Lecture 6.2 Type 2 Reaction Mechanisms

Note Title 9/9/2011

Type 1 Rxn Mechanisms
1) El. rxn ... slow ... R.L.S.
2) El. rxn ... fast
3) El. rxn ... fast

Type 2 Rxn Mechanisms
1) El. rxn fast
2) El. rxn ... slow .. RLS
3) El. rxn fast

Example. Experimentally overall rxn $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ ☆

rate equation: $\text{rate} = k[NO]^2[O_2]$

Proposed Mechanism:

El. Rxn #1 (bimolecular) $2\,NO \rightarrow N_2O_2$ fast ← Type 2!

El. Rxn #2 (bimolecular) $N_2O_2 + O_2 \rightarrow 2\,NO_2$ slow .. RLS

$2NO + N_2O_2 + O_2 \rightarrow N_2O_2 + 2NO_2$ (N_2O_2 Rxn intermediate)

$2NO + O_2 \rightarrow 2NO_2$ ☆ agrees with exp ☺

R.L.S. $1N_2O_2 + 1O_2 \rightarrow 2NO_2$ slow

$\text{rate} = k[N_2O_2]^1[O_2]^1$ ... doesn't match!

↖ cannot contain intermediate

reactants → 1) $2NO \underset{r}{\overset{f}{\rightleftharpoons}} 1N_2O_2$ fast

Large amts of N_2O_2 accumulate

Dynamic Equilibrium

$\text{rate}_f = \text{rate}_r$

2) $N_2O_2 + O_2 \rightarrow 2NO_2$ slow (RLS)

El. Rxn #1 $\text{rate}_f = \text{rate}_r$

$\frac{1}{k_r}\, k_f [NO]^2 = k_r [N_2O_2]^1 \frac{1}{k_r}$

$k_f/k_r\,[NO]^2 = [N_2O_2]$ intermediate! ☺

∴ $\text{rate} = k[N_2O_2]_{\text{intermediate}}[O_2] = k\left(k_f/k_r[NO]^2\right)[O_2] = k[NO]^2[O_2]$ ... agrees with exp