29-7 : chain reactions

Consider $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

with experimentally determined rate law

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr][Br_2]^{-1}}$$

The product decreases the reaction rate as it accumulates. It is thus an inhibitor!

The proposed mechanism, in terms of elementary reactions, is:

$$Br_2 + M \underset{k_{-1} = \text{termination}}{\overset{k_1 = \text{initiation}}{\rightleftharpoons}} 2Br + M$$

$$Br + H_2 \underset{k_{-2} = \text{inhibition}}{\overset{k_2 = \text{propagation}}{\rightleftharpoons}} HBr + H$$

$$H + Br_2 \underset{k_{-3} = \text{inhibition}}{\overset{k_3 = \text{propagation}}{\rightleftharpoons}} HBr + Br$$

The propagation steps are chain reactions involving free radicals.

→ they each produce what the other one consumes

This is also important in polymerization.

To obtain the experimental rate laws from this mechanism, we need to eliminate M, H, and Br from the elementary reactions.

To do this we apply the steady state approx to H and Br, and M ends up canceling out.

Also, we set $k_{-3} = 0$ because it is known this reaction is very slow.

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

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

Add these: $0 = k_1[Br_2][M] - k_{-1}[Br]^2[M]$

$$\Rightarrow [Br] = \left(k_1/k_{-1}\right)^{1/2}[Br_2]^{1/2} = K_1^{1/2}[Br_2]^{1/2}.$$

Sub. this into the $\frac{d[H]}{dt} = 0$ expression to get

$$[H] = \frac{k_2[Br][H_2]}{k_{-2}[HBr] + k_3[Br_2]} = \frac{k_2 K_1^{1/2}[Br_2]^{1/2}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Then we use $\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] + k_3[H][Br_2]$

with the [H] and [Br] steady state expressions to obtain the observed rate law with $k = k_2K_1^{1/2}$; $k' = k_{-2}/k_3$.