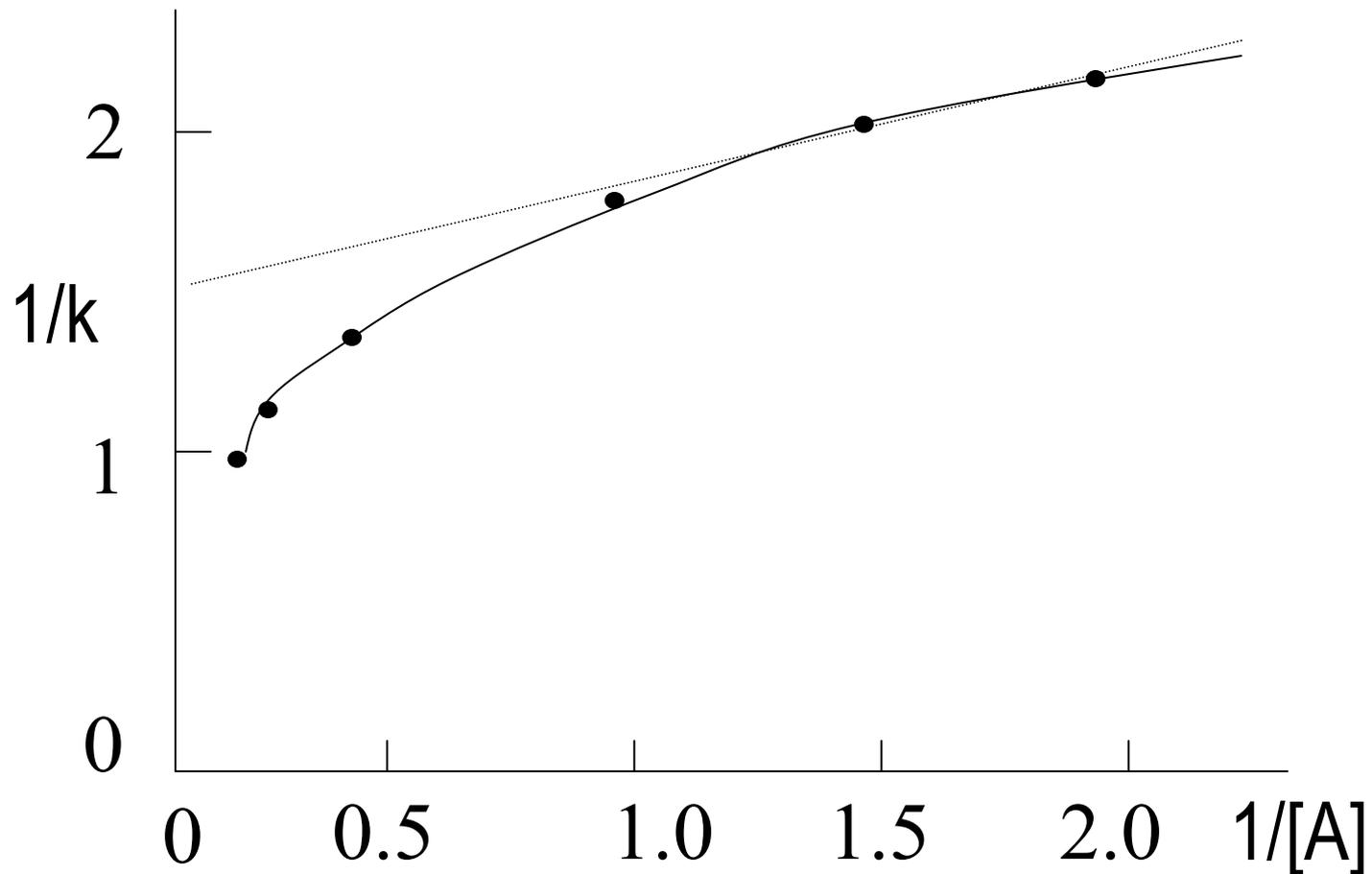
If we write the rate expression as,

$$d[P]/dt = k[A] \quad \text{where} \quad k = k_a k_b [A] / \{k_b + k'_a [A]\}$$

The effective rate constant is,

$$1/k = k'_a / (k_a k_b) + 1/k_a [A]$$

The test for the theory is to get a straight line for $1/k$ vs. $1/[A]$ plot. A typical plot is seen below.



