

How can we distinguish multistep  
from single step?

good example comes from



Real example  $OClO \rightleftharpoons Cl + O_2$



with  $v_f^1 > v_b^1$  and  $v_f^2 > v_b^2$



$$\frac{dA}{dt} = -k_1 A$$

Solve for  $A = A_0$

$$A(t) = A_0 e^{-k_1 t}$$

$$\frac{dI}{dt} = k_1 A - k_2 I$$

$$I(t) = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\frac{dP}{dt} = k_2 I$$

$$P = A_0 - I - A$$

$$= A_0 \left( 1 + \frac{1}{k_1 - k_2} \left( \frac{k_2 e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right)$$

prob 29-5  
not doing

For a single step reaction

$$P = A_0 (1 - e^{-k_1 t})$$

so when can these be distinguished?

If  $k_2 \gg k_1$ ,

$$P = [A]_0 \left[ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]$$

$$\approx [A]_0 (1 - e^{-k_1 t}), \text{ can't distinguish}$$

If  $k_1 \gg k_2$

$$P \approx [A]_0 (1 - e^{-k_2 t})$$

Measure  $-\frac{dA}{dt}$  &  $\frac{dP}{dt}$ , distinguishable!

## Rate determining step

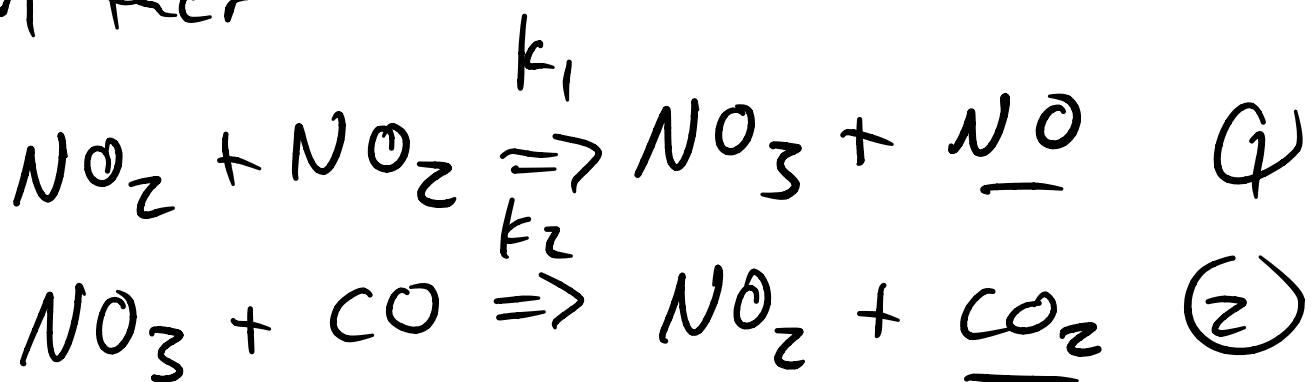
If one step is very slow,  
sets apparent reaction mechanism

