## Free Radical Chain Mechanism

1. 
$$\operatorname{Br}_2 \xrightarrow{k_1} 2 \operatorname{Br}$$
 inititation experimental rate law:

2. Br + 
$$H_2 \xrightarrow{K_2} HBr + H$$
 propagation d[HBr]  $k_2$  [H2][Br2]

3. 
$$H + Br_2 \xrightarrow{k_3} HBr + Br$$
 propagation  $\frac{d[HBr]}{dt} = \frac{k_a [H_2][Br_2]^{1/2}}{k_b + k_a}$ 

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$$Br_2 \xrightarrow{k_2} 2 Br$$
 inititation experimental rate laws

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

3.  $H + Br_2 \xrightarrow{k_4} HBr + Br$  propagation

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

1.  $Br_2 \xrightarrow{k_1} 2 Br$  inititation experimental rate laws

2.  $ar_1 \xrightarrow{k_2} br_2 = br_3$ 

3.  $ar_2 \xrightarrow{k_3} br_4 = br_4$ 

4.  $ar_3 \xrightarrow{k_4} br_5 = br_5$ 

3.  $ar_4 \xrightarrow{k_4} br_5 = br_6$ 

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8.  $ar_5 \xrightarrow{k_5} br_5 = br_6$ 

9.  $ar_5 \xrightarrow{k_5} br_5 = br_6$ 

10.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

11.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

12.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

13.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

14.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

15.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

16.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

17.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

18.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

18.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

19.  $ar_5 \xrightarrow{k_5} br_7 = br_7$ 

5. 
$$2 \operatorname{Br} \xrightarrow{K_5} \operatorname{Br}_2$$
 breaking

I. 
$$\frac{d[HBr]}{dt} = k_2 [Br][H_2] + k_3 [H][Br_2] - k_4 [H][HBr]$$

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

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

IV. 
$$\underline{\text{add II} + \text{III}} : 0 = 2 \text{ k}_1[\text{Br}_2] - 2 \text{ k}_5 [\text{Br}]^2 \Rightarrow [\text{Br}] = \left(\frac{k_1}{k_5} [\text{Br}_2]\right)^{1/2}$$

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

VI. subtract III from I: 
$$\frac{d[HBr]}{dt} = 2 k_3 [H][Br_2]$$

$$\underline{\text{substitute V into VI:}} \quad \frac{d[HBr]}{dt} = \frac{2 k_3 k_2 k_1^{1/2} k_5^{-1/2} [H_2][Br_2]^{1/2} [Br_2]}{k_3[Br_2] + k_4[HBr]}$$

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