The behaviour is in gross agreement with the theory. At high pressures (lower $1/[A]$) the value of k higher (lower $1/k$) than expected from a linear behaviour. The reaction studied is the unimolecular isomerization of trans-CHD=CHD. The Lindemann-Hinshelwood mechanism is the straight line, extrapolation from lower pressure (larger $1/[A]$) to higher pressure (smaller $1/[A]$).

Chain reactions

Chain reactions are examples of complex reactions, with complex rate expressions.

In a chain reaction, the intermediate produced in one step generates an intermediate in another step.

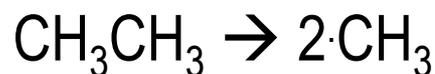
This process goes on.

Intermediates are called **chain carriers**. Sometimes, the chain carriers are radicals, they can be ions as well. In nuclear fission they are **neutrons**.

There are several steps in a chain reaction.

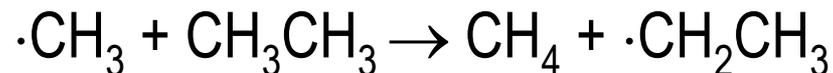
1. Chain initiation

This can be by **thermolysis** (heating) or **photolysis** (absorption of light) leading to the breakage of a bond.



2. Propagation

In this, the chain carrier makes another carrier.



3. Branching

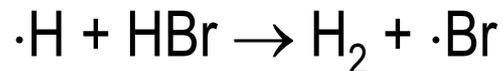
One carrier makes more than one carrier.



(oxygen has two unpaired electrons)

4. Retardation

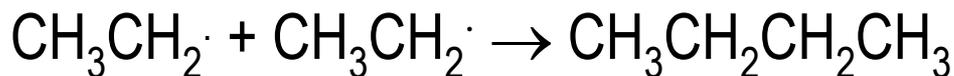
Chain carrier may react with a product reducing the rate of formation of the product.



Retardation makes another chain carrier, but the product concentration is reduced.

5. Chain termination

Radicals combine and the chain carriers are lost.



6. Inhibition

Chain carriers are removed by other processes, other than termination, say by foreign radicals.



All need not be there for a given reaction.

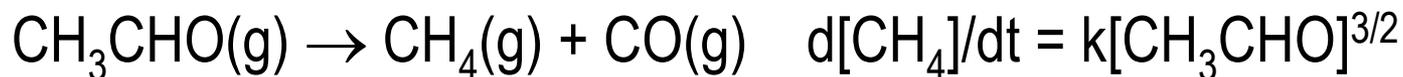
Minimum necessary are,

Initiation, propagation and termination.

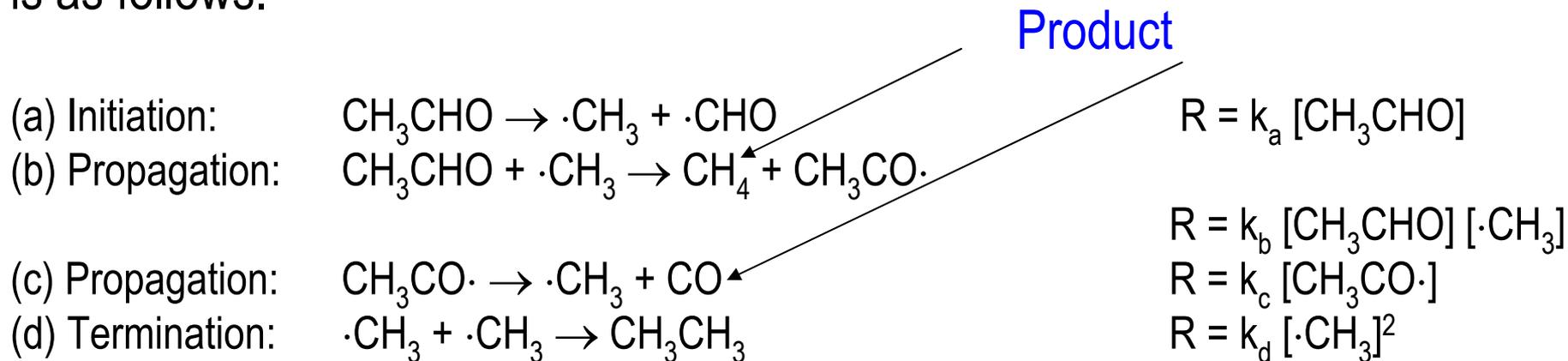
How do we account for the rate of laws of chain reactions?

Look at the thermal decomposition of acetaldehyde. This appears to follow three-halves order in acetaldehyde.

