Free Radical Chain Mechanism

1. $Br_2 \xrightarrow{k_1} 2\,Br$ inititation

2. $Br + H_2 \xrightarrow{k_2} HBr + H$ propagation

3. $H + Br_2 \xrightarrow{k_3} HBr + Br$ propagation

4. $H + HBr \xrightarrow{k_4} H_2 + Br$ inhibition

5. $2\,Br \xrightarrow{k_5} Br_2$ breaking

experimental rate law:

$$\frac{d[HBr]}{dt} = \frac{k_a\,[H_2][Br_2]^{1/2}}{k_b + k_c \dfrac{[HBr]}{[Br_2]}}$$
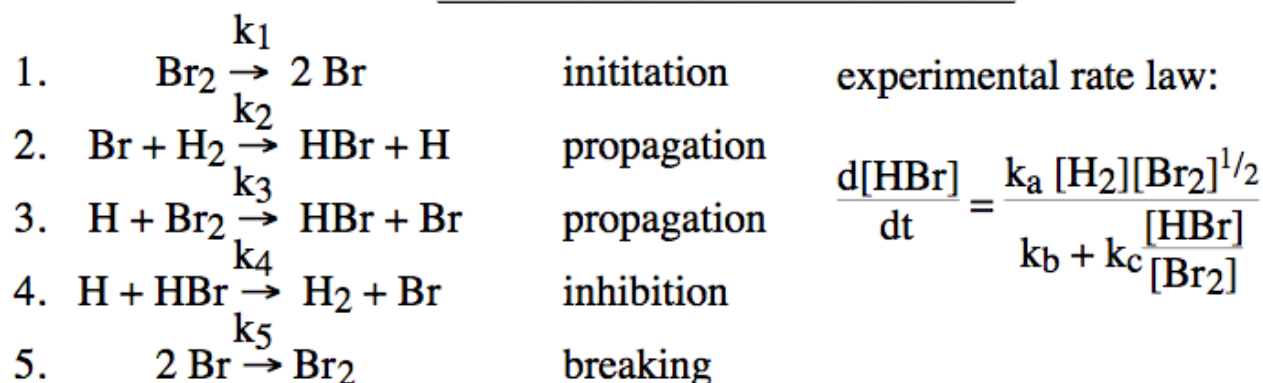
I. $\dfrac{d[HBr]}{dt} = k_2\,[Br][H_2] + k_3\,[H][Br_2] - k_4\,[H][HBr]$

II. $\dfrac{d[Br]}{dt} = 0 = 2\,k_1[Br_2] - k_2\,[Br][H_2] + k_3\,[H][Br_2] + k_4\,[H][HBr] - 2\,k_5[Br]^2$

III. $\dfrac{d[H]}{dt} = 0 = k_2\,[Br][H_2] - k_3\,[H][Br_2] - k_4\,[H][HBr]$

IV. <u>add II + III :</u> $0 = 2\,k_1[Br_2] - 2\,k_5\,[Br]^2 \;\Rightarrow\;$ $[Br] = \left(\dfrac{k_1}{k_5}\,[Br_2]\right)^{1/2}$

V. <u>solve III for [H] :</u> $[H] = \dfrac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} = \dfrac{k_2\left(\dfrac{k_1}{k_5}\right)^{1/2}[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]}$

VI. <u>subtract III from I:</u> $\dfrac{d[HBr]}{dt} = 2\,k_3\,[H][Br_2]$

<u>substitute V into VI:</u> $\dfrac{d[HBr]}{dt} = \dfrac{2\,k_3\,k_2\,k_1^{1/2}\,k_5^{-1/2}\,[H_2][Br_2]^{1/2}\,[Br_2]}{k_3[Br_2] + k_4[HBr]}$

$$\frac{d[HBr]}{dt} = \frac{2\,k_3\,k_2\,k_1^{1/2}\,k_5^{-1/2}\,[H_2][Br_2]^{1/2}}{k_3 + k_4\dfrac{[HBr]}{[Br_2]}}$$