$$\text{Eg} \quad k_{\text{obs}}$$



$$\star \text{not } v = k [\text{NO}_2] [\text{CO}]$$

In fact

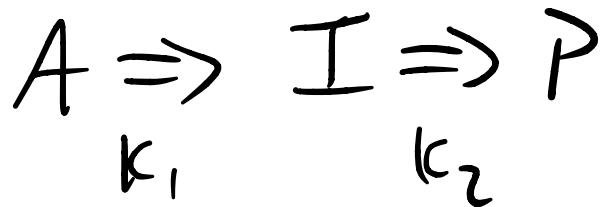


$$v_1 \ll v_2$$

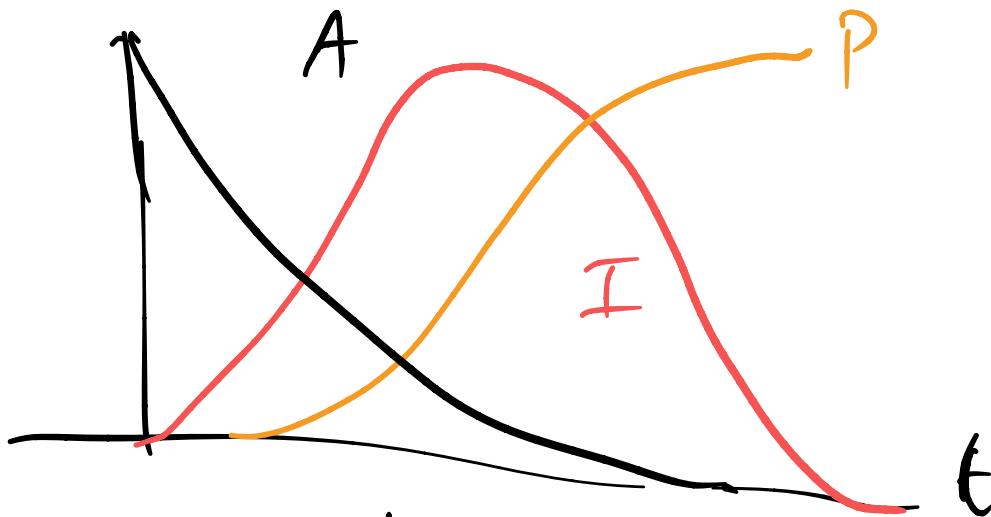
$$\text{so } v = k_1 [\text{NO}_2]^2$$

as long as sufficient CO  
waiting around

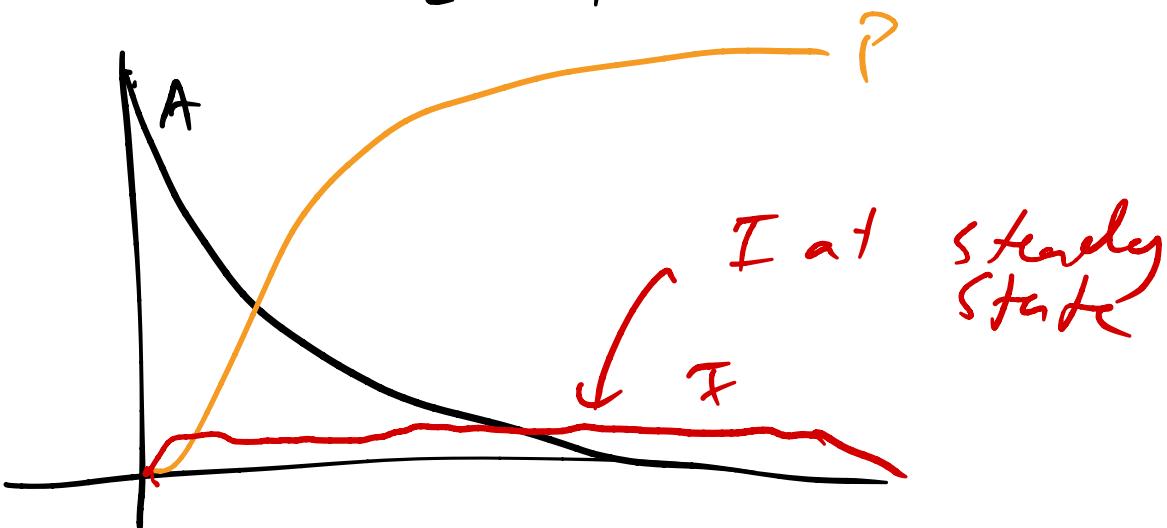
Steady state Approx helps solve  
many rate problems



If  $k_1 \gg k_2$ , get a lot of I,  
which slowly reacts



but if  $k_2 \gg k_1$ ,



Also true for a set of reversible reactions at eq.

