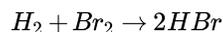


## 29.7: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

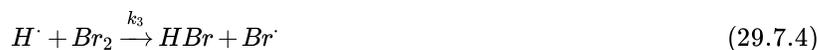
These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction



The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \quad (29.7.1)$$

A proposed mechanism is



Based on this mechanism, the rate of change of concentrations for the intermediates ( $H^\cdot$  and  $Br^\cdot$ ) can be written, and the steady state approximation applied.

$$\frac{d[H^\cdot]}{dt} = k_2[Br^\cdot][H_2] - k_{-2}[HBr][H^\cdot] - k_3[H^\cdot][Br_2] = 0$$

$$\frac{d[Br^\cdot]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^\cdot]^2 - k_2[Br^\cdot][H_2] + k_{-2}[HBr][H^\cdot] + k_3[H^\cdot][Br_2] = 0$$

Adding these two expressions cancels the terms involving  $k_2$ ,  $k_{-2}$ , and  $k_3$ . The result is

$$2k_1[Br_2] - 2k_{-1}[Br^\cdot]^2 = 0$$

Solving for  $Br^\cdot$

$$Br^\cdot = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the  $H^\cdot$  that is generated by solving the steady state expression for  $d[H^\cdot]/dt$ .

$$[H^\cdot] = \frac{k_2[Br^\cdot][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^\cdot] = \frac{k_2 \sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for  $H^\cdot$  and  $Br^\cdot$ , we can substitute them into an expression for the rate of production of the product  $HBr$ :

$$\frac{[HBr]}{dt} = k_2[Br^\cdot][H_2] + k_3[H^\cdot][Br_2] - k_{-2}[H^\cdot][HBr]$$

After substitution and simplification, the result is

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

Multiplying the top and bottom expressions on the right by  $[Br_2]$  produces

$$\frac{[HBr]}{dt} = \frac{2k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [H_2][Br_2]^{3/2}}{[Br_2] + \frac{k_{-1}}{k_3} [HBr]}$$

which matches the form of the rate law found experimentally (Equation 29.7.1)! In this case,

$$k = 2k_2 \sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

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