Achindha (Aditya Chindhade)

1) 1 $I + S \underset{K_{1b}}{\overset{K_{1f}}{\rightleftharpoons}} I \cdot S$ — fast k_1, K_1

2 $\omega + S \rightleftharpoons \omega \cdot S$ → fast k_2, K_2

3 $\omega \cdot S + I \cdot S \rightleftharpoons TBA \cdot S + S$ → slow k_3, K_3

4 $TBA \cdot S \rightleftharpoons TBA + S$ → fast k_4, K_4

∴ Now each step is elementary. $\left(\frac{K_{4f}}{K_{4b}} = K_4\right)$

$$\therefore r_4 = k_4[TBA \cdot S] - \frac{k_4}{K_4}[TBA][S] \quad -④$$

$[TBA \cdot S]$ can't be measured.

$$r_3 = k_3[\omega \cdot S][I \cdot S] - \frac{k_3}{K_3}[TBA \cdot S][S] \quad -③$$

$$r_2 = k_2[\omega][S] - \frac{k_2}{K_2}[\omega \cdot S] \quad -②$$

$$r_1 = k_1[I][S] - \frac{k_1}{K_1}[I \cdot S] \quad -①$$

1.1] For fast reactions, they reach equilibrium fast.

~~$r_1 = 0, r_2 = 0$~~,

$r_1 \to 0$, $r_2 \to 0$, $r_4 \to 0$.

$$\therefore k_1[I][S] = \frac{k_1}{K_1}[I \cdot S] \Rightarrow [I \cdot S] = [I][S]K_1$$

$$k_2[\omega][S] = \frac{k_2}{K_2}[\omega \cdot S] \Rightarrow [\omega \cdot S] = [\omega][S]K_2.$$

$$[TBA \cdot S] = \frac{[TBA][S]}{IK_4}$$

$$r_3 = k_3[\omega \cdot S][I \cdot S] - \frac{k_3}{IK_3}[TBA \cdot S][S]$$

$$r_3 = k_3 IK_1 IK_2 [I][\omega][S]^2 - \frac{k_3}{IK_3}\frac{[TBA][S]}{IK_4}[S]$$

$$r_3 = k_3[S]^2 \left[IK_1 IK_2 [I][\omega] - \frac{[TBA]}{IK_3 IK_4} \right]$$

$$[S_0] = [I \cdot S] + [\omega \cdot S] + [TBA \cdot S] + [S]$$

$$[S_0] = \left[[I][S] IK_1 + [\omega][S] IK_2 + \frac{[TBA][S]}{IK_4} \right] + \theta + [S]$$

$$\frac{[S_0]}{\left([I] IK_1 + [\omega] IK_2 + \frac{[TBA]}{IK_4} + 1 \right)} = [S]$$

$$\therefore r_3 = k_3 \cdot \frac{[S_0]^2}{\left(1 + [I] IK_1 + [\omega] IK_2 + \frac{[TBA]}{IK_4} \right)} \cdot \left[IK_1 IK_2 [I][\omega] - \frac{TBA}{IK_3 IK_4} \right]$$

1.2] Adsorption of isobutylene is rate limiting.

~~$k_1 = [I \cdot S]$~~

$k_1 [\omega][S] = [\omega \cdot S]$ — (1)

$$[TBA \cdot S] = \frac{[TBA][S]}{k_4} \quad — (2)$$

$k_3 [\omega \cdot S][I \cdot S] = [TBA \cdot S][S]$ — (3)

$$\Rightarrow [I \cdot S] = \frac{(TBA \cdot S)[S]}{k_3 [\omega \cdot S]} = \frac{[TBA][S]^2}{k_3 k_4 k_1 [\omega][S]}$$

$$\therefore r_1 = k_1 [I][S] - \frac{k_1}{k_1}[I \cdot S]$$

$$= k_1 [I][S] - \frac{k_1}{k_1}\left(\frac{(TBA)[S][S]}{k_4 \; k_3 k_1 [\omega][S]}\right)$$

$$r_1 = \left[k_1 [I] - \frac{k_1 [TBA]}{k_1^2 k_4 k_3}\right][S] \quad — (4)$$

$$\left[1 + [I]k_2 + [\omega]k_1 + \frac{[TBA]}{k_4}\right]$$

$$[S_0] = [I \cdot S] + [\omega \cdot S] + [TBA \cdot S] + [S]$$

$$= \frac{[TBA][S]}{k_2 k_3 k_4 [\omega]} + [\omega][S]k_2 + \frac{[TBA][S]}{k_4} + [S]$$

$$\therefore [S] = [S_0]\left[\frac{TBA}{k_2 k_3 k_4 [\omega]} + [\omega]k_2 + \frac{[TBA]}{k_4} + 1\right]^{-1} \quad — (5)$$

