Chain Reaction Example

Series of steps involve free radicals reactive intermediates (unpaired electron on atom or molecular fragment)

Example $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

rate law $$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}$$

	Steps	Mechanism	Step rate law
a)	Initiation	$Br_2 \rightarrow 2Br\cdot$ (collision or photon absorption)	$\frac{d(Br)}{dt} = 2k_a(Br_2)$
b)	Propagation	$Br\cdot + H_2 \rightarrow HBr + H\cdot$	$\frac{d(HBr)}{dt} = k_b(Br)(H_2)$
		$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	$\frac{d(HBr)}{dt} = k_b'(H)(Br_2)$
c)	Inhibition	$H\cdot + HBr \rightarrow H_2 + Br\cdot$	$\frac{d(HBr)}{dt} = -k_c(H)(HBr)$
d)	Termination	$Br\cdot + Br\cdot + M \rightarrow Br_2 + M^*$	$\frac{d(Br)}{dt} = -2k_d(Br)^2$

left off · in H· and Br· above

Net rate of formation of product HBr is

$$\frac{d(HBr)}{dt} = k_b(Br)(H_2) + k_b'(H)(Br_2) - k_c(H)(HBr)$$

Apply steady state approximation to reactive intermediates

$$\frac{d(H)}{dt} = k_b(Br)(H_2) - k_b'(H)(Br_2) - k_c(H)(HBr) = 0$$

$$\frac{d(Br)}{dt} = 2k_a(Br_2) - k_b(Br)(H_2) + k_b'(H)(Br_2) + k_c(H)(HBr) - 2k_d(Br)^2 = 0$$

Solve two eq simultaneously 2 eq. - 2 unknowns

Solve for (H) and (Br) from Eqs above

Sub into $\frac{d(HBr)}{dt}$ eq get

$$\frac{d(HBr)}{dt} = \frac{2k_b(k_a/k_d)^{1/2}(H_2)(Br_2)^{3/2}}{(Br_2) + (k_c/k_b')(HBr)}$$

remember a complicated mechanism $\longrightarrow$ complicated rate law

$\hookrightarrow$ Simple rate law