Overall reaction,



The mechanism for this reaction known as **Rice-Herzfeld mechanism** is as follows.



Although the mechanism explains the principal products, there are several minor products such as acetone (CH_3COCH_3) and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$).

The rate equation can be derived on the basis of **steady-state approximation**. The rate of change of intermediates may be set equal to zero.

$$\begin{aligned} d[\cdot\text{CH}_3]/dt &= k_a[\text{CH}_3\text{CHO}] - k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k_c[\text{CH}_3\text{CO}\cdot] \\ &\quad - 2k_d[\cdot\text{CH}_3]^2 = 0 \end{aligned}$$

$$d[\text{CH}_3\text{CO}\cdot]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k_c[\text{CH}_3\text{CO}\cdot] = 0$$

The sum of the two equation is,

$$k_a[\text{CH}_3\text{CHO}] - 2k_d[\cdot\text{CH}_3]^2 = 0$$

The steady-state concentration of $\cdot\text{CH}_3$ radicals is,

$$[\cdot\text{CH}_3] = (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

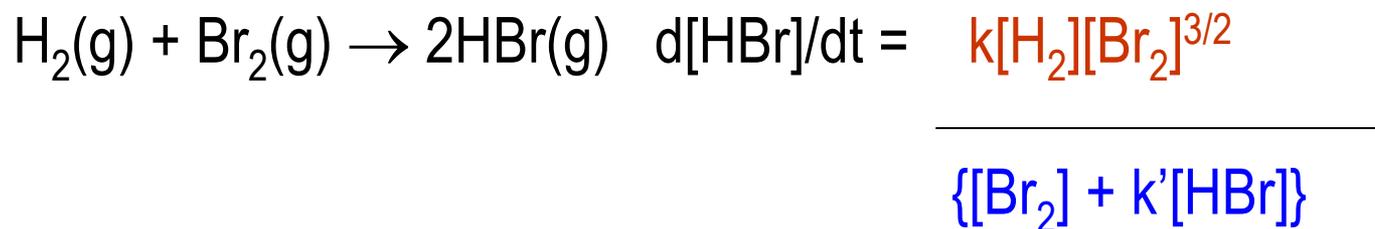
It follows that the rate of formation of CH_4 is

$$d[\text{CH}_4]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_b (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Thus the mechanism explains the observed rate expression. It is sure that the true rate law is more complicated than that observed experimentally.

There are several cases where the reaction is complicated.

An example is,



The following mechanism has been proposed to account for this rate law.

- (a) Initiation: $\text{Br}_2 + \text{M} \rightarrow \text{Br}\cdot + \text{Br}\cdot + \text{M}$ $R = k_a[\text{Br}_2][\text{M}]$
where M is either Br_2 or H_2 .
- (b) Propagation: $\text{Br}\cdot + \text{H}_2 \rightarrow \text{HBr} + \text{H}\cdot$ $R = k_b[\text{Br}\cdot][\text{H}_2]$
 $\text{H}\cdot + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}\cdot$ $R = k'_b[\text{H}\cdot][\text{Br}_2]$
- (c) Retardation: $\text{H}\cdot + \text{HBr} \rightarrow \text{H}_2 + \text{Br}\cdot$ $R = k_c[\text{H}\cdot][\text{HBr}]$
- (d) Termination: $\text{Br}\cdot + \text{Br}\cdot + \text{M} \rightarrow \text{Br}_2 + \text{M}^*$ $R = k_d[\text{Br}\cdot]^2 [\text{M}]$

The third body collision removes the excess energy.

There can be other recombinations also, such as H. + H. and H. + Br..

The net rate of formation of HBr is,

$$d[\text{HBr}]/dt = k_b[\text{Br}\cdot][\text{H}_2] + k'_b[\text{H}\cdot][\text{Br}_2] - k_c[\text{H}\cdot][\text{HBr}]$$

We can apply steady state.

$$d[\text{H}\cdot]/dt = k_b[\text{Br}\cdot][\text{H}_2] - k'_b[\text{H}\cdot][\text{Br}_2] - k_c[\text{H}\cdot][\text{HBr}] = 0$$

$$d[\text{Br}\cdot]/dt = 2k_a[\text{Br}_2][\text{M}] - k_b[\text{Br}\cdot][\text{H}_2] + k'_b[\text{H}\cdot][\text{Br}_2] + k_c[\text{H}\cdot][\text{HBr}] - 2k_d[\text{Br}\cdot]^2 [\text{M}] = 0$$

$$[\text{Br}\cdot] = (k_a/k_d)^{1/2} [\text{Br}_2]^{1/2}$$

$$[\text{H}\cdot] = k_b(k_a/k_d)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2} / \{k'_b[\text{Br}_2] + k_c[\text{HBr}]\}$$