Put (5) in (4)

$$r_1 = k_1\left[[I] - \frac{[TBA]}{\frac{1}{K_2}\frac{1}{K_1}\cdot\frac{1}{K_4}\frac{1}{K_3}}\right][S_0]\left[\frac{[TBA]}{\frac{1}{K_2}\frac{1}{K_3}\frac{1}{K_4}[\omega]} + [\omega]\frac{1}{K_2} + \frac{TBA}{\frac{1}{K_4}} + 1\right]^{-1}$$

3] Eley Rideal ... kinetics

$I \cdot S + W \rightarrow TB \cdot S$ — ④

and the surface reaction is rate limiting

Surface reaction:

$I + S \rightleftharpoons I \cdot S$ — ① fast

$I \cdot S + W \rightleftharpoons TBA \cdot S$ — ② slow

$TBA \cdot S \rightleftharpoons TBA + S$ — ③ fast

$$[I \cdot S] = [I][S]/K_1$$

$$[TBA \cdot S] = \frac{[TBA][S]}{K_4}$$

$$r_2 = k_2[I \cdot S][W] - k_{-2}[TB \cdot S]$$

$k_{-2} \rightarrow 0$

$$r_2 = k_2[I \cdot S][W] - \frac{k_2}{K_2}[TB \cdot S]$$

$$r_2 = k_2\left[[W][I]/K_1[S] - \frac{[TBA][S]}{K_2 K_4}\right]$$

$$= k_2 \cdot \left[[W][I]/K_1 - \frac{[TBA]}{K_2 K_4}\right] \cdot [S]$$

$$[S_0] = [I \cdot S] + [TBA \cdot S] + [S]$$

$$[S_0] = [I][S]/K_1 + \frac{[TBA][S]}{K_4} + [S]$$

$$\therefore [S] = [S_0] \Big/ \left[[I]/K_1 + \frac{[TBA]}{K_4} + 1\right]$$

$$r_2 = k_2 \left[[\omega][I]/K_1 - \frac{[TBA]}{/K_2 /K_4} \right] \left[\frac{[S_0]}{[I]/K_1 + \frac{[TBA]}{/K_4} + 1} \right]$$

$$\boxed{r_2 = \frac{k_2 [[\omega][I]/K_1 [S_0]}{\left[1 + [I]/K_1 + (TBA)/K_4 \right]}}$$

[4]

$$I + S_1 \rightleftharpoons I \cdot S_1 \quad \rightarrow \text{fast}$$

$$\omega + S_2 \rightleftharpoons \omega \cdot S_2 \quad \rightarrow \text{fast}$$

$$I \cdot S_1 + \omega \cdot S_2 \rightleftharpoons TBA + S_1 + S_2 \quad \rightarrow \text{slow}$$

$$IK_1 = \frac{[I \cdot S_1]}{[I][S_1]} \Rightarrow IK_1[I][S_1] = [I \cdot S_1]$$

$$IK_2 = \frac{[\omega \cdot S_2]}{[\omega][S_2]} \Rightarrow IK_2[\omega][S_2] = [\omega \cdot S_2]$$

$$r_3 = k_3[I \cdot S_1][\omega \cdot S_2] - \frac{k_3}{IK_3}[TBA][S_1][S_2]$$

$$= k_3\left[IK_1[I][S_1]IK_2[\omega][S_2] - \frac{1}{IK_3}[TBA][S_1][S_2]\right]$$

$$= k_3[S_1][S_2]\left[IK_1[I]IK_2[\omega] - \frac{[TBA]}{IK_3}\right]$$

$$[S_{1o}] = [S_1] + [I \cdot S_1]$$

$$[S_{1o}] = [S_1] + IK_1[I][S_1]$$

$$\therefore [S_1] = \frac{[S_{1o}]}{(1 + IK_1[I])}$$

$$[S_{2o}] = [S_2] + [\omega \cdot S_2]$$

$$[S_{2o}] = [S_2] + IK_2[\omega][S_2]$$

$$[S_2] = \frac{[S_{2o}]}{(1 + IK_2[\omega])}$$

$$r_3 = \frac{k_3[S_{1o}][S_{2o}]}{(1 + IK_1[I])(1 + K_2[\omega])}\left[IK_1IK_2[I][\omega] - \frac{[TBA]}{IK_3}\right]$$