

Now each step is elementary. ( $\frac{k_{-1}}{k_1} = K_1$ )

$$r_4 = k_4 [TBA \cdot S] - \frac{k_{-4} [TBA] [S]}{K_4} \quad \text{--- (4)}$$

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

$$r_3 = k_3 [W \cdot S] [I \cdot S] - \frac{k_{-3} [TBA \cdot S] [S]}{K_3} \quad \text{--- (3)}$$

$$r_2 = k_2 [W] [S] - \frac{k_{-2} [W \cdot S]}{K_2} \quad \text{--- (2)}$$

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

1.1] For fast reactions, they reach equilibrium fast.

$$\begin{array}{l}
 \cancel{r_1 = 0}, \cancel{r_2 = 0}, \\
 r_1 \rightarrow 0, \quad r_2 \rightarrow 0, \quad r_4 \rightarrow 0.
 \end{array}$$

$$\therefore k_1 [I] [S] = \frac{k_{-1} [I \cdot S]}{K_1} \Rightarrow [I \cdot S] = [I] [S] K_1$$

$$k_2 [W] [S] = \frac{k_{-2} [W \cdot S]}{K_2} \Rightarrow [W \cdot S] = [W] [S] K_2$$

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

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

$$r_3 = k_3 K_1 K_2 [I][W][S]^2 - \frac{k_3}{K_3} \frac{[TBA][S]}{K_4} [S]$$

$$r_3 = k_3 [S]^2 \left[ K_1 K_2 [I][W] - \frac{[TBA]}{K_3 K_4} \right]$$

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

$$[S_0] = \left[ [I][S]K_1 + [W][S]K_2 + \frac{[TBA][S]}{K_4} \right] + [S]$$

$$\frac{[S_0]}{\left( [I]K_1 + [W]K_2 + \frac{[TBA]}{K_4} + 1 \right)} = [S]$$

$$\therefore r_3 = k_3 \cdot \frac{[S_0]^2}{\left( 1 + [I]K_1 + [W]K_2 + \frac{[TBA]}{K_4} \right)} \cdot \frac{[K_1 K_2 [I][W] - \frac{[TBA]}{K_3 K_4}]}{K_3 K_4}$$



1.2] Adsorption of isobutylene is rate limiting.

$$k_1 = \text{[I.S]}$$

$$k_2 [W][S] = [W.S] \quad \text{--- (1)}$$

$$[TBA.S] = \frac{[TBA][S]}{K_4} \quad \text{--- (2)}$$

$$K_3 [W.S][I.S] = [TBA.S][S] \quad \text{--- (3)}$$

$$\Rightarrow [I.S] = \frac{[TBA.S][S]}{K_3 [W.S]} = \frac{[TBA][S]}{K_3 K_4 K_1 [W][S]}$$

$$\therefore r_1 = k_1 [I][S] - \frac{k_1 [I.S]}{K_1}$$

$$= k_1 [I][S] - \frac{k_1}{K_1} \left( \frac{[TBA][S][S]}{K_4 K_3 K_1 [W][S]} \right)$$

$$r_1 = \left[ k_1 [I][S] - \frac{k_1 [TBA][S][S]}{K_1^2 K_4 K_3} \right] \frac{1}{\left[ 1 + \frac{[I] K_2}{K_1} + \frac{[W] K_1}{K_4} + \frac{[TBA]}{K_4} \right]} \quad \text{--- (4)}$$

$$[S_0] = [I.S] + [W.S] + [TBA.S] + [S]$$

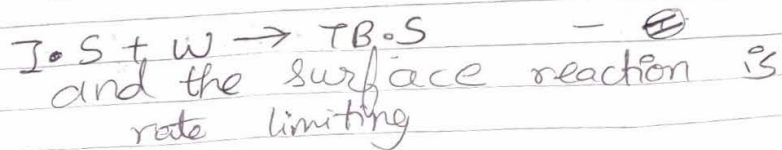
$$= \frac{[TBA][S]}{K_2 K_3 K_4 [W]} + [W][S] K_2 + \frac{[TBA][S]}{K_4} + [S]$$

$$\therefore [S] = [S_0] \left[ \frac{[TBA]}{K_2 K_3 K_4 [W]} + [W] K_2 + \frac{[TBA]}{K_4} + 1 \right]^{-1} \quad \text{--- (5)}$$

