

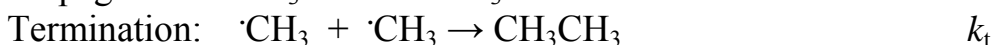
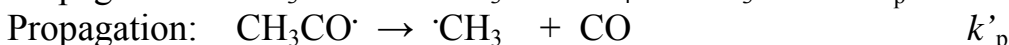
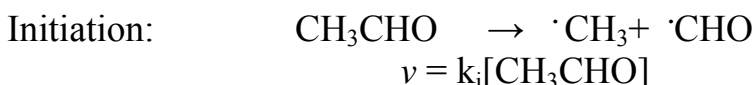
## 26 The kinetics of complex reactions

### 26.1 The rate laws of chain reactions

The thermal decomposition of acetaldehyde



$$v = k[\text{CH}_3\text{CHO}]^{3/2} \quad 26.1.1$$



The net rates of change of the intermediates are:

$$\frac{d[\cdot\text{CH}_3]}{dt} = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot]$$

Applying the steady state approximation to the above two equations

$$0 = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2$$

$$0 = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot]$$

The sum of the above two equations is:

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

thus the steady state concentration of  $[\cdot\text{CH}_3]$  is:

$$[\cdot\text{CH}_3] = \left( \frac{k_i}{2k_t} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

The rate of formation of  $\text{CH}_4$  is:

$$\frac{d[\text{CH}_4]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_p \left( \frac{k_i}{2k_t} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \quad 26.1.2$$

Equation 26.1.2 is in agreement with the three-halves order observed experimentally.

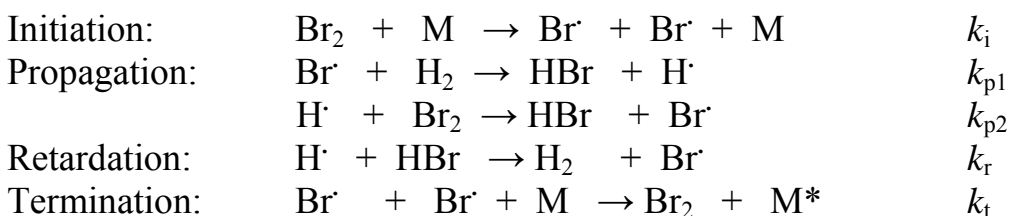
We have discussed earlier that hydrogen-bromine reaction has complicated rate law rather than the second order reaction as anticipated. Now we examine why



*Yield*

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]} \quad \mathbf{26.1.3}$$

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



The net rates of formation of the two intermediates are

$$\frac{d[\text{H}\cdot]}{dt} = k_{p1}[\text{Br}\cdot][\text{H}_2] - k_{p2}[\text{H}\cdot][\text{Br}_2] - k_r[\text{H}\cdot][\text{HBr}]$$

$$\frac{d[\text{Br}\cdot]}{dt} = 2k_i[\text{Br}_2][\text{M}] - k_{p1}[\text{Br}\cdot][\text{H}_2] + k_{p2}[\text{H}\cdot][\text{Br}_2] + k_r[\text{H}\cdot][\text{HBr}] - 2k_t[\text{Br}\cdot]^2[\text{M}]$$

The steady-state concentrations of the above two intermediates can be obtained by solving the following two equations:

$$k_{p1}[\text{Br}\cdot][\text{H}_2] - k_{p2}[\text{H}\cdot][\text{Br}_2] - k_r[\text{H}\cdot][\text{HBr}] = 0$$

$$2k_i[\text{Br}_2][\text{M}] - k_{p1}[\text{Br}\cdot][\text{H}_2] + k_{p2}[\text{H}\cdot][\text{Br}_2] + k_r[\text{H}\cdot][\text{HBr}] - 2k_t[\text{Br}\cdot]^2[\text{M}] = 0$$

$$[\text{Br}\cdot] = \left(\frac{k_i}{k_t}\right)^{1/2} [\text{Br}_2]^{1/2}$$

$$[\text{H}\cdot] = \frac{k_{p1}(k_i/k_t)^{1/2}[\text{H}_2][\text{Br}_2]^{1/2}}{k_{p2}[\text{Br}_2] + k_r[\text{HBr}]}$$

substitute the above results to the rate law of [HBr]

$$\frac{d[\text{HBr}]}{dt} = k_{p1}[\text{Br}\cdot][\text{H}_2] + k_{p2}[\text{H}\cdot][\text{Br}_2] - k_r[\text{H}\cdot][\text{HBr}]$$