Before hand:

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dI}{dt} = k_1 A - k_2 I = 0 \quad \leftarrow \text{if steady state}$$

$$\frac{dP}{dt} = k_2 I \quad \leftarrow \quad \rightarrow I = \frac{k_1 A}{k_2}$$

$$\Rightarrow A = A_0 e^{-k_1 t}$$

$$I_{ss} = \frac{k_1}{k_2} A_0 e^{-k_1 t}$$

$$P = A_0 (1 - e^{-k_1 t})$$

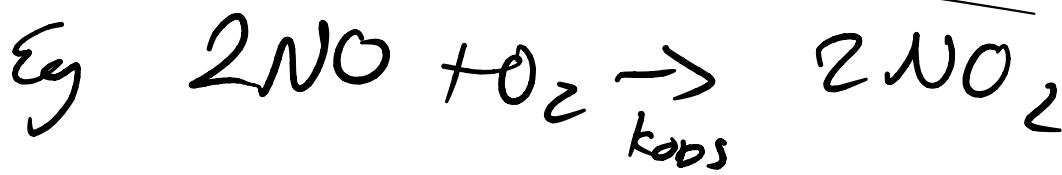
appears  
single step

$$\frac{dI_{ss}}{dt} = -\frac{k_1^2}{k_2} A_0 e^{-k_1 t}$$

so  $\frac{k_1^2}{k_2} A_0$  must  
be small!

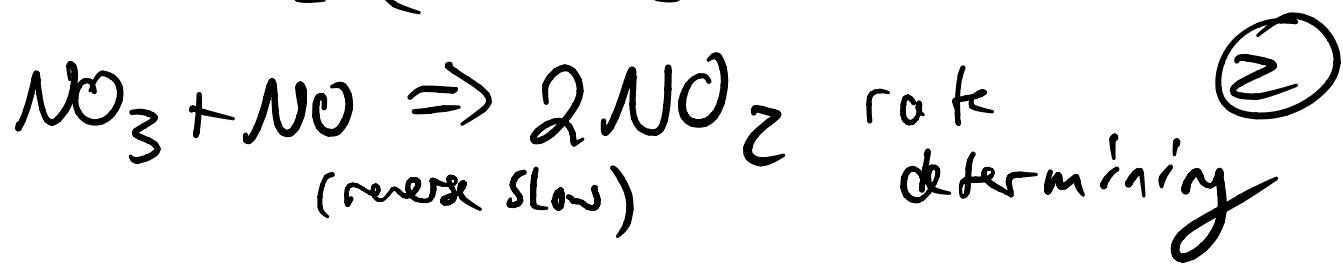
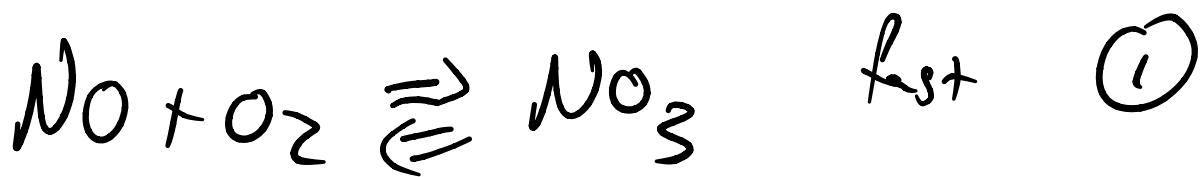
Otherwise not  $\approx 0$

Rate law  $\rightarrow$  mechanism



$$v(f) = k_{\text{obs}} [\text{NO}]^2 [\text{O}_2] \quad ?$$

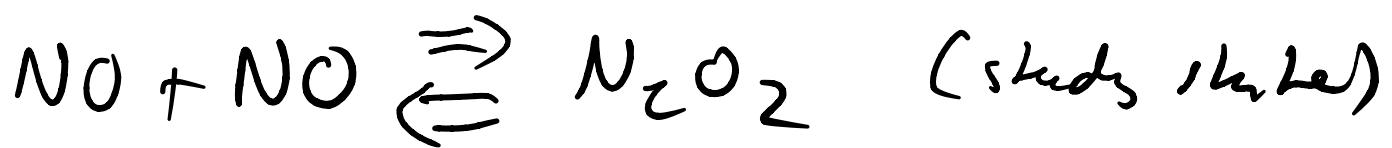
What about mechanism:



$$\textcircled{1} \quad \textcircled{2} \quad \frac{k_f'}{k_b'} = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$$

$$\begin{aligned} \frac{1}{2} \frac{d[\text{NO}_2]}{dt} &= \text{rate} = k_2 [\text{NO}_3][\text{NO}] \\ &= \frac{k_2 k_f'}{k_b'} [\text{NO}]^2 [\text{O}_2] \end{aligned}$$

Alternative, Mech 2



$$\text{rate} = \frac{1}{2} \frac{d[N_2O_2]}{dt} = k_2 [N_2O_2][O_2]$$

Can solve for

$$[N_2O_2]_{ss} = \frac{k_f' [NO]^2}{k_b' + k_2 [O_2]}$$

$$\approx \frac{k_f' [NO]^2}{k_b'} \quad \text{if } k_2 [O_2] \text{ small}$$

$$\text{rate} = k_2 \frac{k_f'}{k_b'} [NO]^2 [O_2]$$

Same as mech 1!