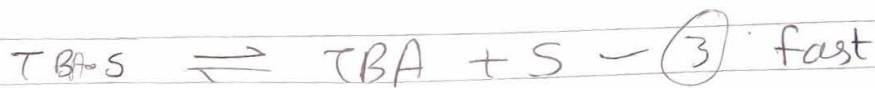
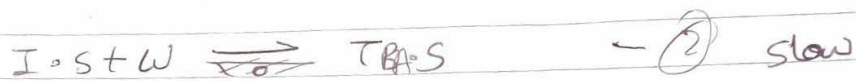
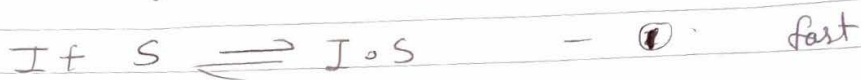
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$$r_1 = K_1 \left( \frac{[I] - [TBA]}{K_2 K_1 K_4 K_3} \right) [S_0] \left( \frac{[TBA]}{K_2 K_3 K_4 [\omega]} + [\omega] \frac{K_2 + TBA + 1}{K_4} \right)^{-1}$$

### 3) Eley Rideal kinetics



Surface reaction:



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

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

$$r_2 = \frac{k_2[I \cdot S][W]}{K_2} = \frac{k_2[I][S]K_1[W]}{K_2} - \frac{k_2[TB \cdot S]}{K_2}$$

$$r_2 = k_2 \left[ \frac{[W][I]K_1[S]}{K_2K_4} - \frac{[TBA][S]}{K_2K_4} \right]$$

$$= k_2 \cdot \left[ \frac{[W][I]K_1 - [TBA]}{K_2K_4} \right] \cdot [S]$$

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

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

$$[S] = \frac{[S_0]}{\left( [I]K_1 + \frac{[TBA]}{K_4} + 1 \right)}$$



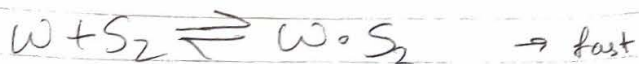
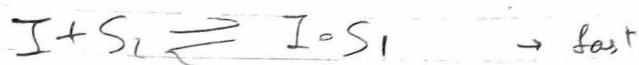
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$$r_2 = k_2 \left[ \omega [I] k_1 - \frac{[TBA]}{k_2 k_4} \right] \left[ \frac{[S_0]}{[I] k_1 + \frac{[TBA]}{k_4} + 1} \right]$$

$$r_2 = \frac{k_2 [\omega] [I] k_1 [S_0]}{1 + [I] k_1 + [TBA]/k_4}$$

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$$K_1 = \frac{[I \cdot S_1]}{[I][S_1]} \Rightarrow K_1[I][S_1] = [I \cdot S_1]$$

$$K_2 = \frac{[W \cdot S_2]}{[W][S_2]} \Rightarrow K_2[W][S_2] = [W \cdot S_2]$$

$$r_3 = \cancel{k_3} K_3 [I \cdot S_1] [W \cdot S_2] - \frac{k_3}{K_3} [TBA] [S_1] [S_2]$$

$$= k_3 [K_1 [I][S_1] K_2 [W][S_2]] - \frac{1}{K_3} [TBA] [S_1] [S_2]$$

$$= K_3 [S_1] [S_2] \left[ K_1 [I] K_2 [W] - \frac{[TBA]}{K_3} \right]$$

$$\begin{aligned} [S_{10}] &= [S_1] + [I \cdot S_1] \\ [S_{10}] &= [S_1] + K_1 [I][S_1] \end{aligned}$$

$$\therefore [S_1] = \frac{[S_{10}]}{(1 + K_1 [I])}$$

$$\begin{aligned} [S_{20}] &= [S_2] + [W \cdot S_2] \\ [S_{20}] &= [S_2] + K_2 [W][S_2] \end{aligned}$$

$$[S_2] = \frac{[S_{20}]}{(1 + K_2 [W])}$$

$$r_3 = \frac{K_3 [S_{10}] [S_{20}]}{(1 + K_1 [I]) (1 + K_2 [W])} \left[ K_1 K_2 [I] [W] - \frac{[TBA]}{K_3} \right]$$