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_{p1}(k_i/k_t)^{1/2}[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + (k_r/k_{p2})[\text{HBr}]} \quad 26.1.4$$

Equation 26.1.4 has the same form as the empirical rate law 26.1.4, so the two empirical rate constants can be identified as

$$k = 2k_p \left( \frac{k_i}{k_t} \right)^{1/2}$$

$$k' = \frac{k_r}{k_{p2}}$$

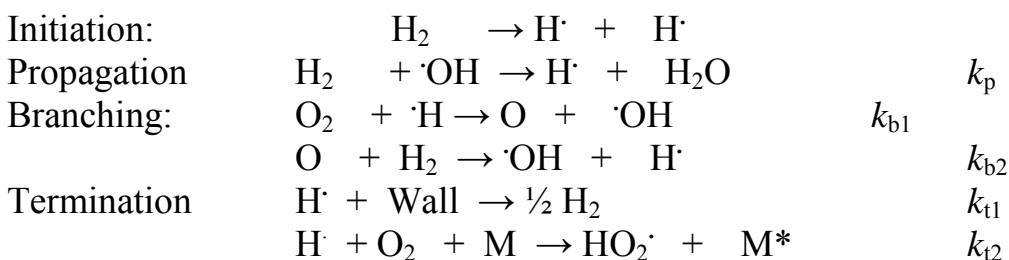
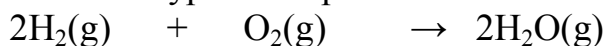
analyzing the effects of HBr, H<sub>2</sub>, and Br<sub>2</sub> on the reaction rate based on equation 26.1.4.

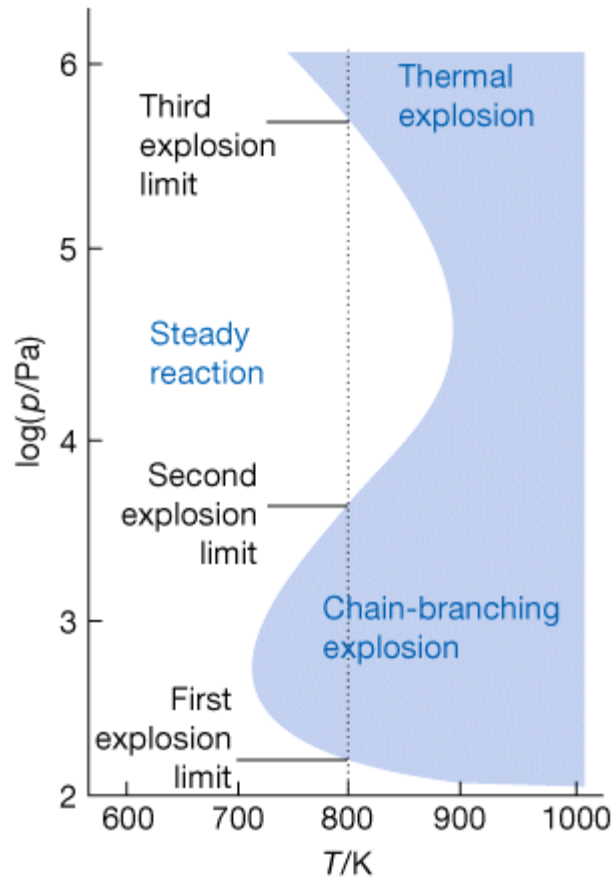
## 26.2 Explosions

A **thermal explosion** is a very rapid reaction arising from a rapid increase of reaction rate with increasing temperature.

A **chain-branching explosion** occurs when the number of chain centres grows exponentially.

An example of both types of explosion is the following reaction





Analyzing the above reaction and show that an explosion occurs when the rate of chain branching exceeds that of chain termination.