KINETICS OF HYDROGEN & BROMINE REACTION

Dr. (Mrs.) Anshumala Vani

School of Studies in Chemistry & Biochemistry

Vikram University, Ujjain (M.P.)

INTRODUCTION

In Chemical kinetics there are two types of reaction

- Elementary reaction (Single step reaction)
- Complex reaction (Many step reaction)

Complex reaction follows two mechanisms

- Equilibrium approximation
- Steady state approximation

KINETICS OF COMPLEX REACTIONS

The study of chemical kinetics becomes highly complicated due to occurrence of complex reactions which involve more than one step. Important among such reactions are the following categories:

- ***Opposing or reversible reactions***
- ***Consecutive reactions***
- ***Chain reactions***

The well known example of chain reaction is Hydrogen & Bromine reaction

Hydrogen & Bromine reaction is the type of complex reaction.

Mechanism of this reaction followed by three steps

- ***Chain initiation***
- ***Chain propogation***
- ***Chain termination***

Kinetics of this reaction mechanism studied by Steady state approximation

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

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]}{[Br_2] + k'[HBr]}$$

MECHANISM OF THE ABOVE REACTION

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

According to steady state approximation rate expression of HBr, H, Br, expressed in equation I, II & III from above reaction mechanism

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

NOTE: Steady state means rate of formation= rate of disappearance

For the formation we involve positive (+) sign for the rate constant and reactant concentration and negative (-) sign involve for the rate constant and reactant concentration in above equation I, II & III

$$\frac{d[H]}{dt} = k_2 [H_2] [Br] - k_3 [H] [Br_2] - k_4 [H] [HBr] = 0 \quad \text{...............(3)}$$

$$\frac{d[Br]}{dt} = k_1 [Br_2] - k_2 [H_2] [Br] - k_3 [H] [Br_2] + k_4 [H] [HBr] - k_5 [Br]^2 = 0 \quad \text{........4)}$$

From equation (3)

$$k_2 [H_2] [Br] = k_3 [H] [Br_2] + k_4 [H] [HBr] \quad \text{...................(5)}$$

From equation (4), we also have,

$$k_2 [H_2] [Br] = k_1 [Br_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - k_5 [Br]^2 \quad \text{...........(6)}$$

From equations (5) and (6), we have

$$k_3 [H] [Br_2] + k_4 [H] [HBr] = k_1 [Br_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - k_5 [Br]^2$$

$$k_1 [Br_2] = k_5 [Br]^2$$

$$[Br]^2 = \frac{k_1}{k_5} [Br_2]$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad \text{.............(7)}$$

Substituting the value of [Br] from equation (7) in (3), we get

Substituting the value of [Br] from equation (7) in (3), we get

or
$$k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}[H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr] = 0$$

or
$$\{k_3 [Br_2] + k_4 [HBr]\} [H] = k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]$$

$$[H] = \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \qquad \text{.........................(8)}$$

Substituting the values of [H] and [Br] from equations (8) and (7) in equation (3), we get the rate expression for formation of hydrogen bromide. This is given by,

$$\frac{d\,[HBr]}{d\,t} = k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2] + k_3 \cdot \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \cdot [Br_2]$$

$$- k_4 \cdot \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \cdot [HBr]$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad \text{..............(7)}$$

$$[H] = \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad \text{..............................(8)}$$

Substitute equation (7) & (8) in the equation (3) given below

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

Substituting the values of [H] and [Br] from equations (8) and (7) in equation (3), we get the rate expression for formation of hydrogen bromide. This is given by,

$$\frac{d\,[HBr]}{dt} = k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}\,[H_2] + k_3 \cdot \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}\,[H_2]}{k_3\,[Br_2] + k_4\,[HBr]} \cdot [Br_2]$$

$$- k_4 \cdot \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}\,[H_2]}{k_3\,[Br_2] + k_4\,[HBr]} \cdot [HBr]$$

$$= k_2 \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2] \left\{1 + \frac{k_3 . [Br_2]}{k_3 [Br_2] + k_4 [HBr]} - \frac{k_4 . [HBr]}{k_3 [Br_2] + k_4 [HBr]}\right\}$$

$$= k_2 . \left(\frac{k_1}{k_5}\right)^{1/2} . [Br_2]^{1/2} [H_2] \left\{\frac{k_3 . [Br_2] + k_4 [HBr] + k_3 . [Br_2] - k_4 [HBr]}{k_3 [Br_2] + k_4 [HBr]}\right\}$$

$$= k_2 . \left(\frac{k_1}{k_5}\right)^{1/2} . [Br_2]^{1/2} [H_2] . \left\{\frac{2k_3 . [Br_2]}{k_3 [Br_2] + k_4 [HBr]}\right\}$$

$$\frac{d\,[HBr]}{d\,t} = \frac{2k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{\frac{k_3\,[Br_2]}{k_3\,[Br_2]} + \frac{k_4\,[HBr]}{k_3\,[Br_2]}}$$

$$\frac{d\,[HBr]}{d\,t} = \frac{2k_2 \cdot \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} [H_2]}{1 + \frac{k_4}{k_3} \cdot \frac{[HBr]}{[Br_2]}}$$

$$\frac{d\,[HBr]}{d\,t} = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + k' \cdot \frac{[HBr]}{[Br_2]}}$$

$k = 2\,k_2\,(k_1/k_5)^{1/2}$ and $k' = k_4/k_3$.

THIS IS THE RATE EXPRESSION OF HYDROGEN BROMINE

$$\frac{d\,[HBr]}{d\,t} = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + k' \cdot \frac{[HBr]}{[Br_2]}}$$

THANKYOU