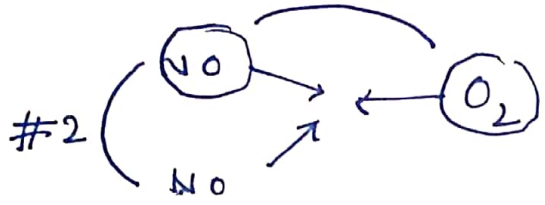
$2\,NO + O_2 \longrightarrow 2\,NO_2$ (gas + base)

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k_{obs}[NO]^2[O_2]$$ Experiment

#1



Mech #1

① $NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3$ fast eqm

② $NO_3 + NO \xrightarrow[k_2]{} 2\,NO_2$ slow / rate det

$$\frac{[NO_3]}{[NO][O_2]} = \frac{k_1}{k_{-1}} = (K_{eq})_1 \Rightarrow [NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

Rate: $v_2 \equiv (Rate)_2 = k_2[NO_3][NO]$

$$= k_2 \times \frac{k_1}{k_{-1}}[NO][O_2] \times [NO]$$

$$k_{obs} = \frac{k_1 k_2}{k_{-1}}$$

$$\boxed{Rate = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]}$$

(HW) ⇒ Same mechanism using SSA for $[NO_3]$

$$\frac{d[NO_3]}{dt} = ? \approx 0\,|_{ss}$$

Mech #2

① $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

② $N_2O_2 + O_2 \xrightarrow[k_2]{} 2\,NO_2$

SSA for $[N_2O_2]$

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2]$$

$$\approx 0 \quad \text{under SS}$$

$$[N_2O_2]\big|_{ss} = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]}$$

$$\text{Rate}: \quad \frac{1}{2}\frac{d[NO_2]}{dt} \equiv v_2 \equiv (\text{Rate})_2$$

$$= k_2[N_2O_2][O_2]$$

$$= k_2 \times \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]} \times [O_2]$$

$$= \frac{k_1 k_2}{k_{-1} + k_2[O_2]}[NO]^2[O_2]$$

$$\approx \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]$$

$NO + NO \rightleftharpoons N_2O_2 \xrightarrow{O_2} 2NO_2$

$v_{-1} \gg v_1, v_2$

$k_{-1}[N_2O_2] \gg k_2[N_2O_2][O_2]$

$k_{-1} \gg k_2[O_2]$

Condition SSA

HW $\Rightarrow$ Same mechanism using eq'n approx

$2\ O_3(g) \longrightarrow 3\ O_2(g)$ CFCs Cl · F ·

① $O_3 + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M(g)$

② $O_3 + O \xrightarrow{k_2} 2\ O_2$

SSA for [O]

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O_3][O]$$

$$\approx 0$$

$$\Longrightarrow [O]_{ss} = \frac{k_1[O_3][M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

$$\frac{1}{3}\frac{d[O_2]}{dt} \equiv v_2 = (Rate)_2$$

$$= k_2[O_3][O]$$

$$= k_2 \times [O_3] \times \frac{k_1[O_3][M]}{k_{-1}[O_2][M] + k_2[O_3]} + \dots$$

$$= \frac{k_1 k_2 [O_3]^2 [M]}{k_{-1}[O_2][M] + k_2[O_3]} + \dots$$

Will discuss the O_3 reaction in detail later

Eqm approx. Rate = ?

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* Rate : $\frac{1}{3}\frac{d[O_2]}{dt} = \frac{1}{3}\left\{ k_1[O_3][M] \times 2\ k_2[O_3][O] \right\}$

(If we take $\frac{d[O_2]}{dt}$ for ALL steps)

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

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

H — H : Difficult to break

Br — Br : Easy to break

(1) $Br_2 + M \xrightarrow{k_1} 2\,Br + M$ Initiation

(2) $Br + H_2 \xrightarrow{k_2} HBr + H$

(3) $H + Br_2 \xrightarrow{k_3} HBr + Br$ } Propagation

(4) $HBr + H \xrightarrow{k_{-2}} H_2 + Br$

X (5) $HBr + Br \xrightarrow{k_{-3}} Br_2 + H$ } Inhibition

(6) $2\,Br + M \xrightarrow{k_{-1}} Br_2 + M$ Termination

(4) $\Rightarrow$ exothermic -70 kJ/mole

(5) $\Rightarrow$ endothermic $+170$ kJ/mole

(HW) $\Rightarrow$ NOT ignoring step #5

$$\left.\frac{d[Br]}{dt}\right|_{ss} \approx 0 = 2k_1[Br_2][M] - k_2[Br][H_2] + k_3[H][Br_2] + k_{-2}[HBr][H] - 2k_{-1}[Br]^2[M]$$

$$\left.\frac{d[H]}{dt}\right|_{ss} \approx 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_{-2}[HBr][H]$$

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

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

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

$$k_2[Br][H_2] - \left\{k_3[Br_2] - k_{-2}[HBr]\right\}[H] = 0$$

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

$$\text{Rate} = \frac{1}{2}\frac{d[HBr]}{dt}$$

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

$$= \frac{1}{2}\left\{k_2[Br][H_2] + k_3\frac{k_2[H_2][Br_2]}{k_3[Br_2] + k_{-2}[HBr]} - k_{-2}\frac{[HBr]k_2[H_2]}{k_3[Br_2] + k_{-2}[HBr]}\right\}$$

$$= \frac{1}{2} \times [Br] \times \left\{k_2[H_2] + \frac{k_3 k_2 [H_2][Br_2]}{k_3[Br_2] + k_{-2}[HBr]} - \frac{k_{-2}[HBr]k_2[H_2]}{k_3[Br_2] + k_{-2}[HBr]}\right\}$$

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

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

$$\boxed{\text{Rate} = \frac{k[Br_2]^{1/2}}{1 + k'[HBr][Br_2]^{-1}}}$$

$$k = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}$$

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