Substitute in the HBr rate law.

$$d[\text{HBr}]/dt = 2k_b(k_a/k_d)^{1/2}[\text{H}_2][\text{Br}_2]^{3/2}/\{[\text{Br}_2] + (k_c/k'_b)[\text{HBr}]\}$$

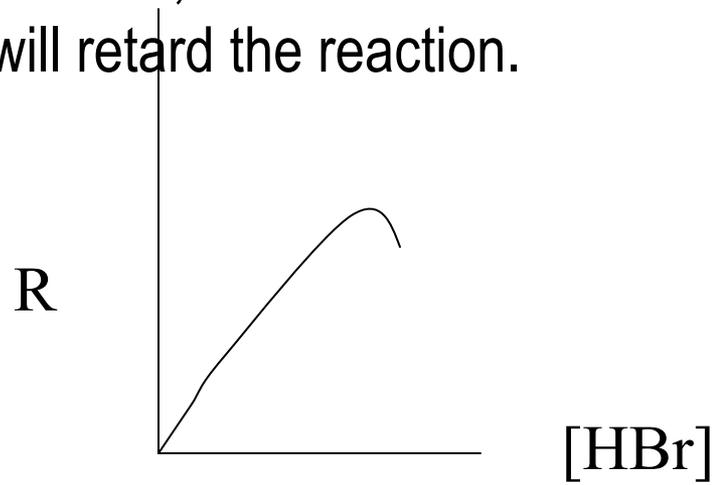
If it is compared with the experimental rate law one can see,

$$k = 2k_b(k_a/k_d)^{1/2} \quad k' = k_c/k'_b$$

Presence of **HBr in the denominator** indicates that it is an **inhibitor**.

Presence of Br_2 in the denominator is because of the fact that its presence removes reactive radicals from the chain mechanism.

If we plot HBr concentration as a function of time, it will reach a maximum as increased presence of HBr will retard the reaction.



Explosions

There are two kinds: thermal and chain-branching.

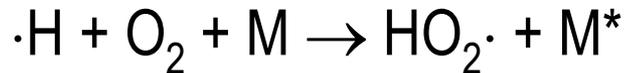
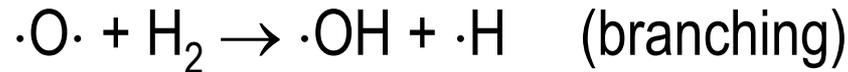
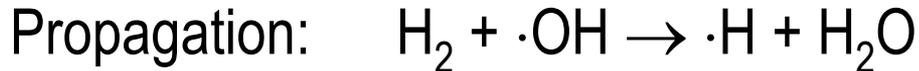
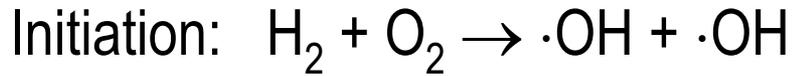
Thermal: This is because in an exothermic reaction if the energy cannot escape, the reaction rate increases fast due to concentration of energy.

Chain-branching: In this case, there are chain branching reactions and the number of carriers grows exponentially.