Other expts favor mech 2

## Lindemann Mechanism

Mentioned previously that  
must have enough energy to  
overcome activation barrier  
- in gases, comes from direct  
collision

Activation barrier can be quite high  
Eg in book  $\text{CH}_3\text{NC} \xrightarrow{\text{heat}} \text{CH}_3\text{CN}$  ( $E = 131$   
 $\text{kJ/mol}$ )

At high conc:

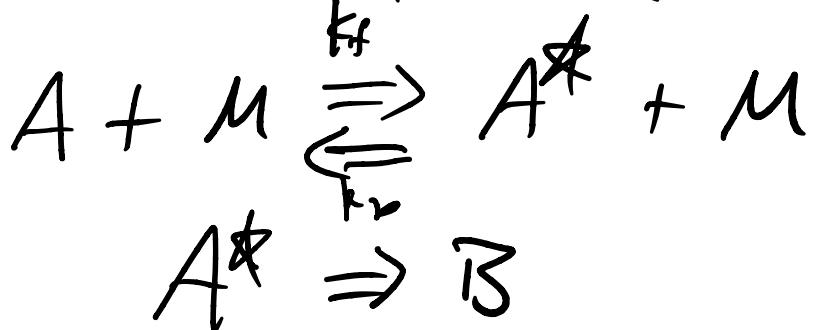
$$v = k[\text{CH}_3\text{NC}]$$

$\propto$  conc

$$v = k[\text{CH}_3\text{NC}]^2$$

Need a collision to get enough  
energy to react

Lindemann proposed activated state  
from collision w/ Molecule M



$$[A^*] \text{ is small so } \frac{d[A^*]}{dt} \approx 0$$

$$\frac{d[B]}{dt} = k_f^2 [A^*] \star$$

$$0 = \frac{dA^*}{dt} = k_f [A][M] - k_f^2 [A^*] \\ - k_b [A^*]$$

$$[A^*] = \frac{k_f' [A][M]}{(k_f' + k_b' [M])}$$

$$\frac{d[B]}{dt} = \frac{k_f^1 k_f^2}{(k_f^2 + k_b' [M])} [A][M] = k_{obs} [A]$$

$$k_{obs} = \frac{k_f^1 k_f^2}{(k_f^2 + k_b' [M])} [M]$$

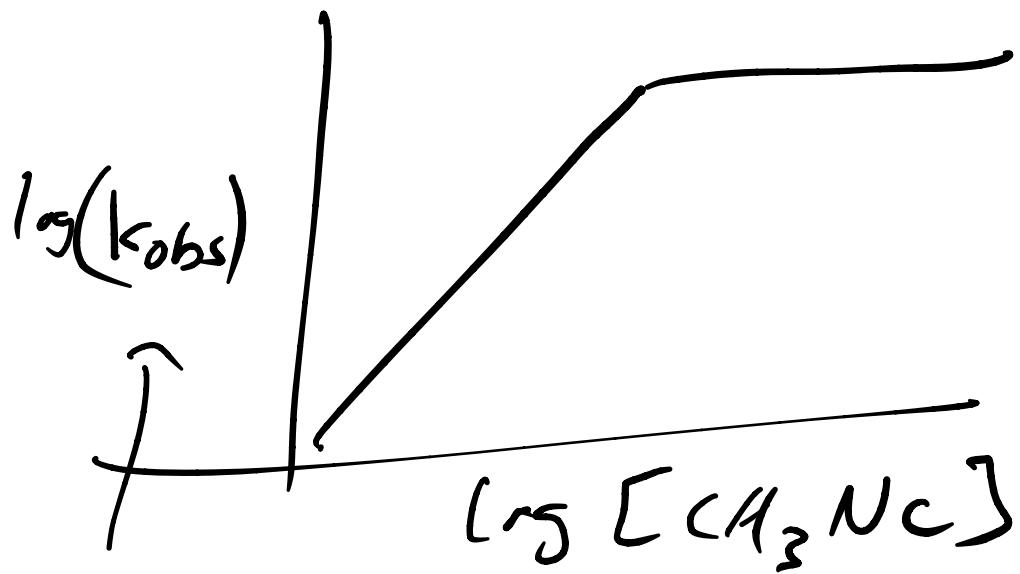
At high concentration  $M$ ,  
often deactivated &