An example of the latter type,

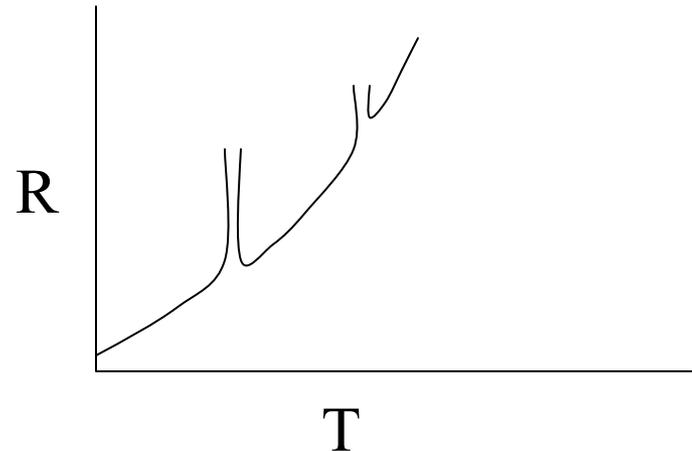


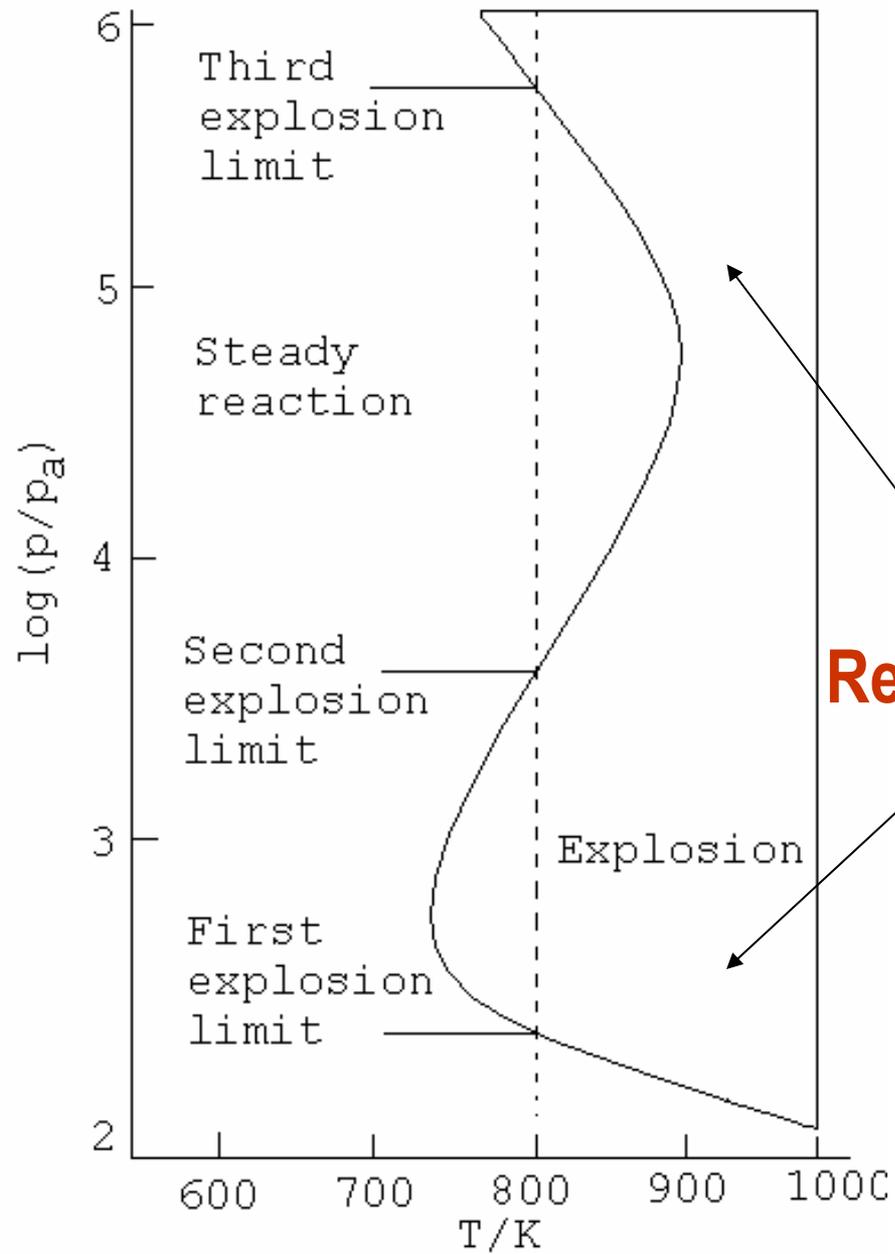
The mechanism is very complex. Yet there are these steps, which explain explosion.



The explosions depend on temperature and pressure.

This is explained in the figure below





Regions of explosion

At low pressures the chain carriers can reach the walls and get lost. No explosion happens. As the pressure is increased along the dotted line shown, the radicals react before reaching the walls and the reaction suddenly becomes explosive. This is the first explosion limit. In the second explosion limit, the pressure of the products is high so that reactions of the type, $O_2 + H \cdot \rightarrow \cdot O_2H$ occur. These recombination reactions become efficient as the excess energy can be removed by three body collisions. Then the reaction goes smoothly. In the third explosion limit, thermal explosion occur. In this limit, reaction such as $HO_2 \cdot + H_2 \rightarrow H_2O_2 + H \cdot$ dominates the elimination of $HO_2 \cdot$ by the walls.