$$k_{\text{obs}} = \frac{k_f' k_f^2}{k_b'}$$

at low conc,  $k_{\text{obs}} = k_f' [M]$

so, second order at low conc

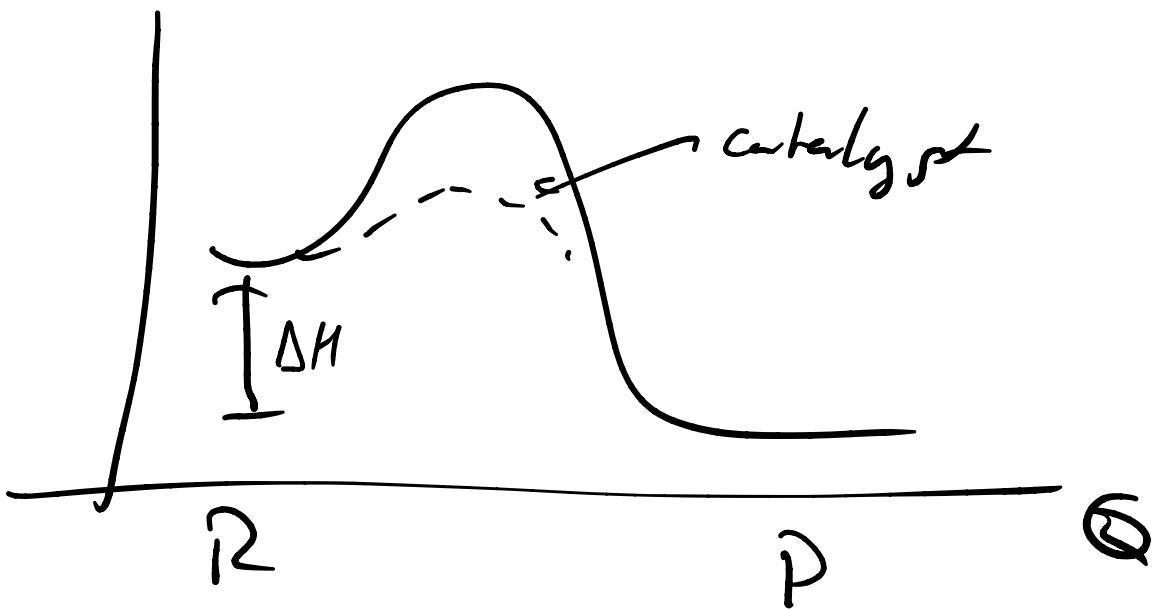
Explains data for  $\text{CH}_3\text{NC}$  isomerization



linear observed rate constant

(skipping chain reactions, 29-7)

# Catalysts



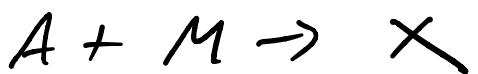
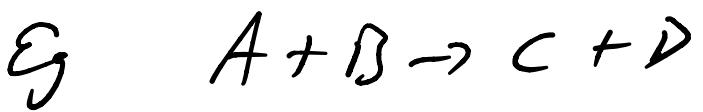
Important - different reaction paths!

Homogeneous catalysis -  
in solution mixed in

Heterogeneous catalysis (different phase)

Eg metal surface

Catalyst takes place in reaction  
but is not used up



Enzymes are biological catalysts

Greatly accelerate reactions

and can be very specific & stereospecific